

Triplet states as key intermediates in light-induced energy conversion – deep spectroscopic insights and photochemical applications

Dissertation
zur Erlangung des Grades eines
Doktor rerum naturalium (Dr. rer. nat.)
im Promotionsfach Chemie

am Fachbereich Chemie, Pharmazie, Geographie und Geowissenschaften
der
Johannes Gutenberg-Universität Mainz

JOHANNES GUTENBERG
UNIVERSITÄT MAINZ



vorgelegt von
Maria-Sophie Bertrams
geboren in Waldshut

Mainz, Juni 2024

Dean: [REDACTED]

First reviewer: [REDACTED]

Second reviewer: [REDACTED]

This work was produced in the time period from October 2020 to June 2024 at the Department of Chemistry of the Johannes Gutenberg University Mainz under the supervision of [REDACTED].

I, Maria-Sophie Bertrams, declare this dissertation was written by myself using only sources and references, which are detailed in the thesis. Passages of text and information taken from published material are referenced accordingly.

Date

Signature

Acknowledgements

At this point, I want to mention the persons, who supervised the thesis, worked together with me in the lab and all the people who supported me throughout the dissertation.

First, thank you, [REDACTED], who is the supervisor of this thesis. Your enthusiasm and motivation for photochemistry and research make you a great mentor and supervisor. This also made our discussions about the current topics of my thesis educational and highly productive. I am grateful to have you as a mentor, for your patience, your always open door, the opportunities and support you provided for me to develop, both as a scientist and as a person. I highly appreciate your policy of asking me and the other PhD students for our opinions on group-related decisions and involving us in the related decision-making. I am very proud that you gave me the chance to be your first PhD student.

Thank you, [REDACTED] for agreeing to be the second examiner and for the interesting discussions throughout the "joint-seminars".

Next to be mentioned are my PhD- and postdoc-friends in the lab of [REDACTED], [REDACTED] (making sure every new person brings at least one cake), [REDACTED] (solid partner for conversations in "badisch-alemannisch"), [REDACTED] (with a relatable mentality on coffee-consumption), [REDACTED] (best word-puns), and [REDACTED] (fixes everything with three screws) and soon [REDACTED]. Thank you for your support, ideas, coffee breaks, and generally for making the time in the lab, office and on conferences so enjoyable. I have had great discussions with all of you, thank you for being so awesome and supportive conversation- and lab-partners. Thanks for the relaxing and fun times we had together with Dana playing games and watching movies. Furthermore, I am very proud of our cooperation projects and had a great time working on them together with you.

Tanks also to my students, [REDACTED] [REDACTED] [REDACTED] [REDACTED] [REDACTED] and [REDACTED] for their motivated work in the lab and interest in photochemistry.

Thank you also to the members of the [REDACTED] group, especially [REDACTED] [REDACTED] [REDACTED] and [REDACTED] for helping me with all my general questions, for being great cooperation partners, for interesting discussions and for the joint spectroscopic measurements.

In relation to this thesis, a huge thank you to all proof readers ([REDACTED] [REDACTED] [REDACTED] [REDACTED] [REDACTED] [REDACTED] [REDACTED] [REDACTED] for your advice and thorough and critical reading. Your comments were very helpful.

Thank you to all my "new" friends in Mainz. [REDACTED] and [REDACTED] for the great time we had watching movies, cooking, hiking, running... I enjoyed our discussions and conversations, which ranged from world issues to taste in music or where to order food.

Thank you, [REDACTED] and [REDACTED] for our small running-group, the deep and funny discussions and the currently developing piano-project. Thank you [REDACTED] for your open nature, for your general support and the fun times at conferences.

Furthermore, I want to thank all the sports groups that I am (more or less reliably) a part of. Several running groups and partners, racing-cycle groups and the calli-park group and the (very) occasional bouldering sessions helped me to clear my head and feel great after a good workout.

Thank you to the [REDACTED] group, who I got to know throughout the last year, for the great time we had and the shared workshops, which were always an insightful and fun community experience. Thank you also to [REDACTED] for your time, support, your opinions and our exciting and inspiring phone calls.

I want to mention my "old" friends, who I had the pleasure to meet during my Bachelor and Master studies or in school, [REDACTED], [REDACTED], [REDACTED], [REDACTED], [REDACTED], [REDACTED], [REDACTED] and [REDACTED]. Thanks for our awesome time during our undergrads and in school, and now with a bit of distance, for our delightful and encouraging phone calls, the occasional visits and especially the "Samichlous-Zmorge".

Außerdem bedanke ich mich bei meiner Familie, meine Cousins, Cousins, Tanten, Onkel, Oma und Neffe. Ihr Lieben macht es so schön immer wieder in die Heimat zurück zu kommen, und ich genieße die Zeit die wir zusammen verbringen, um im Urlaub, am Telefon oder an Geburtstagen Kraft zu tanken. Danke auch für Eure unterstützenden Worte und Telefonate während meiner Promotion.

Zum Schluss möchte ich meinen Eltern und Geschwistern danken. Meistens aus der Ferne, aber auch bei Besuchen und gemeinsamen Urlauben konnte ich mit euch zusammen schöne Momente erleben. Vielen Dank, dass ihr mich immer unterstützt, immer erreichbar seid, mir zuhört und mir immer wieder das ein oder anderen "care-package" zugeschickt habt. Vielen Dank für alles!

Abstract

Light as a driving force for chemical transformations has been of interest in chemistry for over a century. The energy of an absorbed photon promotes a molecule into its excited state, from which various pathways exist for utilizing the photon energy. Manifold light-to-chemical energy conversion mechanisms are employed in modern research fields such as photo(redox) catalysis, waste water treatment, bio-medical research or industrial synthesis. An important property of a molecule in its excited state is the spin multiplicity, which can change from a singlet ground state to a triplet in the excited state. Triplet states possess two highly beneficial properties: i) Kinetic advantages owing to inherently longer lifetimes and ii) higher cage escape quantum yields in photoredox reactions. Both have been exploited for achieving high efficiencies in photochemical mechanisms, photocatalysis or technological devices. Excited triplet states are the focus of this work, including various ways of accessing them and their use in photochemistry.

Chapter 2 presents triplet photochemistry in aqueous solutions, establishing light-driven systems in the most environmentally friendly solvent, which is challenging for photochemical processes. The first project focuses on enhancing the efficiency of a photocatalytic mechanism by combining advantageous properties of metal-based complexes as sensitizers (visible light absorption, fast intersystem crossing) and organic chromophores as photoredox catalysts (long triplet lifetimes, efficient cage escape) in two-component catalyst systems. The two-component approach makes this mechanism highly flexible, which is shown by the elucidation of several combinations of metal complexes (iridium- or ruthenium-based) and organic chromophores (naphthalene, *p*-terphenyl or pyrene derivatives). Out of the tested combinations, one was identified with a substantially increased cage escape quantum yield for generating the key intermediate, compared to using the metal catalyst alone. In the second project, a purely organic triplet photocatalyst for challenging light-driven reactions in aqueous solution is investigated. Structural modification enables enhanced intersystem crossing in the SO₂-bridged terphenyl derivative SO₂TDS, derived from a pure singlet chromophore. Detailed spectroscopic studies revealed the properties of the triplet excited state and its ability to activate substrates *via* two different bimolecular photochemical quenching processes: electron transfer and triplet-triplet energy transfer. The spectroscopic results were complemented by photocatalytic test reactions, providing clear evidence for the dual reactivity. The third project presents an underexplored pathway for switching between two fundamentally different photochemical quenching mechanisms (electron or energy transfer) through replacing metal-based complexes by their dyad congeners. Molecular dyads are covalently linked bichromophores, which in the context of this work consist of a metal complex and an organic chromophore, combining advantageous properties of both subunits in one molecule. The long-lived triplet excited state of the dyad is located on the organic subunit, which results in a drastically modified excited

state reactivity compared to the conventional metal-based complex. Quenching of the triplet excited state with the dicationic phosphonium compound $P-H^{2+}$, a pure singlet state chromophore upon direct excitation, occurred through an electron transfer pathway for the metal complexes, whereas the dyads selectively populate the triplet excited state *via* an energy transfer. The triplet excited state of $P-H^{2+}$ undergoes triplet-triplet annihilation upconversion, which is a unique phenomenon in water. Initial experiments using an iridium-based metal catalyst or dyad further explore this concept for switching the quenching mechanism. The final section focuses on recombination as an additional pathway to produce triplet excited species, besides intersystem crossing and triplet-triplet energy transfer. Recombination is usually an unwanted side reaction directly leading to the ground state, unless sufficient energy is released, which induces population of the triplet excited state. Spectroscopic experiments strongly support an underexplored recombination-based triplet formation pathway for the previously introduced $P-H^{2+}$ combined with a suitable reductive quencher.

Chapter 3 deals with chromophores and their triplet photochemistry in organic solvents or matrices. Insights into their excited state properties enabled applications for versatile purposes. The first project in this chapter provides an in-depth spectroscopic analysis of a molybdenum(0) carbonyl complex with a triplet excited state suitable for bimolecular energy and electron transfer reactions as well as upconversion. This highlights the potential of more abundant second-row transition metals to replace precious metals in light-driven mechanisms. The second project presents a system for blue-to-UV photon upconversion, with literature-known TADF-emitters as sensitizers and triisopropylacetylene (TIPS) substituted benzene derivatives as annihilator structures. Depending on the number and pattern of the TIPS substitution, the excited state properties change significantly, in particular the triplet state energies. Theoretical calculations (DFT and TD-DFT) allowed the prediction of the triplet energies and substantiate experimental findings. The last project in this thesis presents two heteroleptic platinum(II) complexes. Their specific ligand design provides unique properties such as a long-lived, purely ligand-centered triplet excited state, which was characterized in different solvents and a PMMA matrix. Both complexes were employed in triplet-triplet energy transfer quenching experiments and as sensitizers for isomerization reactions.

All projects in this dissertation rely on triplet excited states as key intermediates accessed through different pathways and exploited for the two main photochemical processes, electron and triplet-triplet energy transfer. Detailed mechanistic investigations of the triplet excited states allowed in-depth analyses of the various triplet formation processes and the efficient usage in bimolecular photochemical processes. This thesis thus contributes to a better mechanistic understanding of photochemical processes involving triplet states with implications for photocatalysis, upconversion, devices relying on changes of the spin multiplicity and light-to-energy conversion systems in general.

Kurzzusammenfassung

Die Ausnutzung von Licht als Triebkraft für chemische Umwandlungen ist in der Chemie bereits seit über einem Jahrhundert von Interesse. Mit der Energie eines absorbierten Photons wird ein Molekül in den angeregten Zustand versetzt, welcher über unterschiedliche Prozesse die Nutzung der Photonenenergie ermöglicht. Vielfältige Möglichkeiten für die Umwandlung von Photonenenergie in chemische Energie werden in modernen Forschungsfeldern, wie beispielsweise Photo(redox)katalyse, Abwasser-aufbereitung, biomedizinische Forschung oder industrielle Synthese herangezogen. Eine wichtige Eigenschaft von Molekülen im angeregten Zustand ist die Multiplizität, welche sich ausgehend von einem Singulett-Grundzustand zu einem Triplett im angeregten Zustand ändern kann. Triplett angeregte Zustände besitzen zwei höchst vorteilhafte Eigenschaften: i) Einen kinetischen Vorteil auf Grund der intrinsisch längeren Lebenszeit und ii) eine höhere "cage escape" (engl. für Dissoziation aus der gemeinsamen Lösungsmittelhülle) Quantenausbeute in Photoredoxreaktionen. Beide Effekte wurden für das Erreichen höherer Effizienzen in photochemischen Mechanismen, in der Photokatalyse oder bei technologischen Bauelementen angewendet. Solche angeregten Triplett-Zustände, sowie unterschiedliche Möglichkeiten diese zu erzeugen und deren Ausnutzung für photochemische Mechanismen stehen im Fokus dieser Arbeit.

Kapitel 2 behandelt photochemische Phänomene in wässrigen Lösungen, wobei lichtgetriebenen Systemen im umweltfreundlichsten Lösungsmittel etabliert werden, welches besonders herausfordernd für photochemische Prozesse ist. Das erste Projekt fokussiert sich auf die Effizienzsteigerung eines Photokatalysatormechanismus durch die Kombination vorteilhafter Eigenschaften von metallbasierten Komplexen als Sensibilisatoren (Absorption von sichtbarem Licht und schnelles "intersystem crossing", deutsch: Interkombination) mit organischen Chromophoren als Photoredox-Katalysatoren (lange Triplett Lebenszeit, effizienter "cage escape"-Schritt). Der Zweikomponenten-Ansatz für diesen Mechanismus bringt eine hohe Flexibilität mit sich, was durch die Untersuchung verschiedener Kombinationen von Metallkomplexen (Iridium- oder Rutheniumbasiert) mit organischen Chromophoren (Naphthalin-, *p*-Terphenyl- oder Pyren-Derivate) gezeigt wird. Aus den verschiedenen getesteten Kombinationen wurde eine mit wesentlich höherer Quantenausbeute für die Bildung des Schlüsselintermediates identifiziert, was durch einen Vergleich mit dem herkömmlichen metallbasierten Katalysator deutlich wird. Im zweiten Projekt wird ein rein organischer Triplett-Photokatalysator für herausfordernde, lichtgetriebene Reaktionen in wässrigen Lösungen untersucht. Eine strukturelle Änderung ermöglicht "intersystem crossing" im SO₂-überbrückten Terphenyl-derivat SO₂TDS, welches von einem reinen Singulett Chromophor abgeleitet ist. Detaillierte spektroskopische Studien geben tiefe Einblicke in die Eigenschaften des angeregten Triplett-Zustands und dessen Fähigkeit, Substrate über zwei unterschiedliche photochemische Abfangprozesse zu aktivieren: Elektronen- und Triplett-Triplett-

Energietransfer. Die spektroskopischen Resultate wurden bekräftigt durch photokatalytische Testreaktionen, welche einen klaren Nachweis der dualen Reaktivität erbringen. Das dritte Projekt stellt eine wenig untersuchte Methode vor, bei der durch Ersetzen eines metallbasierten Komplexes mit der zugehörigen Dyade zwischen fundamental unterschiedlichen photochemischen Abfangreaktionen (Elektronen- oder Energietransfer) differenziert wird. Molekulare Dyaden sind kovalent verbundene Bichromophore, welche im Rahmen dieser Arbeit aus einem Metallkomplex und einem organischen Chromophor bestehen, wodurch die vorteilhaften Eigenschaften beider Untereinheiten in einem Molekül vereint werden. Der langlebige angeregte Triplett-Zustand der Dyade befindet sich auf der organischen Untereinheit, was zu drastischen Veränderungen der Reaktivität im angeregten Zustand führt im Vergleich zum herkömmlichen Metallkomplex. Das Abfangen der angeregten Triplett-Zustände mit der dikationischen Phosphonium Verbindung $P-H^{2+}$, ein reiner Singulett-Chromophor nach direkter Anregung, führt zu einem Elektronentransfer im Fall des Metallkomplexes, wogegen die Dyaden selektiv den Triplett-Zustand über einen Energietransfer erzeugen. $P-H^{2+}$ im angeregten Triplett-Zustand durchläuft einen Aufwärtskonversionsmechanismus über Triplett-Triplett Annihilation in Wasser, was in diesem Lösungsmittel höchst selten stattfindet. Weitere explorative Untersuchungen mit Iridium-basierten Metallkomplexen und Dyaden bestätigen das Konzept des Mechanismus-Schaltens (Elektronen- oder Energietransfer). Der letzte Abschnitt stellt die Rekombination als zusätzliche Möglichkeit Triplett-Zustände in wässriger Lösung zu erzeugen vor. Üblicherweise stellen Rekombinationsprozesse eine ungewollte Nebenreaktion dar, welche direkt und unproduktiv den Grundzustand erzeugen. Wenn allerdings ausreichend Energie frei wird, so kann die Besetzung des Triplett-Zustands induziert werden. Spektroskopische Experimente untermauern diesen rekombinationsinduzierten Triplett-Bildungsmechanismus, mit dem bereits vorgestellten $P-H^{2+}$ in Kombination mit geeigneten reduktiven Abfangreagenzien.

Kapitel 3 bezieht sich auf Chromophore und deren Triplett-Photochemie in organischen Lösungsmitteln oder Matrizen. Einblicke in die Eigenschaften der angeregten Zustände legen den Grundstein für eine breite Palette von Anwendungen. Das erste Projekt in diesem Kapitel beschreibt eine detaillierte Analyse eines Molybdän(0)-Carbonyl-Komplexes mit einem angeregten Triplett-Zustand, der sich für bimolekulare Energie- und Elektronentransfermechanismen sowie für die Aufwärtskonversion eignet. Diese Studie unterstreicht das Potential von häufig auf der Erde vorkommenden Übergangsmetallen der zweiten Reihe als Alternative für seltene Metalle in lichtgetriebenen Mechanismen. Das zweite Projekt stellt ein System für die blau-zu-UV Aufwärtskonversion vor, das sich aus einem literaturbekannten TADF-Chromophor als Sensibilisator und triisopropyl-acetylen substituierten Benzolderivaten als Annihilatoren zusammensetzt. In Abhängigkeit von der Anzahl und der Anordnung der Substituenten ver-

ändern sich die Eigenschaften der angeregten Zustände grundlegend; insbesondere ändern sich die Energien der angeregten Triplett-Zustände. Theoretische Berechnungen (DFT und TD-DFT) ermöglichen die Vorhersage der Triplettenergien und bestätigen die experimentellen Resultate. Das letzte Projekt dieser Arbeit stellt zwei heteroleptische Platin(II)-Komplexe vor. Das spezielle Ligandendesign begünstigt besondere Eigenschaften, wie beispielsweise den langlebigen, rein ligandenbasierten angeregten Triplett-Zustand, der in unterschiedlichen Lösungsmitteln und PMMA-Matrix charakterisiert wurde. Die Komplexe wurden in Triplett-Triplett-Energietransfer Abfangexperimenten und als Sensibilisatoren für Isomerisierungsreaktionen eingesetzt.

Alle Projekte dieser Dissertation beziehen sich auf angeregte Triplett-Zustände als Schlüsselintermediate, die durch unterschiedliche Wege zugänglich gemacht werden und für die zwei wichtigsten photochemischen Prozesse – Elektronen- und Energietransfer – genutzt werden. Detaillierte mechanistische Untersuchungen dieser Triplett-Zustände erlauben aussagekräftige Analysen der unterschiedlichen Triplett-Bildungsmechanismen sowie deren effiziente Nutzung in bimolekularen chemischen Prozessen. Daher trägt diese Doktorarbeit zu einem besseren mechanistischen Verständnis von photochemischen Prozessen mit angeregten Triplett-Zuständen bei, was Anwendungsmöglichkeiten bietet und direkte Auswirkungen auf die Gebiete Photokatalyse, Technologien, bei denen Spinmultiplizitäts-Änderungen eine Rolle spielen, oder Aufwärtsskonversion hat und im Allgemeinen bei der Umwandlung von Licht in andere Energieformen von besonderer Bedeutung ist.

Contents

1	Introduction	2
1.1	Motivation of the thesis	2
1.2	Principles of photochemistry	5
1.2.1	Energy diagrams and transitions	5
1.2.2	Intersystem crossing	7
1.2.3	Rate constants and lifetimes	8
1.2.4	Bimolecular quenching	9
1.2.5	Advantages of triplet excited states	14
1.3	Current literature and applications of triplets	19
1.3.1	Photochemistry in water	19
1.3.2	Combining properties of metal complexes and organic chromophores	21
1.3.3	Reactivity control	29
1.3.4	Back electron transfer-induced triplet formation	33
1.3.5	Sensitized triplet-triplet annihilation	35
1.4	Outline of the projects	40
2	Photochemistry of triplet states in aqueous solution	44
2.1	Sensitization-initiated electron transfer	44
2.1.1	Sensitization-initiated electron transfer with blue light	45
2.1.2	Sensitization-initiated electron transfer with green light	52
2.2	Organic photo(redox) catalyst with triplet-mediated energy and electron transfer reactivity	90
2.3	Dyads as mechanistic switch between energy and electron transfer	96
2.3.1	Ruthenium-based dyads	96
2.3.2	Iridium-based dyads	107
2.4	Back electron transfer-induced triplet formation	112
3	Photochemistry of triplet states in organic solvents	118
3.1	Molybdenum complex as triplet sensitizer for upconversion and as photoredox catalyst	118
3.2	Theoretical calculations supporting annihilator design and experimental findings	136
3.3	Insights into properties of triplet excited ligand-centered states in heteroleptic platinum(II) complexes	148

4	Conclusion and future perspectives	162
4.1	Photochemistry of triplet excited states in aqueous solution	162
4.1.1	Sensitization-initiated electron transfer	162
4.1.2	Organic photo(redox) catalysis with triplet-mediated energy and electron transfer reactivity	164
4.1.3	Dyads as mechanistic switch between energy and electron transfer	165
4.1.4	Back electron transfer-induced triplet formation	165
4.2	Photochemistry of triplet excited states in organic solvents	166
4.2.1	Molybdenum complex as triplet sensitizer for upconversion and as photoredox catalyst	166
4.2.2	Theoretical calculations supporting annihilator design and ex- perimental findings	167
4.2.3	Insights into properties of ligand-centered triplet excited states in heteroleptic platinum(II) complexes	167
5	References	169
6	Appendix	184
6.1	General experimental details for unpublished data	184
6.2	Additional data and supporting Information for Sensitization-initiated electron transfer with blue light (Section 2.1.1)	186
6.2.1	General experimental details	186
6.2.2	Synthesis and characterization	186
6.2.3	UV-Vis spectra of iridium-based complexes and naphthalene- and <i>p</i> -terphenyl-based organic chromophores	189
6.2.4	Potentials of water-soluble naphthalenes and terphenyls	190
6.2.5	Excited state kinetics and transient absorption spectra for cat- alytic mechanism in Figure 18:	191
6.2.6	Spectroscopic data for MC–OC systems with enhanced Coulom- bic interactions:	195
6.3	Additional data and Supporting Information for sensitization-initiated electron transfer with green light (Section 2.1.2)	198
6.4	Additional data and Supporting Information for Iridium-based dyads (Section 2.3.2)	201
6.4.1	General experimental details	201
6.4.2	Synthesis and characterization	201
6.4.3	UV-Vis spectra in aqueous solution	204
6.4.4	Lifetimes of the excited states and E_T energies	205
6.4.5	Energetic considerations for potentials of the dyads	207
6.4.6	Additional quenching experiments	208

6.5	Additional data and Supporting Information for back electron transfer-induced triplet formation (Section 2.4)	210
6.5.1	Additional transient absorption spectra with reductive quenchers	211
6.5.2	Additional data for triplet formation after reductive quenching with Br ⁻	212
6.5.3	Additional quenching experiments related to the external heavy atom effect	214
6.6	Additional data and Supporting Information for Molybdenum complex as triplet sensitizer for upconversion and as photoredox catalyst (Section 3.1)	217
6.7	Supporting Information for Sensitization-initiated electron transfer with green light (Section 2.1.2)	219
6.8	Supporting Information for Organic photo(redox) catalyst with triplet-mediated energy and electron transfer reactivity (Section 2.2)	289
6.9	Supporting Information for Dyads as mechanistic switch between energy and electron transfer (Section 2.3)	322
6.10	Supporting Information for Molybdenum complex as triplet sensitizer for upconversion and as photoredox catalyst (Section 3.1)	365
6.11	Supporting Information for Theoretical calculations supporting annihilator design and experimental findings (Section 3.2)	470
6.12	Supporting Information for Insights into properties of triplet excited ligand-centered states in heteroleptic platinum(II) complexes (Section 3.3)	499

List of abbreviations

A	electron acceptor
An	annihilator
ACP	acetophenone
Asc ²⁻	ascorbate dianion
bpy	2,2'-bipyridin
Bz	benzene
CT	charge transfer
D	electron donor
ΔG	Gibbs free energy
DFT	density functional theory
TD-DFT	time dependent-density functional theory
DMA	<i>N,N</i> -dimethylanilin
DPA	9,10-diphenylanthracene
EA	energy acceptor
ED	energy donor
E_{ox}	oxidation potential
E_{red}	reduction potential
E_{T}	triplet energy
ET	energy transfer
eV	electronvolt
η	efficiency
FRET	Förster resonance energy transfer
HAsc ⁻	ascorbate monoanion
$h\nu$	photon
IC	internal conversion
iEnT	intra molecular energy transfer
(b)ISC	(back) intersystem crossing
k_{n}	rate constant for process n
LC	ligand centered
LED	light emitting diode
MC	metal complex
MeOHPhOH	methoxyphenol

MLCT	metal-to-ligand charge transfer
NHE	normal hydrogen electrode
nm	nanometer
nr	non-radiative
OC	organic chromophore
OLED	organic light emitting diode
PC	photocatalyst
PDS	pyrene-1,3,6,8-tetrasulfonate
PDT	photo dynamic therapy
phen	1,10-phenanthroline
ppy	2-phenylpyridine
PS	photosensitizer
Py	5-(pyren-1-yl)1,10-phenanthroline
ϕ	quantum yield
Q	quencher
SCE	saturated calomel electrode
T _n	triplet state at n th vibratory level
TA	transient absorption
TADF	thermally activated delayed fluorescence
TIPS	triisopropyl-acetylene
TMS	trimethyl-acetylene
tpe	tris(pyridyl)ethane
TTET	triplet-triplet energy transfer
τ	lifetime
S _n	singlet state at n th vibratory level
sTTA UC	sensitized triplet-triplet annihilation upconversion
UV	ultra violet
Vis	visible

1 Introduction

1.1 Motivation of the thesis

In photochemistry, interactions between light and molecules are investigated. On a molecular level, those interactions are electronic transitions, which classify those molecules as chromophores. Transitions within a certain energy range are responsible for colors resulting from absorption, transmission or emission processes. After absorption, the energy of visible photons is often transformed in fast decay processes into vibrational energy, finally converting the photon energy into heat. Specific chromophores are promoted into photoactive excited states. This excited state "stores" the energy of the light for a certain period of time, the lifetime of an excited state. Decay of the excited state entails the release of the stored energy, which can be implemented *via* various pathways. This property makes excited states highly interesting and the focus of investigation for photochemistry and all related fields.

Utilizing the energy of visible photons has intrigued researchers since the beginning of the 20th century^[1] and since then the number and complexity of investigated photoresponsible systems or chromophores have increased drastically.^[2-6] Based on fundamental photochemical principles, the results of such research have conceptualized and optimized broadly used technological devices in the form of, for example, (O)LEDs and solar cells.^[7-9] Besides that, photochemistry is relevant in medicinal and biological fields. Within the challenging cellular or aqueous environments chromophores are used for bio-imaging and microscopy techniques or in photo-dynamic therapy (PDT).^[10-14] Another large field of photochemistry is associated to synthesis driven by photocatalysts or photocatalytic systems.^[15,16] In addition to laboratory syntheses^[17,18], photochemistry has been implemented in selected industrial steps out of which probably the most famous example is the production of the anti-malaria drug artemisinin by Sanofi.^[19] Every individual application and technology framework comes with specific and increasingly complex requirements, thereby making photochemistry a diverse and highly relevant field of research.

Photochemistry is often correlated to sustainability and/or "green" chemistry. Historically this linkage has been justified by considering the possibility of driving chemical reactions with light, ideally with light from the sun, instead of fossil fuels.^[1] In the 1990s the term "green chemistry" was defined more strictly and general principles were developed by P. T. Anastas and J. C. Warner (later N. Eghbali).^[20,21] Their concept is a holistic viewpoint on chemical processes, and sustainability within this framework considers aspects throughout an entire process including experiment design, atom economy, waste disposal, energy consumption, solvent disposal or recycling, to name a few. Photochemistry intrinsically agrees well with several of those principles and is therefore

a reasonable starting point for improvement and development of strategies aiming at a broader implementation of sustainability in chemistry.^[3,18,21,22]

Possible developments targetting aspects of the technological fields and sustainability in general are: i) Transition to solvents that are classified as "green", such as water (Figure 1). Besides being considered sustainable,^[23,24] aqueous systems are also interesting for bio-medicinal applications operating in highly complex aqueous environments.^[24–26] ii) Replacing photocatalysts and complexes based on precious metals with either earth-abundant metals or purely organic chromophores (Figure 1). Metal-based chromophores often contain ruthenium, iridium or osmium with limited availability on Earth. Replacing them is therefore interesting from an economic point of view and in a long-term perspective most likely inevitable.^[15,27–29] iii) Increase the overall efficiency of light-driven mechanisms (Figure 1). Efficiency includes several aspects such as energy conversion, photon usage or side product elimination. Those considerations can be decisive for future implementation of photochemistry in industrial and large-scale procedures.^[16,30,31] iv) Development of novel (multiple photon) mechanisms and strategies for highly specified applications in increasingly complex and challenging systems (Figure 1). Sophisticated mechanisms target the optimization of catalytic cycles^[5,32] or for combining the energy of two (or more) photons, such as in sensitized triplet-triplet annihilation up-conversion (sTTA UC). For example mercury-containing UV lamps can be avoided by using blue-to-UV upconversion systems, thereby completely eliminating the hazards entailing the production, use and disposal of such light sources.^[33–35]

To meet such requirements and as prerequisites for implementing photon-based technologies, the underlying processes and mechanisms must be understood in detail. For such insights optical spectroscopic methods are key and within this dissertation, transient absorption (TA) spectroscopy on nanosecond-to-millisecond timescales is the method of choice for providing information about chromophores in their excited states and diffusion-based processes on a temporal and spectral resolution.

Combined with theoretical considerations and test reactions, such investigations have the potential to substantially optimize photochemistry and photochemical processes for example by increased efficiencies,^[36–38] or identification of key reactive species^[39–42]. One fundamental aspect of photochemistry is the spin multiplicity of a chromophore in its excited state. Most organic molecules and the metal complexes that are relevant within the framework of this dissertation exist in a singlet ground state. Exceptions for singlet ground-states are some *d*-metal complexes^[43–46] or oxygen^[47].

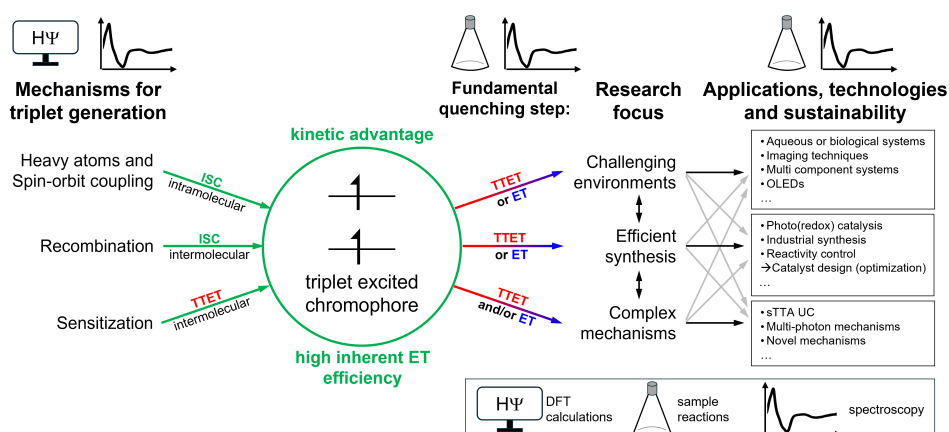


Figure 1: Illustration of triplet excited states, different methods of accessing them (left part), the fundamental quenching steps and possible research areas. The right side of the figure illustrates examples for different fields of application. The arrows indicate the direct (black) or indirect (gray) connection of the individual fields. See text for further explanations.

After light absorption and population of the singlet excited state, the multiplicity can change under certain conditions into a triplet multiplicity through intersystem crossing (ISC, Figure 1, left part).^[48,49] ISC and including triplet excited states had a substantial impact on OLEDs, making devices of the 2nd to 4th OLED generation intrinsically more efficient by up to 75 %.^[7,50] For bimolecular, diffusion-based processes, triplet species have substantial advantages (Figure 1, green circle) with respect to kinetics and the overall efficiency of the quenching process (cage escape). In a broader perspective, those improvements are transferred to all following processes and finally to the applications resulting in more efficient conditions for example in photo(redox) catalysis or multiphoton mechanisms such as sensitized triplet-triplet annihilation upconversion (sTTA UC). The figure also illustrates the pronounced interdisciplinarity of photochemistry, especially when triplet species are involved. For example, thermally-activated delayed fluorescence (TADF) emitters are employed in OLEDs^[7,51], in photo(redox) catalysis^[40,51,52] and as sensitizers in sTTA UC schemes.^[33,53]

Accessing triplet excited states together with their inherent advantages, however, requires certain molecular properties or (and) specific conditions of the chromophore's direct environment (*p. ex.* solvent, additives). Intramolecular prerequisites for ISC include heavy atoms, a high spin-orbit coupling or charge separation (Figure 1 Mechanisms for triplet generation).^[15,51,54,55] Several intermolecular processes are employed to obtain triplet excited states, among which sensitization and recombination are relevant for this thesis (external heavy atom effects or singlet fission are beyond the scope of this thesis).^[5,50,56,57]

1.2 Principles of photochemistry

This second section establishes important fundamental concepts and principles, which lay the grounds for the projects presented in the thesis. Some links and references to current literature are provided, this however will be the focus of Section 1.3.

1.2.1 Energy diagrams and transitions

The transitions that are important for photochemistry and for this work are generally within the energy range of visible photons (400 nm to 750 nm corresponds to 3.1 eV to 1.7 eV) with some extensions into parts of the ultra violet (UV) energy regime (~ 300 nm to 400 nm corresponds to 3.1 eV to 4.1 eV). In visible light spectroscopy transitions between states of different electronic (bold, horizontal lines in Figure 2) and vibrational (thin, horizontal lines in Figure 2) energies (vibronic transitions) are analyzed. Such energy schemes are simplified representations of the energy potentials resulting from solutions of the time-independent Schrödinger equation, assuming no interaction between the nucleus and electrons (Born-Oppenheimer-approximation).^[49,58,59] A transition describes an electron changing its energy level, *e.g.* it is promoted into a higher-lying state upon applying an external stimulus. Consequently, transitions are time-dependent and described in quantum mechanics by perturbation theory.^[49,59] The transitions illustrated in the energy diagram in Figure 2 are based on the following approximation (similar to the Born-Oppenheimer-approximation): It is assumed, that the electronic transition to a different energy level is very fast compared to the nuclear movement. Consequently, the transition occurs within one nuclear framework (vertical transition), which adjusts to the new electronic state only after the transition is finished (Franck-Condon-principle). A transition is only possible if the overlap integral of the wavefunctions of the two involved energy states is non-zero. For that reason, transitions into higher vibrational levels of an electronic state are often more intense than the transition to the vibrational ground state. The squared overlap integral (Franck-Condon-factor) is one of the three factors, contributing to the probability, and therefore intensity of a transition. The other two factors are the transition dipole moment and the electron spin, which both also have to be non-zero for a transition to occur. The latter has to be preserved within the Franck-Condon-principle and spin changes are strictly forbidden, exceptions to this rule are discussed in the next section (Section 1.2.2).^[49,58,60]

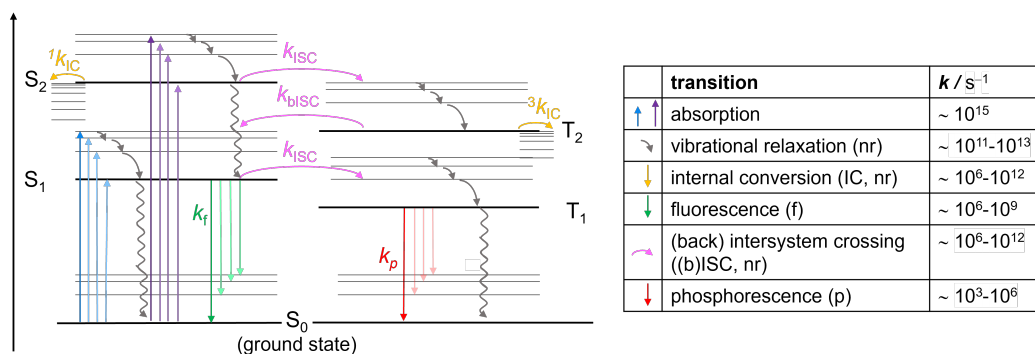


Figure 2: Simplified energy diagram of a molecule in its singlet ground state, the excitation and relaxation processes. The general rate constants and examples for their usual magnitudes^[58,59] are given in the table.

The transitions in Figure 2 illustrate the basic processes for a compound with a singlet ground state. The absorption of a photon promotes an electron into the first (blue), second (violet) or higher-lying orbital, thereby reaching a singlet excited state, which depends on the energy of the photon. The first electronically excited state (S_1) decays *via* fluorescence from its vibrational ground state (green arrows). The gray arrows indicate vibrational, non-radiative decay to the respective vibrational ground state (Kasha's rule). Internal conversion (IC, orange) is the non-radiative transition between electronic states without changing the spin multiplicity. To obtain a full image of the excited state transitions, the figure also shows the multiplicity-changing (back)intersystem crossing ((b)ISC, pink), which is isoenergetic and non-radiative. The transitions shown include triplet excited states (here T_1 and T_2) and the molecular prerequisites for those transitions are detailed in Section 1.2.2. Within the triplet manifold the same non-radiative pathways, internal conversion (IC, orange) and vibrational relaxation (gray) are common. The radiative decay from the electronic state, back to the ground state involves also a change in multiplicity and is called phosphorescence (red).^[48,58,59]

In optical absorption spectroscopy, vertical transitions for the excitation starting from the vibrational ground state (S_0) are resolved, providing information about the energy that required for the transition (wavelength) and the probability of the transition to occur (intensity). The Beer-Lambert law in the following equation 1 gives a linear relation between the absorbance (A) at a given wavelength and the path length of the light through the solution (d), the concentration of the chromophore (c) and the molar extinction coefficient (ϵ), which is a characteristic parameter for a chromophore:^[58,59]

$$A = \lg \frac{I_0}{I} = d \times c \times \epsilon \quad (1)$$

For the physical measurement of the absorbance (A) the decadic logarithm of the original excitation light-intensity (I_0) divided by the light intensity after passing through the

sample (I) is plotted against the wavelength (optical density can also be employed to replace the term absorption)^[58]. The molar extinction coefficient connects the physical measurement to quantum mechanics. ε is proportional to the oscillator strength of the transition, and consequently can be correlated to the transition dipole moment.^[48,58]

The molar extinction coefficient is also useful for calculating the fluorescence decay rates from the excited state back to the ground state.^[59] A Strickler–Berg analysis connects the energy of a transition and the extinction coefficient to its decay rates. Estimations of the excited state decay rates with the (simplified) Strickler-Berg analysis^[48,61,62], have been employed for the project discussed in Section 2.2 and the corresponding publication.^[63]

Insights into the absorption properties and lifetimes of the electronically excited states are provided by transient absorption (TA) spectroscopy. A TA spectrum shows the difference absorption spectrum between the ground state and the excited state and consequently the derived values are the difference in optical density (ΔOD) and the difference extinction coefficient ($\Delta \varepsilon$).

1.2.2 Intersystem crossing

The transitions discussed in the previous section would not explain a change in spin multiplicity, because the transition moment between two states of orthogonal spin vanishes and the transition is therefore spin forbidden.^[48] Intersystem crossing, however, does require a spin contribution and an extension of the descriptive methods used so far. The most famous integration of spin-contributions into vibronic transition is probably spin-orbit coupling. This contribution is derived by coupling the spin and orbital magnetic moments, representing the magnetic field experienced by the electron. A generalized form of the resulting Hamiltonian $\hat{H}$ for spin-orbit coupling is given in the following equation involving the interaction of operators for the spin $\hat{s}$ and orbit $\hat{l}$ angular momentum, and the spin-orbit coupling constant ζ :^[49,58]

$$\hat{H}_{SO} = \sum \zeta \hat{l} \times \hat{s} \quad (2)$$

A direct derivation from this equation is the heavy atom effect. ζ is a constant originating from magnetic field parameters, including atomic number and the charge of the nucleus that is experienced by the electron. The fact that ζ is proportional to the fourth power of the atomic number ($\sim Z^4$) increases the effect of heavy atoms on the hamiltonian ($\hat{H}_{SO} \sim Z^4$) thereby making intersystem crossing more allowed for heavier atoms.¹ Generally, sulfur is already considered a heavy atom and therefore held responsible for

¹The heavy-atom effect is divided into internal and external contributions. Within the framework of this thesis, mostly the internal heavy atom effect will be relevant.

enhanced intersystem crossing in sulfur-containing compounds. For halogens, the effect becomes increasingly stronger going down in the periodic table ($\text{Cl} < \text{Br} < \text{I}$).^[60,64]

A second rule that is related to equation 2 is the El Sayed rule, which states that ISC is efficient if the involved orbitals change their type. In other words, a change in spin is only allowed if the orbital angular momentum also changes. The textbook examples for such transitions are carbonyls involving a multiplicity change, which is possible owing to a transition between orthogonal orbitals $^1\text{n}\pi \rightarrow ^3\pi\pi$ and $^1\pi\pi \rightarrow ^3\text{n}\pi$.^[59,65] Qualitatively, this observation can be rationalized considering the angular momentum operator ($\hat{l}$), which couples only the orthogonal contributions of involved orbitals. For ketones, those are exactly the transitions mentioned before. This consideration is also the explanation for intersystem crossing involving the d -orbitals in transition metal complexes.

Other quantum mechanical considerations, which explain ISC, are spin-spin coupling and hyperfine couplings. Spin-spin couplings (dipole interaction between electronic spins) involve just electronic spin components.^[49,66] Hyperfine coupling (dipole-dipole interaction of nuclear and electronic spin) is considered in ISC processes that involve charge transfer (CT) in collision-based bimolecular processes or in charge-transfer excited states of donor-acceptor structured molecules (Section 1.2.5).^[60,67]

1.2.3 Rate constants and lifetimes

The lifetime (τ) of a species, decaying according to a first-order process, is defined as the time required for the initial concentration (N) to be reduced to $\tau = N/e$. The general relation between a lifetime of a process and the rate constant is:^[48,58]

$$\tau = \frac{1}{\sum_n k_n} \quad (3)$$

The lifetimes measured by optical methods are usually a combination of all possible process. As a consequence, a fluorescence lifetime (τ_0) consists of the following processes: the isolated fluorescence (k_{fl}^0), non-radiative decay (k_{nr}) and ISC (k_{ISC}). The rate constant, derived from lifetime measurements is k_{fl} :^[48,58,59]

$$\tau_0 = \frac{1}{k_{\text{fl}}^0 + k_{\text{nr}} + k_{\text{ISC}}} = \frac{1}{k_{\text{fl}}} \quad (4)$$

With the fluorescence quantum yield, the k_{fl}^0 can be calculated ($\phi_{\text{fl}} = k_{\text{fl}}^0 \times \tau_0$, see Section 1.2.4 for more information and reference [48]). The decay rate for the isolated fluorescence can be Bimolecular processes, such as energy or electron transfer, also have an impact on the lifetime. The quenching process is thus a further possible decay pathway, which depends on the concentration of the quencher molecule ([Q]):

$$\tau_q = \frac{1}{k_{\text{fl}} + k_q[\text{Q}]} \quad (5)$$

The same principles and considerations hold true for the decay of species with a triplet multiplicity (lifetime: τ_T), except the indices are related to triplet based processes with the isolated phosphorescence decay rate (k_p^0), the rate for non-radiative decay (k_{nr}), (the decay rate for the unquenched process, k_T). The lifetime for triplet decay including a quencher is:

$$\tau_T = \frac{1}{k_p^0 + k_{\text{nr}} + k_q[\text{Q}]} = \frac{1}{k_T + k_q[\text{Q}]} \quad (6)$$

Those equations give information about a quenching process at one certain quencher concentration. To analyze bimolecular quenching processes in a reliable way, Stern–Volmer-quenching experiments are performed.^[48,58,59]

1.2.4 Bimolecular quenching

Stern–Volmer:

A Stern–Volmer analysis gives information about a single-step bimolecular quenching process between a chromophore in its excited state and a quencher molecule. Besides the quenching rate constant (k_q) this type of study can provide also information about the static or dynamic nature of the mechanism.^[68,69] For this thesis, Stern–Volmer-studies are employed for electron or energy transfer quenching and depending on the underlying mechanism the general quenching rate constant (k_q) is related to the respective mechanism (k_{TET} for triplet-triplet energy transfer and k_{ET} for electron transfer, the mechanisms and thermodynamic requirements are detailed later in this section).

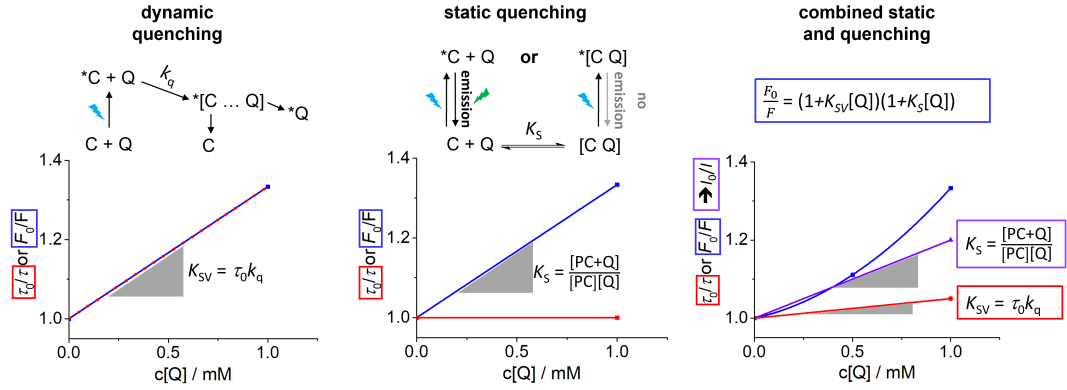


Figure 3: Schematic Stern–Volmer plots in different quenching scenarios for lifetime-based (τ_0/τ , red) or emission intensity- based (F_0/F , blue) data: For purely dynamic quenching and static quenching the respective key mechanistic steps are shown using a chromophore (C) and a quencher (Q). The equations allow to calculate the involved variables. For more information see text below.

The dynamic or diffusional quenching mechanism (left part of Figure 3) is operating if only the excited state of the chromophore (*C) interacts with the quencher. In the exemplary mechanism shown, the excited quencher (*Q) is produced (equations and principle are equally valid for photon induced electron transfer). An equal decrease in lifetime and emission intensity (τ_0/τ or F_0/F) can be measured. According to the Stern–Volmer- equation, the detected decrease can be fitted in a linear plot with the slope K_{SV} out of which the quenching rate k_q for the system under investigation can be extracted:^[48,58,68,70]

$$\frac{\tau_0}{\tau} = \frac{\frac{1}{k_0}}{\frac{1}{k_0 + k_q[Q]}} = 1 + \frac{k_q[Q]}{k_0} = 1 + \tau_0 k_q[Q] = 1 + K_{SV}[Q] \quad (7)$$

In static quenching, the lifetime is unchanged upon quencher addition, but the emission intensity is reduced. This intensity decrease is caused by preassociation, which results in an equilibrium between free chromophor molecules (C) in solution and the coordinated version chromophor - quencher ($[CQ]$). For this boundary case, the emission of free chromophores (C) is completely unaffected by the quencher (no change in lifetime, indicated by the green lightning in the figure), whereas chromophores coordinated to the quencher do not decay in a radiative process after excitation (no emission, gray arrow in the figure). As a result, the number of free, emissive chromophores – and therefore the emission intensity – changes with quencher concentration due to the prassociation process. The slope of the intensity-based Stern–Volmer plot gives the association constant K_S , whereas the lifetime-based plot remains unchanged. Most systems feature a combination of static and dynamic quenching. In this case, the emission intensity-based

Stern–Volmer plot can be fitted quadratically with respect to the quencher concentration ($[Q]$), and combined with the linear lifetime-based plot, all characteristic variables (k_{SV} and K_S) can be determined.^[68,69]

Efficiency and quantum yield:

The efficiency (η) of a photokinetic step is defined as the rate constant of one step (k_x) in relation to the sum of all rate constants for all possible competing processes originating from the excited state (equation 8).^[58] The quenching efficiency provides information on the ratio of initiating species that collides with a quencher and therefore depends on the quencher concentration. Using the Stern–Volmer-equation (7), equation 8 can be rearranged to equation 9 and this method for calculating the efficiency of a quenching step is used in Section 1.2.5:

$$\eta_x = \frac{k_x}{\sum_i k_i} \quad (8)$$

$$\eta = \frac{\tau_0 - \tau}{\tau_0} \quad (9)$$

In addition to the quenching efficiency, also success of the quenching ("efficiency for quenching-product formation") must be taken into account, *i.e.* the ratio between collisions of the quencher and the initiating species and generated desired product. This consideration takes into account that several quenching pathways are possible, out of which not all are productive (more explanations in Section 1.2.5).²

The quantum yield (ϕ_x , equation 10) provides information about the fraction of photons that induce a process (x) out of all absorbed photons, in other words, the absorption efficiency (ϕ_{abs}) multiplied by the efficiency of a process:^[48,58]

$$\phi_x = \frac{\# \text{ processes}}{\# \text{ absorbed photons}} \sim \phi_{abs} \times \eta_x \quad (10)$$

For a quantum yield after consecutive photoninduced processes the efficiencies of the individual steps are multiplied (as an example see quantum yield for upconversion equation 14 in Section 1.3.5). The distinction between quantum yield and efficiencies is of great importance: A quantum yield is related to the photons invested in a light-induced process (*e.g.* ϕ_{CE} in Section 2.1.2 takes absorption and sensitization into account).^[58] Efficiency on the other hand is only related to one quenching and/or formation step (see above). In bimolecular processes, high efficiencies are prerequisite for high quantum yields. This becomes relevant in the following section (Section 1.2.5) and the distinction will also be made for the project presented in Section 2.3.

²Both efficiencies are referred to in Section 2.1.2 as quenching efficiency (η_{q1} and η_{q2}) and cage escape efficiencies (η_{CE1} and η_{CE2}).

In addition to the quantum yield, the energy ratio comparing the energy of a photon with the energy of the reaction-initiating species is also important. For a quantitative comparison, the energy of the photon (in eV) will be compared to the redox potential provided by the reactive species to drive the reaction (measured as potentials relative to the normal hydrogen electrode, V vs NHE), which will be referred to as efficiency of input-photon energy usage. Those comparisons will be especially important for Section 2.1. Even though the values of the redox potentials depend on the reference electrode, thereby making the value change depending on the employed reference, this comparison is useful and possible for the following two reasons: i) The normal hydrogen electrode was defined as reference point for several energetic and electrochemical considerations.^[71] ii) To determine the redox potential of compounds, they have to be measured against an electrode, which in literature is often not the normal hydrogen electrode. Comparing the efficiency of input-photon energy usage between two compounds, requires the potentials to be referenced against the same reference. For this thesis the reference will be the normal hydrogen electrode, see i). This comparison would also be possible with respect to a different electrode, which would only change the absolute values, but not the relative "ranking" of the compared compounds.

Energy transfer quenching:

There are three fundamental pathways for energy transfer processes between an excited chromophore and a quencher: Emission - reabsorption, Dexter energy transfer^[22,72] and Förster resonance energy transfer (FRET)^[73,74] out of which the two latter are relevant for the thesis and schematically illustrated in Figure 4.

During a **reabsorption** (sometimes trivial energy transfer) the excited chromophore emits a photon, which is absorbed by a second molecule.^[48]

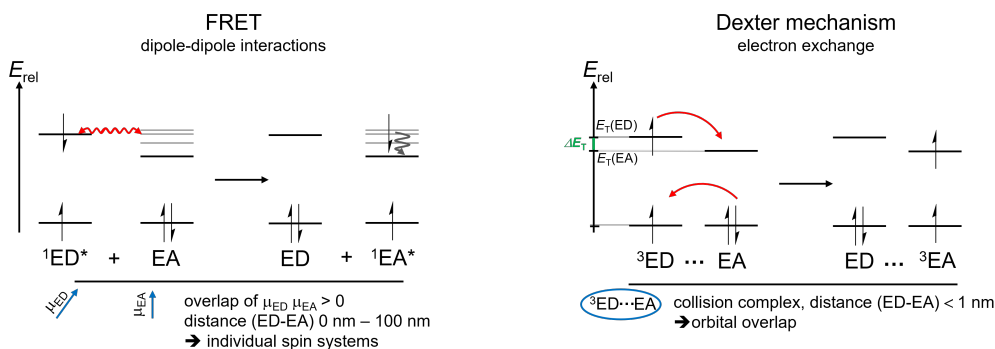


Figure 4: Mechanistic scheme for Förster resonance energy transfer (FRET, left) and Dexter energy transfer (right). The red arrows indicate the fundamental step between energy donor (ED) and acceptor (EA): electron exchange for Dexter, resonance for FRET. Interactions between ED and EA are highlighted in blue: orbital overlap for Dexter, transition dipole moments for FRET.

FRET is a radiationless dipole-(induced)dipole interaction between an excited energy donor and an acceptor in the ground state (Figure 4, left part). For a successful FRET, the orientational factor of the transition dipole moments must be unequal zero (indicated by the blue arrows in the figure), and because molecular rotations are fast in solution, this contribution is an averaged value.^[59] Immediately after the energy transfer the acceptor is vibronically excited, which decays fast to the lowest vibratory level (gray, wavy arrow in the figure). Owing to the fact, that FRET is a long-range (0 nm to 100 nm)^[59,68] resonance-based interaction between excited donor and acceptor, the two molecules are considered individual spin systems. The individual spins are conserved throughout the process and for that reason, FRET is observed almost exclusively for singlet-singlet energy transfer.^[22]

As a consequence, FRET occurs with a high likelihood if the overlap integral of the energy donor emission and absorption of the energy acceptor is non-zero. This consideration indicates that the energy for excitation of EA must be equal or smaller than the E_{00} of ED for a successful FRET.

The **Dexter** mechanism describes a triplet-triplet energy transfer. The energy donor and acceptor have to be in close proximity, such that their orbitals overlap (collision complex $^3\text{ED} \cdots \text{EA}$) and an electron exchange is possible (red arrows in Figure 4, right). Owing to the orbital overlap between donor and acceptor, conservation of the total spin becomes relevant (opposed to the individual spins in FRET), which makes this mechanism well suited for triplet-triplet energy transfer. The relevant spectral overlap therefore includes the phosphorescence spectrum of the ^3ED and the singlet to triplet absorption of EA.^[22,59] The feasibility for a Dexter-type energy transfer is estimated thermodynamically using the triplet energies of donor and acceptor (see relative energies in Figure 4)^[22]:

$$\Delta E_T = E_T(\text{EA}) - E_T(\text{ED}) \quad (11)$$

The rate constant for triplet-triplet energy transfer (k_{TET}) can be described as a Boltzmann distribution with respect to the energy difference (ΔE_T) and the rate constant for diffusion.

For $\Delta E_T < 0$ the energy transfer is thermodynamically feasible and k_{TET} is close to the diffusion limit. For the opposite case $\Delta E_T > 0$, the energy transfer becomes slow and quickly drops below the diffusion limit. For $\Delta E_T = 0$, k_{TET} should be exactly half the diffusion rate constant.^[22,59,68,75]

Such considerations allow the relative estimation of the excited state energies based on quenching experiments. More sophisticated models of the Boltzmann distribution allow the corrections for experimental variances from the ideal assumptions (*e.g.* substantial structural differences between singlet and triplet structures).^[42,59,75–77]

Electron transfer quenching:

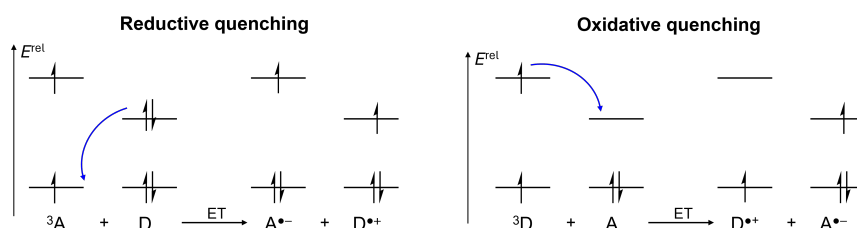


Figure 5: Mechanistic schemes for reductive (left) and oxidative (right) electron transfer (ET) quenching of triplet-excited molecules. Either of the molecules, acceptor (A) or donor (D), can be excited, thereby facilitating the electron transfer.

In their excited state, chromophores are both better oxidizing and reducing agents and the quenching process depends to a great extent on the thermodynamics (Figure 5, the spin contributions are discussed in detail in Section 1.2.5).^[59,65] The thermodynamic feasibility of a photoinduced electron transfer reaction is derived from the Rehm–Weller equation, which correlates ΔG_{ET} to the rate constant (k_{ET}) and is given by:^[65,78,79]

$$\Delta G_{ET} = E_{ox}(D^{\bullet+}/^0) - E_{red}(A^0/^{\bullet-}) - E_{00} - w \quad (12)$$

E_{ox} and E_{red} are the respective ground state oxidation and reduction potentials of the electron donor (D) or acceptor (A), E_{00} is the excited state energy and w is an electrostatic term, representing a solvent-dependency. w depends on the charge of reactants and products and the dielectric constant of the solvent (inverse relation). The first contribution to w becomes zero if an uncharged species is involved in the process and the second becomes small (<0.1 eV) in highly polar solvents (like water).^[65] As for collision-based energy transfer, the quenching rate (k_{ET}) can be correlated to the Gibbs free energy of the electron transfer (ΔG_{ET}) in a Rehm–Weller plot. Those plots allow determining unknown redox potentials by comparative quenching experiments.^[79–82]

For quenching rates at the diffusion limit ($k_{ET} = k_{diff}$), the driving force for the electron transfer is smaller than zero ($\Delta G_{ET} < 0$). For small and slightly positive driving forces ($\sim -0.1 < \Delta G_{ET} < 0.3$) rate constants can differ by orders of magnitude (below the diffusion limit) of the employed solvent.^[78,83]

1.2.5 Advantages of triplet excited states

Kinetic advantage:

For an efficient photochemical reaction, it is essential that the excited state has a sufficiently long lifetime in order to encounter a suitable reaction partner in solution. The likelihood of an encounter increases with the lifetime of the excited species. This qualitative consideration is rationalized by considering the efficiency of a quenching process

(“likelihood of an encounter” η , Equation 9) and the lifetime of a species in the presence of a quencher (solving Equation 7 for τ):

$$\eta_q = \frac{\tau_0 - \frac{1}{\frac{1}{\tau_0} + k_Q[Q]}}{\tau_0} = 1 - \frac{1}{1 + \tau_0 k_Q[Q]} \quad (13)$$

The quenching efficiency η can be expressed as a function of the quencher concentration ($[Q]$) at a given quenching rate ($k_q = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, diffusion limit in water)^[48] and τ_0 . Figure 6 is a simulation for quenching efficiencies η_Q based on equation 13 with respect to the concentration of the quencher, assuming a diffusion limited process. The differently colored curves represent different lifetimes (τ_0) of the excited state.

The benefits of dyad-based long triplet excited state lifetimes were utilized by the Kerzig group in two recent publications. Taylor-made dyads allowed an efficient photocatalytic sensitization of $^3\text{O}_2$, which has an intrinsically low solubility under standard conditions.^[36,48,84] These studies contain similar kinetic simulations, however the efficiency η_τ was plotted as a function of τ_0 at a fixed O_2 concentration (in water 0.27 mM)^[48] for different quenching rate constants.^[36,84]

The possibility to work at low quencher concentrations and at the same time at high η_q enabled by a long lifetime of the excited state is essential in several diffusion-based photochemical processes and applications, such as sTTA (avoiding filter effects, Section 1.3.5), limited solubility (Section 1.3.1), or overall reaction efficiency (high η is the prerequisite for a high ϕ_{UC}). Moreover, the study presented in Section 2.3 and the corresponding reference [85] provides experimental data for nearly identical quenching rate constants at inherently different lifetimes of the sensitizer, which is of great benefit for the subsequent upconversion mechanism.

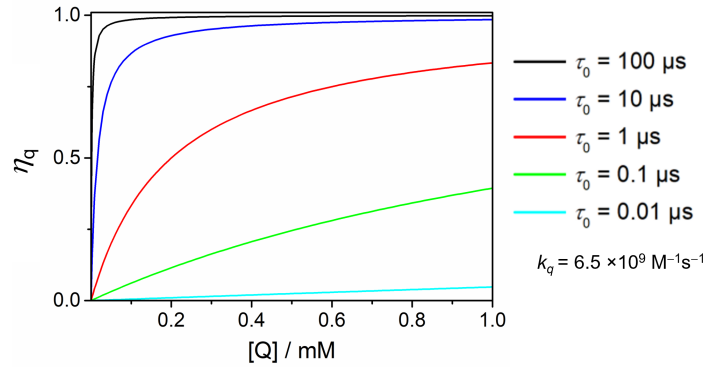


Figure 6: Simulation of η_q (equation 13) depending on the concentration of a quencher $[Q]$ according to equation 13 with $k_q = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

As for the rate constants, η_q is a general term for any quenching process. The quenching mechanism is implied by the index if the quenching mechanism is known (η_{ET} for electron transfer, η_{TTET} for triplet-triplet energy transfer).

Cage escape efficiency of ET reactions:

The previous section (1.2.4) sets the thermodynamic framework for electron transfer reactions and describes the kinetics of the bimolecular quenching step. In this section, the focus is laid on the quenching product and the efficiency of its formation (cage escape efficiency). As indicated by the equations (Section 1.2.3), the rate constants of all possible decay pathways contribute to the lifetime of an excited state. In other words, usually several processes are present and therefore possible unproductive competing decay pathways. The observed mechanism depends on thermodynamics and fast kinetics in favour of one quenching process. This section details how radical pair ISC and efficiency of dissociation from the solvent cage can influence the kinetics and rate constants in thermodynamically feasible reductive photon-induced electron transfer reactions (Section 1.2.4). The general concept is equally applicable to oxidizing reactions.^[86]

Figure 7 presents key mechanistic steps and intermediates for an electron transfer quenching in more detail.³ The reactants are a photocatalyst (PC) in its triplet excited state and a quencher that acts as an electron donor (D) in its ground state.

In a diffusion-based process, 3PC is quenched by electron transfer from D forming a spin-correlated radical pair (Figure 7). This step greatly benefits from a long lifetime of the triplet excited state as detailed in the previous section (kinetic advantage). Within the spin-correlated pair, the spins are not considered separate anymore but can be described in a total spin momentum. Respecting spin conservation, the correlated radical pair has the same multiplicity as the excited state of the photocatalyst, which is a triplet ($^3[PC^{\bullet-} \cdots D^{\bullet+}]$).

³Sometimes, more intermediates are included in the electron transfer mechanism,^[86] such as the solvent separated (ion)pair (PC and D share one spin momentum but are separated by one layer of solvent molecules) or the encounter complex (PC and D are in direct contact share one spin momentum and a solvent shell, but the electron transfer has not occurred yet). Those intermediates are not considered in the discussion of the mechanism. Generally, their initial multiplicity is also a triplet (conservation of the spin). With heavy atoms present, ISC into the singlet manifold is facilitated thereby making unproductive pathways available.

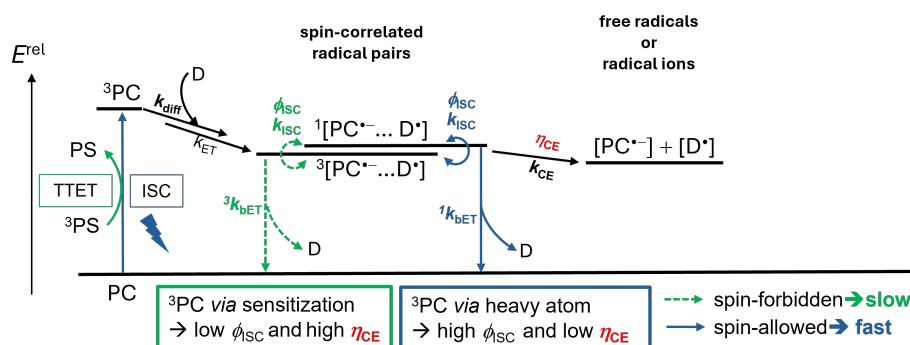


Figure 7: Schematic reaction mechanism for photoinduced electron transfer. Molecules involved are a photocatalyst (PC), an electron donor (D) and a photosensitizer (PS). The black arrows indicate the mechanistic steps, which occur regardless of PC multiplicity (diffusion-based encounter, k_{diff} ; electron transfer, k_{ET} ; cage escape, k_{CE}). The green arrows and box highlight the processes, that are relevant for a PC without intrinsic ISC: In this case, radical pair ISC is slow and unproductive recombination within the singlet multiplicity become irrelevant. The blue arrows and box highlight the processes that are relevant for a PC with intrinsic ISC based on a heavy atom: Within the radical pair, ISC is fast and unproductive pathways *via* singlet species become detrimental side reactions.

Three possible processes can follow the formation of the spin-correlated radical pair and the initial electron transfer: i) Dissociation of the spin-correlated radical pair forming the PC ground state and releasing the donor. This is a spin-forbidden process, therefore slow and non-competitive (green dotted arrow ${}^3k_{\text{bET}}$) ii) Intersystem crossing to the essentially energetically equal singlet radical pair, ${}^1[\text{PC}^{\bullet-} \cdots \text{D}^{\bullet+}]$ (k_{ISC} blue or dotted green round arrows in Figure 7). The efficiency of this process (ϕ_{ISC}) depends on the two reactants, which can enable fast ISC (see also Section 1.2.1). For heavy atom-containing PCs, often metal catalysts, radical pair ISC is still efficient and the dissociation from the resulting singlet manifold is spin allowed, and therefore a main competing pathway (blue arrow). For PCs without heavy atoms present, often organic chromophores, ISC is slow in the solvent cage and the dissociation would involve spin-forbidden processes. Consequently, this pathway is also slow and non-competitive. iii) The desired release of the free, uncorrelated ions, which is possible from both triplet and singlet manifold (cage escape, k_{CE}). Since recombination of single radical pairs is a competitive process (${}^1k_{\text{bET}} \geq k_{\text{CE}}$), the cage escape efficiency is inherently lower compared to that of the triplet radical pairs.^[69,86–89]

The described processes within the spin-correlated radical pair usually take place at shot (< 1 ns time scales).^[89–91] Diffusion-based recombination between the free ions is also a possible and unproductive pathway but in applications has mostly only minor contributions. The radical ions are usually consumed rapidly in the following reaction (for the $\text{D}^{\bullet+}$) or regeneration steps (for the $\text{PC}^{\bullet-}$).^[86,87,92]

The competing pathways originating from the singlet manifold of the spin-correlated radical pair are only possible for efficient ISC in the spin-correlated radical pair. This can be found especially if heavy atoms are involved in the PC, such as for ruthenium-, iridium-, or osmium-based metal complexes but also for heavy atom containing quenchers.^[87,92,93] A high ϕ_{CE} can be achieved by eliminating such pathways and avoiding the direct influence of heavy atoms in reaction intermediates. This has been done by Neumann *et al.* by designing a molecular dyad with a ruthenium-based metal complex, a xylene spacer and an anthracene organic chromophore. That way, the ruthenium part of the molecule provided a high ϕ_{ISC} and favourable energetics ensured fast energy transfer to the anthracene moiety. Sufficient spatial separation between ruthenium and the triplet reaction center located on the anthracene was provided by the xylene bridge, which enabled an increased ϕ_{CE} .^[92] A bimolecular approach is discussed in 2.1 with the corresponding publication.^[36]

1.3 Current literature and applications of triplets

1.3.1 Photochemistry in water

The solvent choice is an important factor in solution-based photochemistry. To introduce a "green" chemistry aspect, life cycle analyses help to classify and rank solvents regarding their sustainability.^[21,23,94] Literature provides several possibilities for replacing (halogenated) organic solvents with more sustainable alternatives including supercritical carbon dioxide, ionic liquids or liquid polymers to name a few.^[23,95]

According to green chemistry principles, water fulfills several sustainability criteria of a solvent.^[21,96] In literature it is discussed whether or not water can be classified as even "the greenest" solvent.^[23,24,96] However, inherent properties of water prevent its broad usage in synthesis and industry. The high polar and protic nature of water is responsible for precipitation or aggregation of apolar chemicals, and some reaction types, catalysts or intermediates do not tolerate water because reactands and intermediates decompose.^[97] An important factor in industry is the heat capacity of water resulting in high costs for heating or cooling.^[21,23] A clear advantage of water is its non-toxic nature, which is in line with the principle of utilizing safe solvents.^[21] However, if polluted throughout a chemical reaction, careful efforts and regulations for recycling and purification are required. Despite those challenges, water is a cost-efficient, broadly available, non-flammable and non-volatile solvent, which makes the solvent interesting for synthesis.^[23,24,98]

A second field for photochemistry in water is the relevance of chromophores in biological environments. For applications, such as bio-imaging, photodynamic therapy or the release of biologically active compounds, the photosensitizers and photoactive compounds have to be compatible with the aqueous and cellular environments.

In the following, four photochemistry-specific aspects are elaborated that need to be taken into account for photochemistry in water and sometimes even result in improved reactivities or reaction conditions (*e.g.* Section 2.1.2):

i) The high polarity of water has a major impact on photochemical properties of chromophores^[81,99] (Section 2.1.1) and their reactivities.^[100,101] Stabilizing charged compounds and intermediates leads to competing or preferred electron transfer reactivity over energy transfer mechanisms.^[25,86,102,103] Despite this, photocatalytic energy transfer reactions are still possible and successful in water.^[36,63,102] Modification of the electron transfer reactivity was explored by Nauman and Goez, who discovered a higher redox potential of ruthenium-based photocatalysts using water as a solvent compared to acetonitrile.^[81]

ii) To ensure water solubility, apolar compounds can be substituted with ionic groups, which in some cases change the redox potentials and reactivities in ground and excited state.^[25,104–106] This holds especially true for aromatic hydrocarbon derivatives.^[36,63]

Further options to enable water-solubility are supramolecular environments, such as micelles^[63,107–111] or cyclodextrin(-related) molecules^[25,112,113].

iii) Water molecules can act as quenchers for excited organic molecules, particularly for emission energy regimes above 600 nm (below 2.1 eV). In 2021, Maillard *et al.* identified resonant energy transfer (FRET) to O–H vibrations as mainly responsible for the quenching effects.^[114] The emission quenching can be utilized for determining the water content within organic solvents.^[115] A more direct impact of water molecules is their property to act as possible ligands for metal-based chromophores. In *d*-block metal complexes such coordination effects can be avoided by chelating ligands.^[116] Another example for quenching processes by solvents is excited Cu(phen)₂⁺. Planarization in the excited state allow nucleophilic solvents, such as acetonitrile to quench the excited state. More bulky substituents in the 2-position of the ligands prevent this process, and hence prohibit quenching processes by nucleophilic solvents.^[46,117]

iv) Diffusion-based reactions and their rate constants are influenced by the ionic strength of a solution, which qualitatively speaking is a measure for the concentration and charge number of dissolved ions. For bimolecular reactions between two ions with a charge of the same sign, a high ionic strength is beneficial due to better stabilization and reduced Coulombic repulsion. For bimolecular reactions between two oppositely charged ions, a high ionic strength can stabilize the individual ions thereby slowing the quenching processes down.^[118,119] Such effects can be utilized to influence reaction rates by intentionally adding or omitting charged species (Section 2.1).^[5,36,63]

Water therefore has the capacity to be employed as a "green" solvent. The "green" solvent was explored for laboratory-scale synthetic chemistry^[25,63,84,120], for the decomposition of quaternary ammonium compounds in water^[102] or in hydrogen generation reactions^[121]. Section 2 presents four systems for photochemistry in water, making use of the solvation of highly charged species (Section 2.1), utilizing the "green" solvent for photochemical transformations (Section 2.2), achieving reactivity control with molecular dyads (Section 2.3) or investigating a recombination induced triplet formation mechanism (Section 2.4).

1.3.2 Combining properties of metal complexes and organic chromophores

The previous Sections 1.2.4 and 1.2.5 show several concepts for improving efficiencies in photon-driven bimolecular reactions: long excited state lifetimes and high cage escape efficiencies are beneficial and both can be achieved by employing a catalytically active species with a long-lived triplet excited state. The second aspect of efficiency is energy-related – efficient conversion of the energy of the input photon – and also taken into account for the overall efficiency of a process. This section provides general considerations and strategies towards achieving highly efficient photochemistry concerning cage escape and energy conversion.

General properties of metal complexes and organic chromophores:

Photosensitizers (PSs) or photocatalysts (PCs) can be subdivided into two general groups, depending on whether they are metal-based or purely organic. The following sections cover the general properties of the two chromophore classes and show how the beneficial properties can be combined and utilized for applications. One aspect that will be addressed is the efficiency of converting the energy of the photons used to drive a reaction into redox potentials for substrate activation. The two values that are compared are the redox potential in V vs NHE and the energy of the initiating photons (eV). The photon energy is usually obtained from the peak wavelength of LEDs^[63,81,122] or the wavelength of a laser^[5]. If the excitation light involves broad-band excitation, the E_{00} was used as initial energy replacing the excitation energy.^[30,123,124]

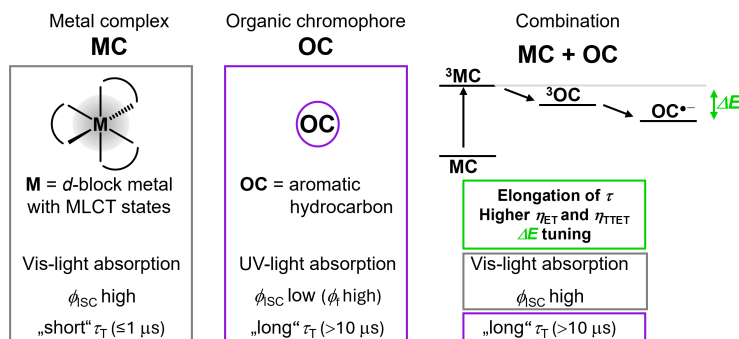


Figure 8: Key properties of the excited states of metal complexes (MCs) and organic chromophores (OCs) together with the combined properties of the two. The right part of the figure highlights a possible reaction scheme combining MC and OC as well as the resulting advantages and options for optimizing catalytic schemes.

Metal complexes (MCs, Figure 8, left part), for this thesis, address *d*-block metal-containing photo(redox) catalysts with visible light absorption. Especially 4*d* and 5*d* MCs, such as ruthenium-, iridium- or osmium-containing complexes, provide high

ϕ_{ISC} (close to unity)^[125] due to the heavy atom effect, and absorption bands in the visible region (often charge-transfer bands from metal-to-ligand charge transfer, MLCT). Generally, those properties make them very well-suited for visible-light photo(redox) catalysis and applications in optical devices. However, the high ϕ_{ISC} also enables radical pair ISC, lowering ϕ_{CE} (Figure 7).^[86,87,92] Comparatively short triplet lifetimes often require high quencher concentrations to obtain high efficiencies (compare Figure 6).

Further aspects come into play when considering sustainability. The availability especially of ruthenium, iridium and osmium on Earth is low, which makes them precious metals that should either be replaced or employed in the lowest possible concentrations for widespread usage. Charged ruthenium, iridium, osmium or copper-based MCs are water soluble^[84,102,126,127] and can in principle be used as photo(redox) catalysts in the "green" solvent.

Throughout the process of excitation upto obtaining the reactive species, energy gets lost. The conversion of the initial photon energy into redox potential that is available for the chemical reaction is often around 50 % or lower (Table 1 lists some examples).^[128]

Table 1: Comparison of photon energy ($h\nu_{exc}$) to redox potential ($E_{1/2}$) provided for chemical reductions using metal-based catalysts.

$h\nu_{exc} / \text{nm}$ ($E_{h\nu} / \text{eV}$)	reactive species ($E_{1/2} / \text{V vs NHE}$)	$\eta = \frac{E_{1/2}}{E_{h\nu}}$	reference
460 (2.70)	$[\text{Ru}(\text{bpy})_3]^+ (-1.30)^a$	0.48	[81]
405 (3.06)	$^3[\text{Ir}(\text{ppy})_3] (-1.49)^{b, c}$	0.49	[104, 129]
405 (3.06)	$^3[\text{Ir}(\text{sppy})_3]^{3-} (-1.65)^{b, c}$	0.54	[104, 129]

^aReduction potential. ^bCalculated from V vs SCE by adding 0.24 V^[71]. ^cExcited-state oxidation potential.

In summary, desired properties of an MC for efficient photo(redox) catalysis are the visible light absorption and the high ϕ_{ISC} , while the lifetime, conversion of the input photon energy and cage escape efficiency can be improved.

Organic chromophore (OC, Figure 8, middle part) generally is a broad term including purely aromatic hydrocarbons,^[30,123,124] natural and nature-derived compounds^[65,130,131] or specially designed chromophores^[55,65,132]. OCs are employed as replacements for noble-metal photocatalysts,^[2,18,28,52,133–135] which is often also based on the population of triplet excited states due to heavy atom effects,^[136–138] or structural motifs^[139] such as carbonyl groups^[138] or charge transfer states (CT, in TADF emitters,^[51,54,132,140] acridinium and phenoxazine dyes,^[37,133,141] organic dyads^[142,143] or certain BODIPY-dyes^[55,144]). The absence of heavy atoms makes high cage escape efficiencies *via* a

triplet excited OC feasible because within the radical pair, intersystem crossing is a slow process (Figure 7).^[92] Organic chromophores, however, frequently suffer from poor conversion efficiencies of the input photon energy into redox power and from low stabilities in electron transfer reactions.^[40,145] Furthermore, water-solubility is often a property that needs to be introduced by suitable ionic groups to an OC, thereby modifying the properties of the excited state.^[36,63]

Table 2: Comparison of photon energy ($h\nu$) with the redox potential ($E_{1/2}$) provided for chemical reductions for organic chromophores.

$h\nu / \text{nm}$ ($E_{h\nu} / \text{eV}$)	radical anion ($E_{1/2} / \text{V vs NHE}$)	$\eta = \frac{E_{1/2}}{E_{h\nu}}$	reference
< 310 (> 3.99) ^a	<i>p</i> -terphenyl ^{•−} (-2.39) ^{b, c}	< 0.59	[63, 123]
< 438 (> 2.83) ^a	perylene ^{•−} (-1.43) ^{b, c}	< 0.51 ^b	[30, 48, 124]
390 (3.18)	SO ₂ TDS ^{•−} ^d (-1.75)	0.55	[63]
525 (2.36)	³ EosinY (-0.91) ^{b, e}	0.39	[65, 146]

^a E_{00} . ^bCalculated from V vs SCE by adding 0.24 V^[71]. ^cReduction potential. ^dFor structure and more details see Section 2.2 and corresponding reference[63]. ^eExcited state oxidation potential, measured in MeOH.

To optimize photo(redox) catalysis, OCs need to be identified that complement the previously established properties of the MCs (visible-light absorptivity and high ϕ_{ISC}). Consequently, suitable OCs have a long lifetime of the triplet excited state (τ_{T}), no pronounced heavy atom effect for high cage escape efficiencies in ET reactions and possibly high redox potentials for efficient usage of the initial photon energy. Such properties can often be found in aromatic hydrocarbons such as naphthalene, perylene or *p*-terphenyl (Section 2.1 and Table 2). Those, however, are not water-soluble and to ensure catalysis in this "green" solvent, ionic groups can be introduced into the organic structures. This again has an impact on the redox potentials and energies of the excited state (Section 2.1).

The two previous paragraphs set the frame for taking the best out of the MC and OC properties aiming at efficient photo(redox) catalysis (Figure 8, right part). An ideal system combines a metal complex with visible light absorptivity and highly efficient intersystem crossing with an organic chromophore with a long triplet lifetime and a high redox potential. For a successful catalysis, the energy levels and redox potentials of the excited states of MC and OC need to be respected: i) To ensure fast energy transfer from ³MC to the OC, the triplet energy of ³OC needs to be slightly below that of the metal complex (Section 1.2.4, energy transfer quenching). ii) Overall energy

loss can be avoided by choosing OCs with highly energetic radicals (or radical ions)^[36] (Section 2.1) or the triplet species^[31,36]. iii) Ideally, back electron or energy transfer processes are thermodynamically disfavored and therefore slow, avoiding competing and unproductive reactions.

This thesis presents two strategies to combine MC and OC. The corresponding previous work is presented in the following two paragraphs of this section, and the further development and novel findings of this strategy are presented in Sections 2.1 and 2.3.

Bimolecular strategy:

This section focuses on a bimolecular approach towards combining the beneficial properties of metal complexes and organic chromophores. From a mechanistic point of view, the catalytic steps are distributed over the individual compounds, MC and OC: A visible-light absorbing MC with quantitative ISC is excited into the triplet state and sensitizes an OC *via* TTET to the long-lived ³OC. This key species was employed in substantially different catalytic pathways in literature as illustrated in Figure 9:⁴

In 2017, Kerzig and Goez^[5] presented an aqueous system with a ruthenium-based photosensitizer and a water-soluble pyrene-carboxylate as an organic chromophore (Figure 9, a)). After green-light excitation and sensitization, the ³OC was reduced by a sacrificial electron donor. The resulting radical species was excited by a second green photon, which induced the release of a solvated electron as reactive species regenerating the pyrene derivative. Incorporating the organic chromophore significantly increased the quantum yield for hydrated electron generation compared to a system with only the metal complex present.^[5,149]

A similar catalytic system in organic solvents employing a ruthenium-based metal complex and pyrene as organic chromophore was presented by König *et al.*^[150] Later, Moore *et al.*^[122] published mechanistic studies for the same combination of MC and OC (Figure 9, b)). The species for substrate activation in this system is the reduced chromophore (OC^{•-}), whereas the system from Kerzig and Goez released a solvated electron. The difference between the mechanisms of König and Moore is the reduction step of ³OC. In Königs mechanism (green arrow in the figure) an electron transfer from a sacrificial electron donor was proposed, which, however, is thermodynamically disfavored. This led to a two-photon based upconversion mechanism being proposed and investigated later.^[150,151] Moore presents a thermodynamically feasible reduction of ³OC (violet ar-

⁴This thesis only takes mechanisms into account that rely on a long-lived ³OC species. There are several more two-photon-based strategies producing highly reactive radical species out of which the two most important ones are briefly explained for a clear distinction: A) The Z-scheme is a concept based on processes within photosynthesis and involves a photocatalyst as a reducing sensitizer for an OC. The OC^{•-} is excited by a second photon and generates the reactive species ²*OC^{•-}.^[32,131] B) The ConPET mechanism involves only one chromophore that, after excitation, is reduced by a sacrificial electron donor and then excited by a second photon. This mechanism also generates an excited radical species, relying however, on only one chromophore.^[147,148]

rows) by incorporating a reduced form of the ruthenium-based metal complex. As a consequence, a ^3MC is quenched, either by energy transfer to the OC (TTET), or by electron transfer from a sacrificial electron donor (ET). The latter produces in the reduced ruthenium species ($\text{MC}^{\bullet-}$), which again can reduce the ^3OC to the $\text{OC}^{\bullet-}$ that is then used for substrate activation.

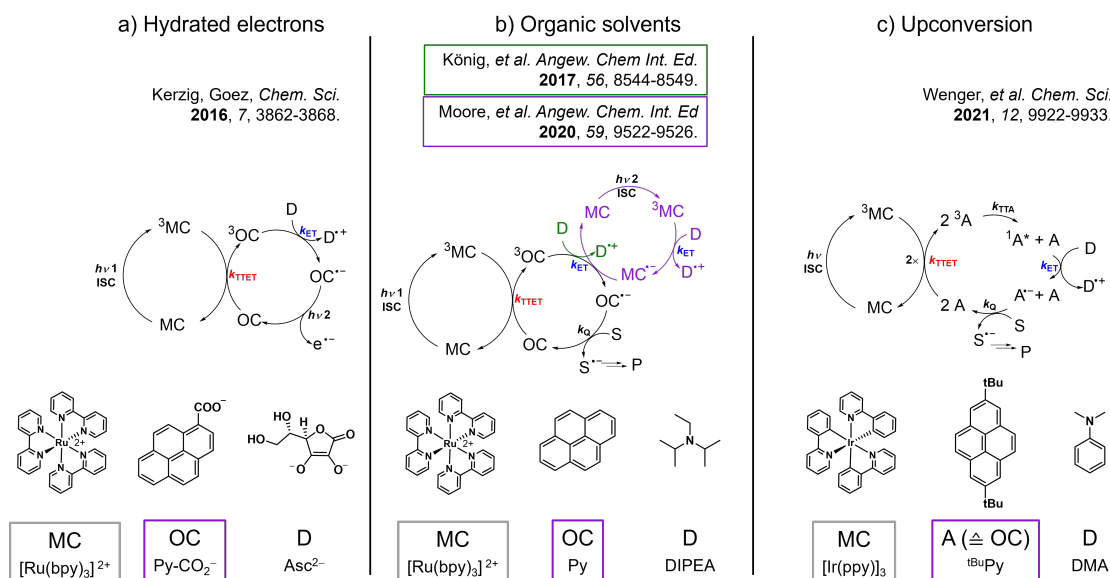


Figure 9: Reaction schemes and key components of bimolecular catalytic systems combining metal catalysts and organic chromophores with the relevant publications (MC: metal complex, OC: organic chromophore, D: electron donor). a) Presents a biphotonic mechanism for the production of hydrated electrons using the ascorbate dianion (Asc^{2-}) as an electron donor.^[5] b) Mechanism in organic solvents, with a (initially regarded as monophotonic^[150,151]) biphotonic mechanism and *N,N*-diisopropylethylamine (DIPEA) as an electron donor.^[122] c) Upconversion mechanism with iridium-based MC preventing competing reactions with *N,N*-dimethylaniline (DMA) as an electron donor.^[57]

Finally, an upconversion-based mechanism in organic solution has been discovered by Glaser, Kerzig and Wenger including a pyrene-based organic chromophore (Figure 9, c)).^[57] This case already differs slightly from the catalytic mechanisms before, because the reduction of the organic chromophore to obtain $\text{OC}^{\bullet-}$ occurs from the singlet excited state instead of the triplet. The triplet excited organic chromophore in this case is classified as an annihilator (A, the detailed mechanism of sTTA UC is further explained in Section 1.3.5).

One possible drawback of such elaborate catalytic systems is the occurrence of various unproductive decay pathways originating from the involvement of two photoactive chromophores and several steps until the reactive species is obtained. This, however, can be

addressed by detailed analysis of the unproductive quenching pathways^[36,38,57] and the production of the radical species could be identified as the most productive pathway.^[5,57] Careful choice of the involved chromophores with special emphasis on the respective excited state energies, potentials and quenching rates further supports this bimolecular approach (see Section 2.1).

This bimolecular strategy has the potential for highly efficient catalytic systems concerning the overall energy conversion and cage escape yields. The mechanisms presented in Figure 9 were optimized for a "green" production of solvated electrons,^[5] or studies combined with reactivity tests were the focus of the respective publications.^[122,150] Considering the energy of the input photon in relation to the potential of the reactive intermediate, however, those mechanisms could still be improved.

Table 3: Comparison of photon energy ($h\nu$) with the oxidation potential ($E_{1/2}$) provided for reduction reactions relying on sensitization-initiated electron transfer reactions (see Figure 9).

$h\nu / \text{nm}$ ($E_{h\nu} / \text{eV}$)	reactive species ($E_{1/2} / \text{V vs NHE}$)	$\eta = \frac{E_{1/2}}{E_{h\nu}}$	Figure 9
2×532 (4.66)	$e_{\text{aq}}^{\bullet-}$ (−2.77)	0.59	a) ^[5,118]
2×450 (5.51)	$\text{Py}^{\bullet-}$ (−1.86)	0.34	b) ^[122]
2×477 (5.20)	$^{\text{tBu}}\text{Py}^{\bullet-}$ (−1.86)	0.36	c) ^[57]

To optimize the usage of the input photon energy, one-photon-driven reaction mechanisms (instead of using two photons, see Figure 9) and the choice of the reactive radical can be considered. Therefore, the scope of OCs is extended to water-soluble *p*-terphenyl, naphthalene and pyrene derivatives (specific energy considerations are presented in Sections 2.1, 2.3 and corresponding publications). Such aromatic hydrocarbon-chromophores can be excited directly and after reduction, the reactive radical species catalyzes ET reactions (Table 2).^[30,63] With a potential of $E_{\text{red}} > -2.39 \text{ V vs NHE}$, the radical anion of *p*-terphenyl was used for CO_2 reduction and successfully employed for the synthesis of non-natural amino acids.^[123,152] Table 2 shows the low efficiencies in photon energy to reactive radical conversion after direct excitation. The potential of the radical is also provided by reducing the triplet excited state, which can be obtained by triplet energy transfer from a suitable iridium-based metal complex (Table 1). In this sensitized strategy, the excitation energy is a blue photon (2.75 eV), which produces a reducing species with $E_{1/2} = -1.96 \text{ V vs NHE}$ resulting in an efficiency of 71 % for the energy conversion (see also Section 2.1).

Molecular dyads:

Molecular dyads within the frame of this thesis are bichromophores consisting of a metal complex linked to an organic chromophore: One of the ligands is covalently attached to an organic unit as shown in Figure 10 (there are also metal-based triads and tetrads respectively substituted with two or three organic chromophores^[55,142,153]). Similar to the previous section, the purpose of this design principle is to utilize the advantages of both subunits, which are visible light absorption and high ϕ_{ISC} for the MC and the long triplet lifetime (Sections 1.2.2 and 1.2.5). The benefits of molecular dyads compared to their metal complex congeners have been exploited in rare-metal complexes such as Ru-based^[84,154–159], Os-based^[153,160–162], Ir-based^[163–166] or earth-abundant 3d metal complexes (including copper-based, iron-based or chromium-based dyads).^[167–170]

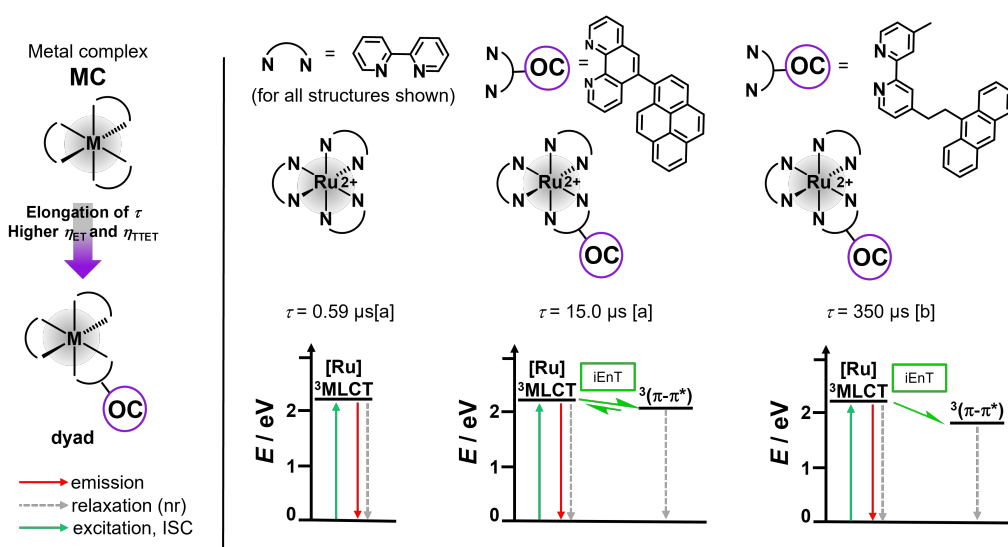


Figure 10: Principle of molecular dyads (left) and examples for ruthenium-based dyads with different lifetimes (right). The left side represents the general idea of molecular dyads including a metal center, which is attached to an organic chromophore for extension of the triplet excited state lifetime, resulting in higher efficiencies for energy and electron transfer reactions. The right side shows the chemical structures of Rubpy ([a] from references [84, 85]) and derived dyads by attaching pyrene or anthracene ([b] reference [159]). Below the structures are the resulting lifetimes together with the corresponding energy diagrams.

As indicated earlier, the choice of organic chromophore has a great impact on the energetics and therefore the reactivity of the molecular dyad (Figure 10, energy diagrams): For similar triplet energies of MC and OC ($\Delta E_T < 0.2$ eV), an equilibrium between the 3MC and 3OC can be observed.^[84] For an OC (or ligandsphere) with high differences in triplet energy to the MC, this back energy transfer can not be observed, thereby eliminating one deactivation pathway and elongating the lifetime of the excited state.^[154,171]

This, however, also entails a loss in energy and depending on the demands for the dyad, optimization on minimum energy loss or lifetime extension can be achieved.

Similar to the sections above, water solubility and challenges combined with this solvent are discussed briefly for molecular dyads. For an increasing size of the organic substituent(s), the water solubility decreases. However, high concentrations of long-lived dyads are often not required, especially when employed as catalysts, and can lead to lifetime-lowering self-quenching effects.^[84] The di-cationic nature of ruthenium-based dyads with small organic chromophores provides sufficient water solubility – in particular when Cl^- counter ions are employed – to allow photochemistry in the "green" solvent. Several dyads have already been developed and investigated for usage in aqueous solutions.^[84,85,92,155]

The fact that the triplet excited state is localized on the organic chromophore leads to modified redox properties in the excited state, besides the lifetime elongation. So far, mostly the lifetime extension was utilized, however, changed redox properties allow the differentiation between inherently different quenching pathways. This effect is detailed in Section 2.3 and the corresponding reference [85].

1.3.3 Reactivity control

Mechanistic, thermodynamic and kinetic considerations in the previous sections illustrate versatile possibilities for triplet excited state photochemistry. Advantages of triplet excited states and the differentiation between two fundamental quenching steps, namely electron transfer or energy transfer, are discussed. This section presents photocatalysis and corresponding studies to achieve different reactivities and reaction products in (synthetic) photoredox catalysis or photochemistry in general.

Photosensitizer as a mechanistic switch:

Photoinduced reactions are highly responsive to their surroundings and modified reactivity can be achieved by choosing different reaction conditions or a different photosensitizer, for example switching between two different metal-based complexes.^[17] The photosensitizer change often requires adaptation and optimization of the reaction conditions and examples, where only the photocatalyst or catalytic system, is exchanged are scarce.^[17,37] By changing the metal catalyst from copper-based to osmium-based using the same organic chromophore (di-cyanoanthracene, DCA), Glaser and Wenger were able to differentiate between oxidative and reductive substrate activation in red light-driven photocatalysis (Figure 11, left part).⁵ For the copper-based photocatalysis, DCA was reduced (ET) and the resulting $\text{DCA}^{\bullet-}$ intermediate was activated with a second photon, producing the highly reducing reactive species $^*\text{DCA}^{\bullet-}$. In the osmium-based photocatalytic system, DCA was sensitized (TTET) and a subsequent upconversion mechanism produced $^1\text{DCA}^*$, with an oxidative reactivity towards substrates. This mechanistic change was found using acetonitrile as a solvent and the upconversion mechanism was optimized for higher efficiency using dichloromethane as solvent.^[32,38] Section 2.1 presents an electron transfer to energy transfer reactivity switch by exchanging a ruthenium-based metal catalyst for its dyad derivative (see Figure 10). Such examples for reactivity changes^[32,37,38,85] require detailed mechanistic analyses of the individual systems and thereby contribute generally to a deeper understanding of photocatalytic mechanisms.

⁵The mechanism shown in Figure 11 is predominantly observed in acetonitrile. A minor fraction of an energy transfer from $^3[\text{Cu}]^{2+}$ followed by the reduction of ^3DCA with DIPEA leads to the $\text{DCA}^{\bullet-}$, which is equally excited by the second photon.

Isomerization reactions:

An extension within this subsection are energy transfer-based *cis/trans*-isomerization reactions (Figure 11, right part). Irradiation reactions do not lead to different products (as seen before), but to different ratios of the *cis/trans* isomers. This product distribution is due to the fact that the triplet energy of the *cis*-isomer is above that of the *trans*-isomer. Depending on the photosensitizer's triplet energy relative to the two isomers, the corresponding quenching rates differ. Two scenarios are relevant for isomerization reactions:

a) The triplet energy of the sensitizer is close to that of the lower energy isomer, (Figure 11, PC1 and the *trans*-isomer). Quenching with the *cis*-isomer (higher triplet energy) is therefore slow, which leads to a selective activation of the *trans*-isomer and an accumulation of the energetically higher-lying *cis*-isomer (*cis/trans* > 1).

b) The triplet energy of the photosensitizer is greater than that of both isomers (PC2). Sensitization by the triplet excited PC2 occurs with similar rate constants and in irradiation reactions this leads to a 1:1 *cis/trans* ratio.

In these scenarios, reactivity control is considered regarding the isomeric ratio, which depends on the chosen sensitizer and the related triplet energy.^[22,42,102] As a consequence, the product ratio in irradiation reactions, after reaching an equilibrium (photo-stationary state), provides information about the triplet energy of the photosensitizer (Section 3.3 and reference [172]).^[42,102]

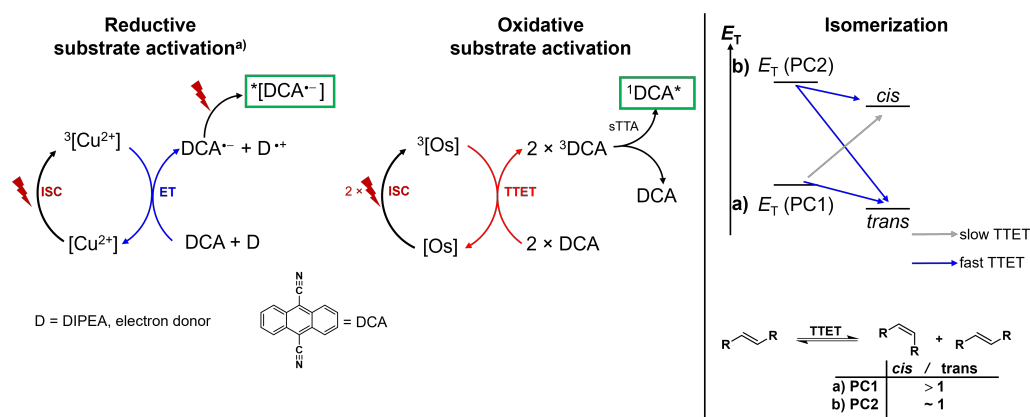


Figure 11: Examples for reactivity switch based on changed photosensitizer. Left part: Comparison of catalytic mechanisms with a copper-based metal complex ($[\text{Cu}^{2+}]$) for reductive substrate activation (via $^*\text{DCA}^{\bullet-}$; a) this mechanism is predominantly observed in acetonitrile) to an osmium-based metal complex ($[\text{Os}^{2+}]$) for oxidative substrate activation (via $^1\text{DCA}^*$).^[32,38] Right part: comparison of triplet energies of two photocatalysts (PC1 and PC2) for *cis/trans* isomerization reactions together with the resulting distribution of isomers after an energy transfer-based isomerization reaction.

Influence of reaction conditions:

Driving reactions with light *via* photocatalysts in their excited states is highly dependent on the rate constants of the quenching steps. To achieve high selectivity, suppression of competing reactions is key, which on the other hand can also be viewed as possibility towards versatility: The choice of additives in solutions enables different quenching pathways and products and allows one photocatalyst to be employed in electron or energy transfer reactions, as shown by the examples in Figure 12: With a suitable sacrificial electron donor, $^3[\text{Ru}(\text{bpy})_3]^{2+}$ is reduced and employed in electron transfer reactions. Goetz and Naumann performed successful pinacol coupling reactions of aromatic ketones and aldehydes (S = benzaldehyde, more examples in the publication), which were activated by the reduced ruthenium-based complex.^[81] On the other hand, in the absence of an electron donor the same $^3[\text{Ru}(\text{bpy})_3]^{2+}$ can be used for TTET followed by an annihilation process, both in aqueous solution (see figure)^[156] and organic solvents^[173]. In 2023, Zysmann-Colman *et al.* published a sulfone-bridged TADF emitter (pDTCz-DPmS) and showed highly versatile reactivity, including triplet-triplet energy transfer, oxidative and reductive substrate activation and dual catalysis with a nickel-based co-catalyst.^[132] Unlike this direct comparison showing the versatility of a photocatalyst within one study, mostly unrelated publications employ one photocatalyst for different reactivities according to their individual requirements *e.g.* organic chromophores (Section 2.2)^[37,63,130,174,175], other TADF emitters^[51,52,132], or earth-abundant metal complexes (Section 3.1).^[17,44,176]

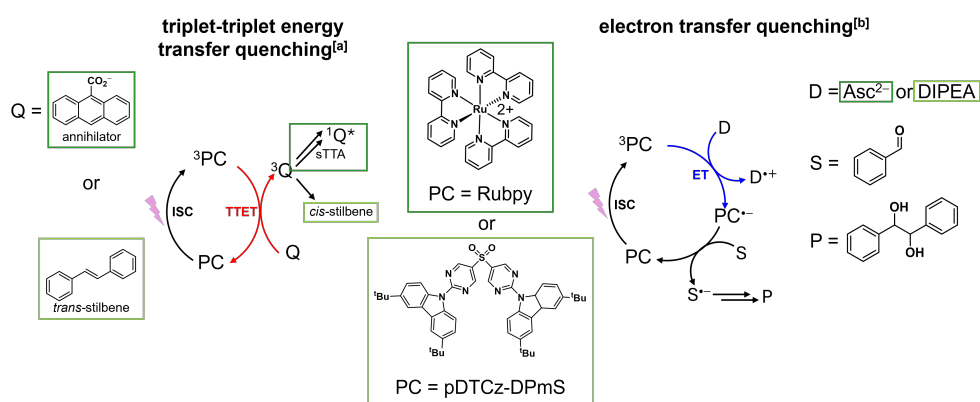


Figure 12: Examples for reactivity switches based on changed additives using $[\text{Ru}(\text{bpy})_3]^{2+}$ (dark green) or pDTCz-DPmS (light green) as photocatalysts (PC). Left part: Triplet-triplet energy transfer-based mechanism. The quencher is either an annihilator structure (Q=anthracene carboxylate) and upconversion was observed^[156] or *trans*-stilbene (an energy acceptor), which isomerized to the *cis*-product.^[132] Right part: Electron transfer-based mechanism using either the ascorbate dianion (Asc^{2-})^[81] or DIPEA^[132] as a sacrificial electron donor and benzaldehyde (and derivatives) as substrates (S) for pinacol coupling reactions.^[81,132]

Further interesting possibilities to change between reaction products were identified when considering the excitation light, which are discussed briefly.^[17] In the first study, high light intensities enabling two photon-based reactions are distinguished from lower light intensities inducing one photon-driven reactions. Switching the light intensity allowed Kerzig and Wenger to control the reaction products, which resulted from a two photon-based reaction mechanism (reactive species: hydrated electrons) or from one photon-based reaction mechanisms (reactive species: triplet excited state of the photosensitizer).^[177] The following two publications revealed different reactivities upon changing the excitation wavelength between blue and green photons.^[178,179] Schmermund *et al.* observed that depending on the excitation wavelength different transitions are enabled ($n-\pi^*$ for green photons and $\pi-\pi^*$ for blue photons), which yielded different substrate activation energies and thus reaction products.^[178] Finally, Gosh and König investigated different reactivities after irradiation with blue or green LEDs using a rhodamin catalyst. The selective absorption of a blue photon by a reaction intermediate allowed the activation of that intermediate under blue-light irradiation, whereas this second activation was prohibited using green photons. The differentiation between the intermediate (green light-driven) and the excited intermediate (blue light-driven) for substrate activation also lead to two different reaction products.^[179] Often more than one parameter needs to be changed in order to obtain high selectivity towards different reaction products.^[17,38] Typical examples are the temperature^[180,181], or additives and co-catalysts.^[44,63,174]

Replacing photocatalysts based on precious metals is of great interest, for sustainability reasons and because of the high costs that are related to such metals (especially for large-scale usage).^[21,28] Several examples of organic and earth-abundant metal catalysts for successful replacement of precious-metal catalysts have been published.^[18,28,44,176,182] Examples for versatile photocatalysis at different reaction conditions, in terms of different quencher molecules are presented in purely organic catalyses in Sections 2.2 and 3.2, and Section 3.1 introduces a versatile catalyst based on a more earth-abundant metal.

1.3.4 Back electron transfer-induced triplet formation

For chromophores with singlet excited state reactivity, electron transfer quenching can occur equivalent to the mechanism described in Section 1.2.4, producing the one-electron reduced (or oxidized) photocatalyst and electron donor or acceptor species, respectively. Unlike the unproductive recombination processes introduced previously (Section 1.2.5, Figure 7), following the electron transfer, a recombination-based pathway can take place producing a triplet excited species, which would not be possible without the recombination step.^[86,90,143,183] In monomolecular systems (often dyad-like donor-acceptor compounds) the intersystem crossing is caused throughout the recombination process by couplings, which enable El-Sayed allowed transitions^[184] or hyperfine couplings.^[60] For bimolecular systems, ISC is often enhanced by electron transfer and explored in combination with magnetic field effects, which enhance the hyperfine couplings.^[90,185] Figure 13 provides a clearer picture of the overall process and the spin-multiplicities included. An additional intermediate, the encounter complex, was included in the mechanistic scheme compared to the mechanism described earlier in Figure 7.^[90,185,186] In principle, the reaction pathway proceeds similar to that described earlier (Figure 7), except for the fact that the excited chromophore starts in a singlet excited state (Figure 13): In a diffusion-based step, the excited photocatalyst (PC) and donor (D) form an encounter complex in a singlet multiplicity because of the spin conservation ($^1[\text{PC} \cdots \text{D}]^*$). Electron transfer leads to the spin-correlated radical pair again with a singlet multiplicity ($^1[\text{PC}^{\bullet-} \cdots \text{D}^{\bullet+}]$). Typically, without a heavy atom present, the spin-correlated pair recombines and decays into the ground state PC and D or cage escape forms the desired radical species (compare Section 1.2.5). Despite the lack of a heavy atom, intersystem crossing can take place, such that the nearly isoenergetic triplet radical pair is formed ($^3[\text{PC}^{\bullet-} \cdots \text{D}^{\bullet+}]$). Under certain conditions, back electron transfer is followed by the release of the two molecules into the solution, populating the triplet state of the PC ($^3\eta_{\text{diss}}$).^[90,91,187]

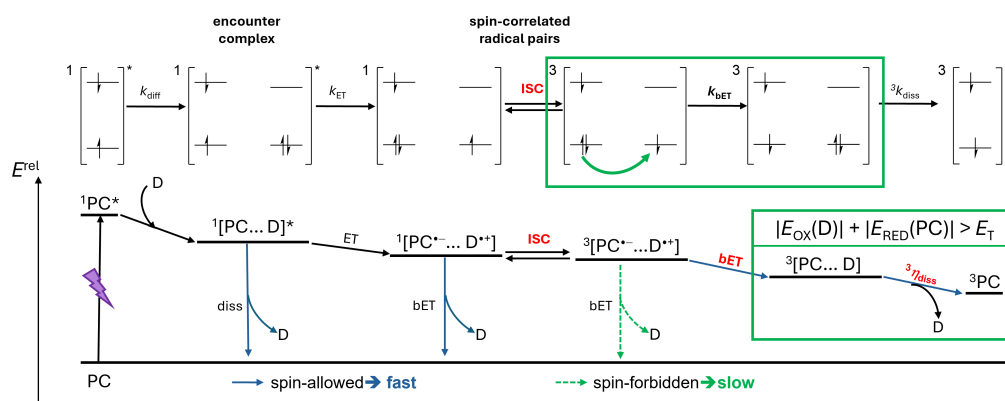


Figure 13: Reaction scheme and energetics of a back electron transfer (bET) or recombination induced triplet formation together with the frontier orbitals representing the spin multiplicities. Direct excitation of a photocatalyst (PC) into the singlet excited state is followed by electron transfer quenching with an electron donor (D). The green box highlights the thermodynamic requirements for the formation of ^3PC . Differences to the electron transfer mechanism in Figure 7 are discussed in the text.

This process is only observed if certain criteria are met. The most important argument is the thermodynamic feasibility of the recombination: The energy released upon recombination to form the triplet species ($\Delta G_{\text{bET}} = E_{\text{T}} - E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{PC})$) can be expressed as a rearrangement of the Rehm–Weller derived equation (Equation 12) and therefore $|E_{\text{ox}}(\text{D})| + |E_{\text{red}}(\text{PC})| > E_{\text{T}}$.^[188] Depending on the individual triplet energies, either the quencher molecule or the photocatalyst can be promoted into the triplet excited state.^[86,188]

Solvent properties, such as reorganization energies, polarity or viscosity impact the stabilization energies of the intermediate^[67,183] and dissociation rate constants^[67,86,88,90].

The recombination-induced ISC is enabled by hyperfine coupling effects or by ultrafast heavy atom induced spin-orbit coupling.^[67,189,190] For systems in organic solution, ISC of chromophores was enhanced by such effects on nano-second and sub-nano-second timescales and were combined with magnetic field effects.^[90,183,185,186,191] Section 2.4 presents a bimolecular aqueous system, with a pure singlet chromophore, which shows strong triplet signals after a recombination process.

1.3.5 Sensitized triplet-triplet annihilation

General mechanism and parameters:

In sTTA UC schemes, the energy of two low-energy photons is combined to produce one photon of higher energy (Figure 14). Such mechanisms consist of two chromophores: A photosensitizer (PS), which absorbs the low-energy photons and forms efficiently the triplet excited state (high ϕ_{ISC}). The second chromophore is an annihilator molecule (An), which quenches the 3PS *via* triplet-triplet energy transfer. If two 3An encounter, they form an encounter complex with the three possible spin-states $^1(An \cdots An)^*$, triplet $^3(An \cdots An)$ and quintet $^5(An \cdots An)$, each with a statistical likelihood of 1/9, 3/9 or 5/9, respectively (f : spin statistical factor). Theoretically, only the singlet encounter pair produces the wanted delayed emission from the $^1An^*$, thereby limiting the overall quantum efficiency of the process to 0.11.^[76,173,192,193] The quintet encounter complex dissociates back into the individual triplets, because disfavoured energetics prevent access to the quintet states of one individual annihilator.^[194,195] For favorable energetics and molecular prerequisites in the annihilator, the triplet encounter pair $^3(An \cdots An)$ also contributes to the delayed emission *via* ISC from higher excited triplet states to the singlet multiplicity, and depending on their coupling interaction and orientation, they can contribute to increasing the spin statistical limit above 0.11.^[53,195] That way, the theoretical limit of the upconversion quantum yield (ϕ_{UC}) can be surpassed.^[53,76,194,196]

The quantum yield of an sTTA UC process is usually determined experimentally using a reference compound. Its biphotonic nature inherently limits the overall quantum yield of sTTA UC to a maximum of $\phi_{UC}=0.5$ compared to the direct emission of the reference compound. The quantum yield can also be considered as the product of the quantum yields of all steps involved, which results in the following equation:^[76,192,197]

$$\phi_{UC} = f \times \phi_{ISC} \times \phi_{TTET} \times \phi_{TTA} \times \phi_F \quad (14)$$

ϕ_{UC} is the upconversion quantum yield, ϕ_{ISC} is the quantum yield for ISC of the sensitizer, ϕ_{TTET} is the quantum yield for the energy transfer, ϕ_{TTA} is the quantum yield for the annihilation process and ϕ_F is the fluorescence quantum yield of the directly excited annihilator (color-code identical to Figure 14).

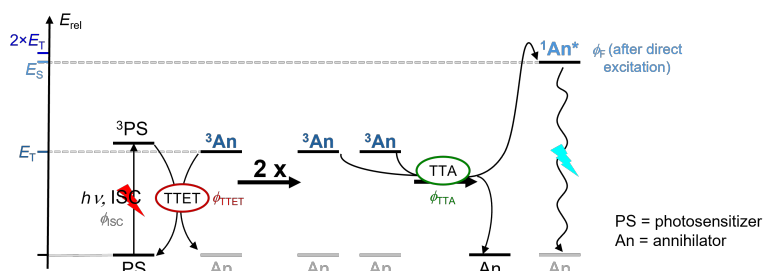


Figure 14: Energy scheme of the sTTA UC mechanism for a photosensitizer (PS) and annihilator (An) including a scale for the relative energies. The scale contains markings for the triplet energy of the annihilator (E_T), the singlet energy of the annihilator (E_S) and the double triplet energy of the annihilator ($2 \times (E_T)$), see text for further explanation. Key parameters for every individual step are the intersystem crossing quantum yield of the sensitizer (ϕ_{ISC}), the quantum yields for energy transfer (ϕ_{TTET}), the quantum yield for annihilation (ϕ_{TTA}) and the fluorescence of the singlet-excited annihilator (ϕ_F).

Three out of the five factors from equation 14, (f , ϕ_{ISC} and ϕ_F) are inherent properties of annihilator and sensitizer. Triplet-triplet energy transfer is the first bimolecular step of an upconversion scheme, and the efficiency of this step is essential for the entire mechanism. For a high ϕ_{TTET} the concentration of the annihilator must be chosen sufficiently high and/or the triplet excited state of the sensitizer must be long-lived (Equation 13). High annihilator concentrations however, cause filter effects, which can be detrimental for the efficiency of an sTTA UC system.^[31,76] As a result long lifetimes of the triplet-excited sensitizer are essential in order to work at high energy transfer efficiencies and at the same time low annihilator concentrations (Section 1.2.5 and Figure 6).

The thermodynamic prerequisite for the annihilator is the relation of triplet and singlet energy. For a successful triplet-triplet energy transfer, the annihilator's triplet energy should be below that of the sensitizer. Additionally, the energy of two triplet excited states must be above the singlet excited state of the annihilator (*i.e.* $2 \times E_T > E_S$).^[76,192] The annihilation process is highly dependent on the concentration of ^3An also from a kinetic point of view, because two triplet-excited annihilators are required for annihilation. At low light intensities, the concentration of ^3An is also low, which is why the observed upconversion signals depend quadratically on $[^3\text{An}]$. The quadratic dependency in the low-power excitation regimes is often used and accepted as confirmation for the biphotonic nature of the annihilation process.^[33,44,85,192,197] At higher light intensities the concentration of ^3An is sufficiently high and the ϕ_{UC} depends linearly on the light intensity. Qualitatively speaking, under those conditions the concentration of ^3An is considered "constant" and every newly formed ^3An annihilates, which is why the formation of the encounter complex only depends on the formation of one new ^3An .^[194,195,198]

sTTA UC in organic solvents:

The concept of combining the energy of two low energy photons to obtain one photon of higher energy is known since the second half of the 20th century^[76,156,199] and since then has found its place in many research fields such as improving the efficiency of solar devices^[8,200,201], chemical syntheses^[35,38,202], combined with supramolecular environments and/or in bio-medicinal applications^[160,161,203].

Those applications and technologies benefit from advantages of the sTTA UC mechanism *e.g.* the penetration depth of lower energy excitation light (especially red-to-blue upconversion for bio-medical applications within the "biological window"^[161,170,204] see also next section), milder reaction conditions and selectivity (compared to direct excitation, utilizing low energy photons allows selectivity because usually ¹A* reacts directly as sensitizer^[38,57] or as FRET-donor^[33]) or avoiding hazardous and inefficient UV lamps by directly applying blue-to-UV upconversion in solution^[34].

General **requirements for sensitizers** are efficient ISC after photon absorption, sufficiently long lifetime of the triplet excited state (Section 1.2.5), possibly low filter effects for the upconverted light,^[34,76,192,195] and within a sustainability-framework replacing precious-metal photosensitizers by organic chromophores or earth-abundant metals. TADF emitters^[34,53] and several metal complexes^[43,107,170,205] have met such requirements and the molybdenum-complex presented in Section 3.1^[44] is a further step towards replacing rare metals.

Requirements for annihilator compounds are the energy gap between singlet and triplet energy ($2 \times E_T > E_S$ see Figure 14) and a low tendency for excimer formation. Finding such properties in possible annihilator structures is non-trivial, however compared to aqueous systems several organic chromophores have been identified as suitable annihilator compounds.^[206] Excimer formation is successfully avoided by substituting the aromatic hydrocarbons with alkyl or TIPS groups.^[207–209] This however leads to a (substantial)^[33,210] lowering in the energies of the annihilator's excited triplet states. Being aware of such effects and building on previous studies, allows a rational approach towards annihilator design. Section 3.2 provides detailed insights into DFT-based, energetic considerations for the design of a blue-to-UVB annihilator.

sTTA UC in water:

The first sTTA UC system in pure water was published by El Roz and Castellano in 2017.^[156] Since then only four more systems in pure water have been developed.⁶ The annihilator structures consist of an organic chromophore (naphthalene, anthracene or pyrene) substituted with ionic groups to provide water solubility (Figure 15).^[102,155,156,213] The reason for such few sTTA systems in water is related to the inherent solvent properties as discussed previously (Section 1.3.1) and out of those the following are relevant for sTTA:

i) The high polarity of water promotes competing ET reactions^[86, 156] limiting the initial TTET step (red circle in Figure 14). Thus the accumulation of a sufficiently high concentration of triplet excited annihilators is prohibited, which is a key factor for successful upconversion systems.^[76,192]

ii) Excimer formation as competing mechanism is more efficient in polar solvents and makes the wanted sTTA mechanism inefficient.^[214] In organic solvents, excimers can often be avoided by substituting the annihilators with aliphatic or TIPS groups (previous paragraph). For aqueous solutions, annihilator structures are decorated with ionic groups to provide water solubility. This does not prevent excimer formation and for several possible annihilator structures, excimer formation was the main observed mechanism instead of the wanted upconversion. Kerzig and Wenger^[155] and a few years later Pfund *et al.*^[102] have tested several water-soluble naphthalene, biphenyl, anthracene and terphenyl derivatives, out of which three were identified for efficient upconversion. All other tested annihilators showed an overall low (or no) upconverted emission due to side reactions such as excimer formation or competing ET reactivity.

iii) Limited solubility of the annihilator can set an upper limit for the maximum concentration.^[102] Long lifetimes of the sensitizers are therefore highly desirable to ensure efficient energy transfer quenching (Section 1.2.5 and Figure 6).

⁶If supramolecular environments or molecular assemblies like micelles or nanoparticles are involved the number of successful systems becomes much larger.^[6,107,203,211,212]

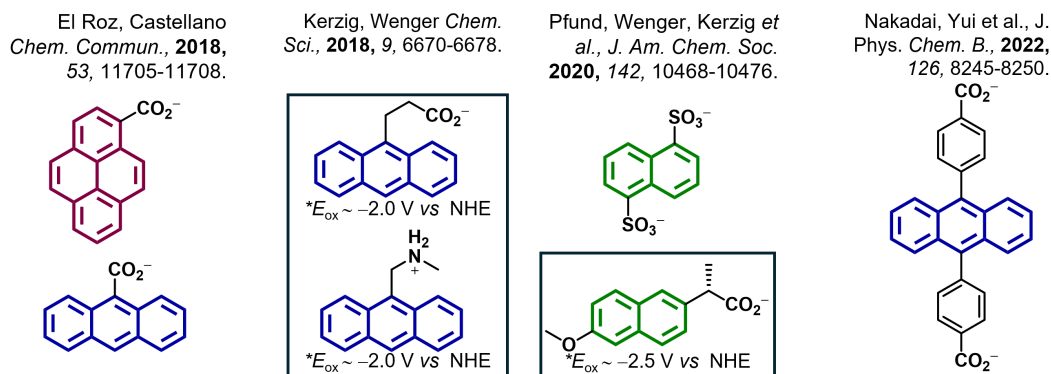


Figure 15: Annihilator structures for sTTA UC systems in pure water, together with the relevant publications. The boxes highlight annihilator structures that were employed in substrate activation reactions owing to their reducing properties in the singlet excited state together with the excited state potential ($^*E_{ox}$).

Some of the aqueous sTTA UC systems have been employed in substrate reduction (ET) reactions using the singlet excited annihilator as catalytically active species in dehalogenation reactions^[102,155] and decomposition of a quarternary ammonium compounds^[102]. Three of the annihilator structures in Figure 15 were employed in sTTA UC-driven photocatalytic electron transfer reactions for pollutant degradation and provide highly reducing properties (< -2.0 V vs NHE) from the singlet excited state. However, oxidative properties in this context have not been reported so far and will be addressed in Section 2.3 and reference [85]

sTTA UC-systems that are compatible with water can be employed for waste-water treatment^[102] and a second huge field of applications is located in bio-medicinal contexts. PDT,^[212] bioimaging,^[160] and photon-triggered processes^[32,38] within this context are limited by the absorption of tissues, and only light within the "biological window" ($>>600$ nm) can pass this barrier and therefore be employed for those purposes.^[204] Photons within this range carry energies below 2.0 eV, which is the thermodynamic limit for one-photon applications. The annihilator structure presented in Section 2.3 has a triplet energy, which is well-suited for potential applications within the "biological window".

1.4 Outline of the projects

This thesis is divided into two main chapters out of which the first presents triplet photochemistry in aqueous environments and the second chapter focuses on systems in organic solvents.

Water is a highly polar and protic solvent and it possesses advantages like non-toxicity, low price and ubiquitous availability. However, water as a solvent provides general challenges like insolubility, aggregation or incompatible reaction conditions, which are added to the photochemistry-specific problems, solvatochromism, modified excited-state decay pathways and the fact that water itself can act as a quencher^[114].

The first project in Section 2.1 presents a concept towards the efficiency increase of a photocatalytic mechanism. Beneficial properties of iridium- and ruthenium-based metal complexes (MCs), such as visible light absorption and fast, quantitative ISC, are combined with the long triplet excited state lifetimes of organic chromophores (OCs). In the investigated bimolecular mechanism, an organic chromophore is sensitized *via* triplet-triplet energy transfer (TTET) from the triplet excited metal complex. This step is followed by a reductive electron transfer (ET) to the triplet excited OC. That way, the one-electron reduced intermediate ($\text{OC}^{\bullet-}$) is formed, which is capable of activating substrates. The modular design of this concept allows the combination of different MCs and OCs enabling optimization of the catalytic system. Two criteria are considered for the effectiveness of this mechanistic strategy. One is the efficient conversion of photon energy into energy available for substrate activation. The second aspect is a high quantum yield for the conversion of absorbed photons into catalytically active species. Beneficial Coulombic interactions paved the way for identifying a highly efficient MC - OC combination with a cage escape efficiency of close to unity for the reactive OC species.

The second project in Section 2.2 focuses on a detailed spectroscopic analysis of a water-soluble, purely organic chromophore with triplet reactivity (SO_2TDS). ISC in this molecule is enabled by introducing an SO_2 -bridge into a formerly pure singlet chromophore. Detailed spectroscopic analyses and NMR scale irradiation experiments confirm the dual TTET and ET reactivity of the SO_2TDS triplet.

In the third aqueous system (Section 2.3), ruthenium-based molecular dyads enable the identification of a novel, highly oxidizing annihilator structure in water. Molecular dyads are bichromophores, consisting of a metal complex (ruthenium-based) with a covalently linked organic chromophore (pyrene), thereby combining the benefits of the two entities within one molecule. The long-lived triplet state of the dyads originates from a fast intramolecular energy transfer to the lower-lying triplet of the pyrene subunit. The resulting lifetime elongation drastically increases the efficiency of the desired quenching step at low quencher concentrations, which is highly relevant for sTTA systems. Furthermore, a fundamentally different reactivity of the triplet excited metal

complex (ET) compared to the dyad (TTET) was observed. The energy transfer quenching pathway allowed the implementation of $P-H^{2+}$ in an sTTA scheme, thereby adding the compound to the very limited number of annihilator structures for sTTA in water. In contrast, the more redox-active metal complexes undergo electron transfer quenching. That way, employing a ruthenium-based dyad or the metal complex congener facilitates a reactivity switch (TTET vs ET). Initial experiments to further investigate this concept employing iridium-based complexes and dyads are presented at the end of this section. The fourth and final aqueous system (Section 2.4) sheds light on a bimolecular pathway to access triplet excited species in molecules without inherent ISC. The annihilator structure of the previous project ($P-H^{2+}$) is highly oxidizing in its singlet excited state and can be reduced by weak electron donors. Fast recombination of the photo-induced electron transfer products (oxidized donor and reduced chromophore) is usually an unproductive and detrimental pathway. In this case, however, recombination with suitable electron donors releases sufficient energy to populate the triplet excited state, which can be observed on nanosecond-toicrosecond timescales. Initial experiments confirm this triplet-forming mechanism and possibly reveal an underexplored pathway for reactivity control and triplet formation.

The second main chapter (Chapter 3) is divided into three sections each containing one project on triplet photochemistry in organic environments. The three sections present ns-TA spectroscopy for an earth-abundant molybdenum complex replacing precious ruthenium complexes, DFT-calculations guiding the design of annihilator structures and ns-TA spectroscopy of Pt(II)-based chromophores for OLED applications.

Section 3.1 focuses on a molybdenum(0) complex capable of replacing ruthenium complexes. The ruthenium and the molybdenum complexes are isoelectronic and using ns-transient absorption spectroscopy, combined with theoretical calculations, the molybdenum triplet excited state was identified and characterized. This triplet excited molybdenum complex sensitizes a literature-known annihilator, thereby replacing a Ru-based sensitizer in an sTTA UC scheme. Furthermore, the complex was employed in an electron transfer driven dehalogenation reaction, as an example for the versatile usage of the molybdenum complex for electron or energy transfer reactions.

The second project (Section 3.2) presents DFT calculations supporting the design and experimental results for annihilator compounds in a blue photon-driven sTTA UC system generating UVB light. Such high-energy-producing multiphoton mechanisms are highly relevant for activating substrates under mild reaction conditions. The annihilator structures under investigation were tris-isopropyl acetylene (TIPS) substituted benzenes. The triplet energies of differently substituted benzenes were calculated, which allowed the prediction of the most promising molecules to guide synthesis.

Finally, in Section 3.3 the excited states of two heteroleptic platinum complexes, which were designed as blue-emitting chromophores for OLEDs, were spectroscopically ana-

lyzed. The ligand-centered triplet nature was confirmed in a polymer matrix as well as in solution and a specially designed cyclometallating ligand containing a spirobifluorene-unit introduced unexpected excited state properties. Beyond spectroscopy, both complexes were also employed in a sample energy transfer photocatalytic reaction (TTET).

All projects are focused on triplet excited species, different access (ISC, sensitization or recombination) and decay pathways (energy and electron transfer or annihilation) and their individual characterization. The detailed analysis of each chromophore or chromophore system is essential for individual optimization and effective usage in photo(redox) catalysis. The projects also show the interplay of theoretical calculations (DFT), spectroscopic measurements and experiments as synergistic methods for obtaining a deep mechanistic understanding. The insights gained throughout the thesis are relevant for many photochemistry-related fields, including biological systems (sTTA schemes in water), catalysis and sustainability (aqueous systems, reactivity control, purely organic catalysis and earth-abundant metal complexes) and even for light-emitting devices (platinum complexes for OLEDs).

2 Photochemistry of triplet states in aqueous solution

This chapter presents four triplet-photochemistry projects realized in aqueous solution. In Section 2.1 a catalytic concept combining energy and electron transfer is explored using combinations of iridium- or ruthenium-based metal complexes and naphthalene, *p*-terphenyl, or pyrene derived organic chromophores. Section 2.2 introduces a purely organic compound with triplet-based photo(redox) chemistry. Section 2.3 combines metal complex and organic chromophore in one compound (dyad), which besides the increased triplet lifetime also introduces a modified reactivity. In the last section (Section 2.4) recombination is explored as a way to access the triplet excited state in a chromophore that normally only populates the singlet excited state.

2.1 Sensitization-initiated electron transfer

This section presents different bimolecular systems consisting of iridium- and ruthenium-based MCs combined with different OCs exploring a combined TTET and ET mechanism. Figure 16 provides the general catalytic cycle (as already discussed in Section 1.2), which will be referred to throughout this section. The goal of this concept is to make use of the visible light absorption and fast ISC of MCs in combination with the long lifetime of the ³OCs. This key intermediate is obtained *via* TTET from the triplet excited metal-based complexes. In previous work (Section 1.2),^[5,57,122,150,151] various pathways for a combined TTET and ET for photoredox catalytic cycles have been investigated. Most of these examples rely on multi-photon mechanisms, whereas for this dissertation the focus is turned to a one-photon mechanism and towards increasing the efficiency of the catalytic cycle.

The first section (Section 2.1.1) introduces a blue-light driven catalytic system combining Ir-based photosensitizers with charged naphthalene and *p*-terphenyl derivatives (as OCs) in aqueous solution. In the presence of a sacrificial electron donor (D), this combination of catalysts allows the formation of highly reactive radical anions (OC^{•-}), aiming at an efficient usage of the photon energy provided by the input light. A high conversion of the photon energy into redox potential available for substrate activation requires careful selection of the individual components (MC, OC and D) for thermodynamically feasible ("downhill") energy and electron transfer steps, while minimizing the energetic loss throughout the overall process.

In the second part (Section 2.1.2), the same mechanistic concept is employed in a similar system with a Ru-based sensitizer and pyrene tetrasulfonate (PTS) as organic chromophore, in a green-light driven catalysis. The overall quantum yield of the sensitization-initiated electron transfer mechanism exceeds the quantum yield of the direct pathway with only the MC as photocatalyst, which is shown spectroscopically and in model reactions.

High cage escape efficiencies and ultimately quantum yields in the individual catalytic steps is achieved by exploiting static quenching caused by the Coulombic interactions between the dicationic ruthenium complex and a tetra-anionic pyrene derivative.

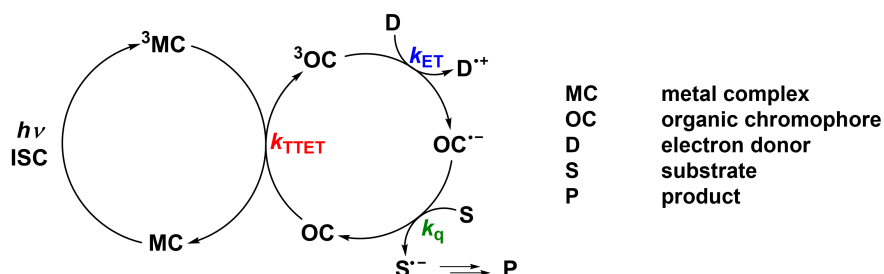


Figure 16: General scheme for a sensitization-initiated electron transfer mechanism. The catalytic cycle consists of a metal-based complex (MC) and an organic chromophore (OC). The individual steps include: excitation and ISC of the MC, TTET (red) to the OC, reduction of the OC (ET, blue) and then the substrate activation step (k_q , green).

2.1.1 Sensitization-initiated electron transfer with blue light

Photons in a wavelength range from 400 nm to 450 nm are the most energetic visible photons, contain energies between 3.09 eV to 2.76 eV and are assigned the colors blue and violet⁷.^[71,215,216] In efficient systems, the photon energy is converted to over 50 % into reduction or oxidation potential for substrate activation (compare Section 1.3.2).^[128] For blue light, this translates to potentials in the range of 1.3 V *vs* NHE to 1.5 V *vs* NHE. As sensitizers, iridium-based complexes with high triplet energies of 2.5 eV to 2.9 eV and fast and quantitative ISC were chosen as sensitizers for photoredox catalysis with blue light.^[102,217,218] The OCs should possess a triplet energy close to that of the Ir-sensitizer, a long τ_T and a high reduction potential, which makes naphthalene ($E_T = 2.62$ eV^[48]) and *p*-terphenyl ($E_T = 2.50$ eV^[48]) derivatives the most promising candidates.^[123,163] After the energy transfer step (compare Figure 16), a sacrificial electron donor reduces the triplet OC to the OC^{•-}. For the catalytic systems presented in this section, the water-soluble ascorbate monoanion (HAsc⁻) was selected as a suitable electron donor. The reduction potential of ascorbate is highly dependent on the *pH* of the solution since the dianion in alkaline surroundings is much more reducing compared to HAsc⁻,^[5,63,219] which is present at *pH* $\approx$ 7. To maintain a constant *pH* (at 7.2), all experiments were performed in a buffered solution, which also maintained a constant ionic strength (Section 1.2).

⁷Depending on the reference, the assignments of colors to wavelength ranges differs slightly. Visible light up to 420 nm to 430 nm is usually classified as violet and blue photons reach $\sim$ 500 nm.^[71,215,216]

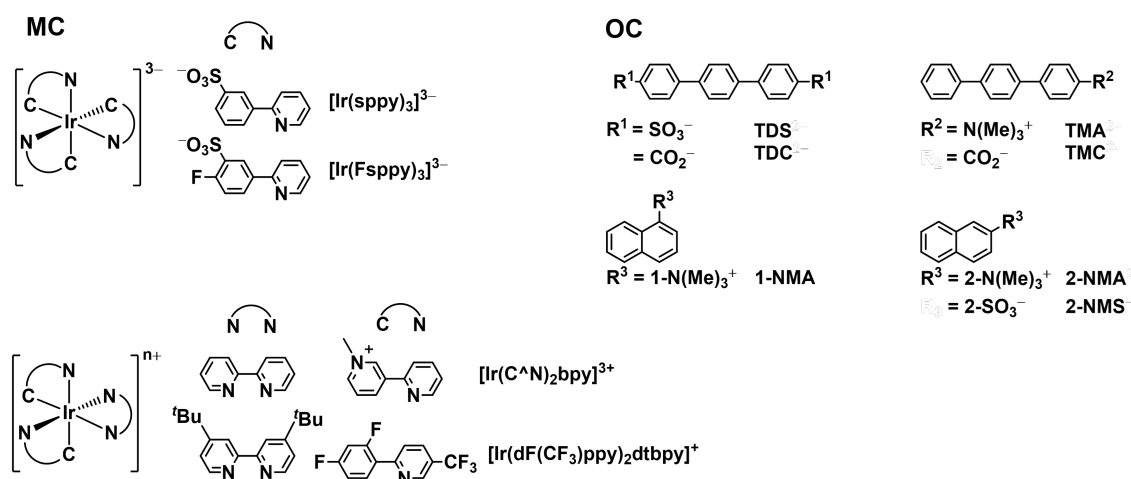


Figure 17: Iridium-based MC and terphenyl or naphthalene-based organic chromophores investigated in this study for a sensitization-initiated electron transfer to generate highly reactive radical anion species for substrate activation.

All uncharged chromophores were substituted with ionic groups to ensure a reasonable solubility in water, while for the overall charged (heteroleptic) complexes conventional counter ions were sufficient (Na^+ , Cl^- or PF_6^-). Structures of all metal complexes and organic chromophores together with their abbreviation are displayed in Figure 17. Introducing ionic groups results in redox potential shifts and modified triplet energies when comparing a substituted chromophore to its uncharged congener. The key photophysical properties of both substituted and unsubstituted chromophores are listed in Table 4. Determining exact redox potentials in an aqueous solution is challenging because of the self-oxidation and -reduction of the solvent.^[220] Thus DFT calculations provided theoretical E_T and the potentials were estimated based on comparative quenching experiments (details are provided in Section 1.2.4, Section 6.2 and the supporting information of reference [63]).

The conversion of the energy of the input photon into redox potential for substrate activation is comparatively high (Section 1.2). Test reactions can be driven using LEDs with a peak wavelength of 440 nm, which corresponds to 2.82 eV. The potentials of the radical anion intermediates for substrate activation are all estimated at -2.0 V vs NHE (Table 4). This corresponds to an efficiency of at least 70 %, which is above the efficiency of the two photon-driven mechanisms (Section 1.2) and above the efficiency when MC or OC is used as a single photocatalyst.

Table 4: Key photophysical parameters of iridium-based metal complexes and the OCs, naphthalene and *p*-terphenyl (derivatives), in aqueous solution at room temperature. Listed are the triplet energy (E_T), the triplet lifetime (τ_T), the ground and excited state reduction potential (E_{red}).

OC or MC	E_T / eV	τ_T / μs	$E_{\text{red}}(\text{C}^{0/\bullet-})$ / V vs NHE	$E_{\text{red}}(^3\text{C}/\text{C}^{\bullet-})$ / V vs NHE
Ir(ppy)_3 [104,218]	2.50	1.9	−1.96 ^a	0.54
<i>p</i> -terphenyl ^[48,123]	2.50	-	−2.39 ^a	−0.13
naphthalene	2.62 ^a	-	−2.34 ^[48]	0.26
$[\text{Ir(sppy)}_3]^{3-}$ [102,104]	2.65	1.66	-	-
TDS ^[63] b,c	2.60	~100	< −1.88	0.81
$[\text{Ir(Fsppy)}_3]^{3-}$ [102,104]	2.76	2.17	-	-
2-NMS	2.50 ^c	14	> −2.4 ^e	> 0.14 ^e
2-NMA	2.58 ^d	16 ^b	> −2.4 ^e	> 0.14 ^e
1-NMA	2.62 ^d	13 ^b	> −2.5 ^e	> 0.14 ^e
$[\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{bpy}]^{3+}$ [127]	2.91	3.5	−0.78 [221]	-
$[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{dtbpy}]^+$ [123,217]	2.68	2.3	−1.13	1.45
TDC ^b	2.52 ^f	-	-	-
TMA ^b	2.48 ^f	-	-	—
TMC ^b	2.30 ^f	-	-	-

^aMeasured in acetonitrile, calculated from V vs SCE by addition of 0.24 V.^[71] ^bDetermined in this project. ^cDFT calculations (B3LYP/6-31+G(d,p)) by Jun.-Prof. C. Kerzig. ^dDFT calculations (B3LYP/6-311+G(d,p)). ^eLower limits for potentials in water for exact derivation see Section 6.2. ^fDFT calculations (B3LYP/6-31+G(d,p)).

$[\text{Ir(sppy)}_3]^{3-}$ and TDS:

The first investigated catalytic system for sensitization-initiated electron transfer in aqueous solution consisted of $[\text{Ir(sppy)}_3]^{3-}$ and TDS. This one-photon-driven mechanism generates the $\text{TDS}^{\bullet-}$ radical anion, which provides a potential of −1.88 V vs NHE.^[123] The system shows a good usage of the input photon energy of >>50 % comparing the estimated reduction potential of $\text{TDS}^{\bullet-}$ (−1.88 V vs NHE) to that of a blue photon (~2.8 eV). Catalysis and spectroscopy were performed in an aqueous potassium acetate buffer solution to maintain a constant *pH* and a high ionic strength (unless indicated otherwise, 50 mM). All elementary reaction steps of the catalytic cycle were

analyzed using transient absorption spectroscopy and together with the corresponding kinetic data, the quenching rates revealed the general feasibility of the mechanism (Figure 18). The rate constants of all key steps are below the diffusion limit in water ($k_{\text{diff}} = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^[48] This can be attributed to the Coulombic repulsion between the anionic metal complex and organic chromophore.^[118] The TTET from $^3[\text{Ir}(\text{sppy})_3]^{3-}$ to TDS also suffers from a comparatively small driving force ($\sim 0.05 \text{ eV}$ in Table 4), which is a further cause for a comparatively small quenching rate constant ($k_{\text{TTET}} = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, Table 5). The rate constants of all wanted quenching pathways allowed optimization of the concentration of each component for maximum overall efficiency.

Spectroscopic analysis of the possible competing mechanistic pathways (Figure 18, gray arrows and entries Table 5 two bottom entries) revealed that $^3[\text{Ir}(\text{sppy})_3]^{3-}$ is reduced by HAsc^- under selected conditions, and this pathway therefore has no relevant impact on the overall reaction progress. Also, possible energy or electron transfer quenching of ^3TDS and ACP would be thermodynamically disfavoured ($E_{\text{T}}(\text{ACP}) = 3.2 \text{ eV}$)^[222]. In contrast, the highest bimolecular quenching rate constant in our investigated system was found for the excited state quenching of $^3[\text{Ir}(\text{sppy})_3]^{3-}$ by the substrate acetophenone (ACP). Despite the quenching being fast, this step is unproductive due to recombination (Appendix, Figures 42 to 44) but eventually converts a certain amount of ACP into the pinacol product. In general, recombination in electron transfer reactions *via* triplet excited photocatalysts containing, in this case iridium, is facilitated by the heavy atom as detailed in Section ???. This is in line with ^1H NMR data, where the control experiment employing only the Ir-catalyst without TDS showed a $\sim 30 \%$ product formation. Employing the full catalytic system with $^3[\text{Ir}(\text{sppy})_3]^{3-}$ and TDS and thereby avoiding recombination enabled by the influence of iridium heavy atom yielded almost full conversion and close to quantitative product formation ($\sim 90 \%$ product formation, Figure 43).

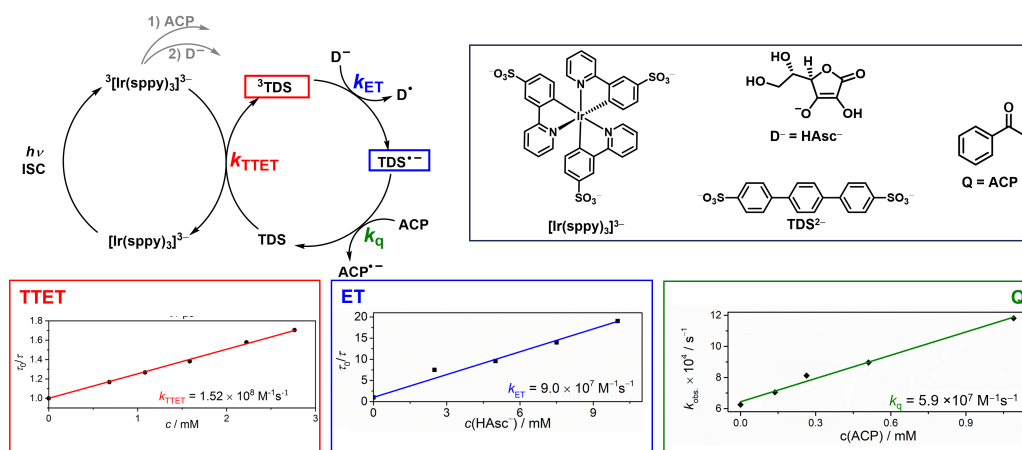


Figure 18: Top left displays the catalytic cycle and the involved chromophores ($[\text{Ir}(\text{sppy})_3]^{3-}$ and TDS) and quenchers ($\text{HAsc}^{\bullet-}$ and ACP) are displayed in the black box. The color-coded quenching plots for k_{TTET} , k_{ET} and k_q are listed in Table 5 (original data in Figures 40–42). The gray arrows 1) and 2) indicate possible competitive quenching pathways of the species involved, which are also addressed in Table 5 and Figure 42.

Table 5: Rate constants for the different elementary steps investigated in a sensitization-initiated electron transfer mechanism using $[\text{Ir}(\text{sppy})_3]^{3-}$ and TDS.

Elementary reaction step	$k_q / \text{M}^{-1} \text{s}^{-1}$	Figure
$^3[\text{Ir}(\text{sppy})_3]^{3-} + \text{TDS} \xrightarrow{\text{TTET}} ^3[\text{Ir}(\text{sppy})_3]^{3-} + ^3\text{TDS}$	1.5×10^8	18
$^3\text{TDS} + \text{HAsc}^{\bullet-} \xrightarrow{\text{ET}} \text{TDS}^{\bullet-} + \text{HAsc}^{\bullet}$	9.0×10^7	18
$\text{TDS}^{\bullet-} + \text{ACP} \xrightarrow{\text{ET}} \text{TDS} + \text{ACP}^{\bullet-}$	5.0×10^7	18
$^3[\text{Ir}(\text{sppy})_3]^{3-} + \text{HAsc}^{\bullet-} \xrightarrow{\text{ET}} [\text{Ir}(\text{sppy})_3]^{4-} + \text{HAsc}^{\bullet}$	1.1×10^6	45
$^3[\text{Ir}(\text{sppy})_3]^{3-} + \text{ACP} \xrightarrow{\text{ET}} [\text{Ir}(\text{sppy})_3]^{2-} + \text{ACP}^{\bullet-}$	2.5×10^9	42

In summary, these results highlight the general feasibility of the single-photon driven combined TTET and ET with an iridium-based sensitizer under blue light irradiation (LED, 440 nm; $E_{h\nu} = 2.82 \text{ eV}$) and $\text{TDS}^{\bullet-}$ as catalytically active intermediate ($E_{1/2} = -1.99 \text{ V vs NHE}$) with a generally high conversion of the energy of the input photon

($\eta \sim 0.7$). Further improvements in this system can be achieved by increasing the energy transfer rate of the initial step and suppressing the direct and unproductive quenching of the triplet excited photosensitizer.

Enhanced Coulombic interaction between iridium-based metal complexes and organic chromophores:

Two main strategies were pursued to overcome the challenges identified in the previous system and to enhance the overall performance of the Ir-complex-based TTET-ET mechanism. The first modification of the system aimed for higher energy transfer rate constants (k_{TTET}) by inverting the Coulombic repulsion and introducing attractive Coulomb interactions between MC and OC. This possibility was investigated using the established $[\text{Ir}(\text{sppy})_3]^{3-}$ and the fluorinated $[\text{Ir}(\text{Fsppy})_3]^{3-}$ as MC in combination with cationic OCs such as the naphthalene derivatives 1-TMN or 2-TMN. For comparing the Coulombic interactions in the TTET step, the anionic 2-NMS was employed as reference OC. The alternative option is to inverse the overall charges by using a cationic MC ($[\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{bpy}]^{3+}$ or $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{dtbpy}]^+$) together with an anionic OC (TDC, TMC, TDS and for comparison TMA). This second strategy involved the usage of surfactants (DTAC, SDS and TX-100)^[5,223], which served for multiple purposes: Besides reducing the Coulombic repulsion between chromophores with charge of equal sign, the surfactants were also intended to reduce the direct quenching of the MC by the substrate and improve the solubility of the water-soluble organic chromophore.

All of the proposed pathways were unsuccessful, mostly for system-inherent reasons. The initial step for the two cationic amine-derivatives of naphthalene proceeded as expected and TA spectroscopy revealed the triplet species using either $^3[\text{Ir}(\text{sppy})_3]^{3-}$ or $^3[\text{Ir}(\text{Fsppy})_3]^{3-}$ as MC. In accordance with the triplet energies (Table 4) of the two sensitizers, the rate constant for energy transfer differed. Using $^3[\text{Ir}(\text{sppy})_3]^{3-}$ as sensitizer ($E_{\text{T}} = 2.65 \text{ eV}$)^[102] resulted in a lower rate constant compared to using $[\text{Ir}(\text{Fsppy})_3]^{3-}$ ($E_{\text{T}} = 2.75 \text{ eV}$)^[102] as a sensitizer, at otherwise identical conditions. Hence, $[\text{Ir}(\text{Fsppy})_3]^{3-}$ was selected as sensitizer for the following investigations. The improved Coulombic interaction for TTET was found with the fluorinated Ir-catalyst and the expected increase in quenching rate, comparing the triplet energy transfer rate with 2-NMS ($k_{\text{TTET}} = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) to that with 2-NMA ($k_{\text{TTET}} = 6.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, original data in Figure 47). The key difference between those two naphthalene derivatives is their overall charge and thus either repulsive (for 2-NMS) or attractive (for 2-NMA) Coulombic interactions towards the negatively charged $[\text{Ir}(\text{Fsppy})_3]^{3-}$ as MC. The almost identical triplet energies (Table 4) of the two naphthalenes lead to identical thermodynamic prerequisites for the energy transfer. Consequently, the observed k_{TTET} for 2-NMA exceeding that of 2-NMS is mainly attributed to the Coulombic interactions. However, the subsequent reduction using Asc^{2-} as a suitable electron donor, did not result in the formation of a long-lived radical species. Despite the detectable reductive quenching of $^32\text{-NMA}$

by Asc^{2-} in time-resolved spectroscopy, only traces of the one electron reduced species were detected. In protic solvents, unsubstituted naphthalene radical anions are rapidly protonated, resulting in a fast decay of the reactive intermediate and subsequently in a decomposition of the naphthalene-derived OC.^[224,225] A similar decomposition might be possible for naphthalene derivatives in an aqueous solution (spectroscopic data in the appendix Section 6.2.6).

As a consequence, improving the *p*-terphenyl derivatives (Figure 17) was considered including studies with surfactant molecules and cationic iridium sensitizers. For all approaches using *p*-terphenyl-derivatives as OC, solubility or aggregation issues prevented a successful application in the catalytic system. The surfactants (DTAC, SDS or TX-100) were added, which however also precipitated eventually or caused unwanted side reactions. Even with two ionic substituents the water-solubility of the terphenyl derivatives is limited to small ($\sim < 10$ mM) concentrations. These restrictions caused by the system design prevented a successful investigation of an improved catalytic combination with iridium sensitizers and charged organic chromophores under conditions suitable for photocatalysis.

This blue light-driven mechanism is generally feasible as evidenced by the results of this section and especially using the combination of $[\text{Ir}(\text{sppy})_3]^{3-}$ as MC and TDS as OC. Furthermore, this mechanism provides highly reactive radical species (the respective $\text{OC}^{\bullet-}$) transforming the energy of the catalytic photon efficiently into redox potentials, which can be used for substrate activation. Systemic challenges, which lower the efficiency of the catalytic mechanism can be overcome by testing further combinations of MC and OC or by optimizing the combination of OC and surfactant.

Author contributions: M.-S. Bertrams synthesized and characterized TDS, performed the optical spectroscopy and irradiation experiments for the $[\text{Ir}(\text{sppy})_3]^{3-}$ – TDS system. Parts of this system were already analyzed during the master thesis of M.-S. Bertrams, supervised by C. Kerzig. M.-S. Bertrams supervised, supported and assisted the synthesis and investigation of the naphthalene-derived OCs (performed by A. König) and the amino- and carboxy *p*-terphenyl derivatives (performed by J. Fetzer). A. S. Sell provided the $[\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{bpy}]^{3+}$. C. Kerzig conceptualized the project idea and provided overall guidance throughout the project realization.

2.1.2 Sensitization-initiated electron transfer with green light

This section presents:

Efficient Energy and Electron Transfer Photocatalysis with a Coulombic Dyad

Matthias Schmitz, Maria-Sophie Bertrams, Arne C. Sell, Felix Glaser, Christoph Kerzig, manuscript under revision.

The blue light-driven system achieved an efficient conversion from photon energy into reduction power. Unproductive competing reactions and decomposition effects however hampered a further optimization of the system. To further pursue the concept of efficient energy conversion *via* the sensitization-initiated electron transfer mechanism, an alternative system with ruthenium instead of iridium complexes combined with charged pyrene derivative was considered, avoiding the drawbacks observed in the iridium-catalyzed systems. Tris-(1,10-phenanthroline)ruthenium(II) ($[\text{Ru}(\text{phen})_3]^{2+}$) was used as a well-known sensitizer. For the organic counterpart the tetraanionic pyrene-1,3,6,8-tetrasulfonate (PTS) was chosen because of its water solubility and the suitable energies and potentials, which are expected to fulfill the thermodynamic prerequisites (see the following section) for a successful realization of the catalytic scheme (chemical structures are shown below in Figure 19).

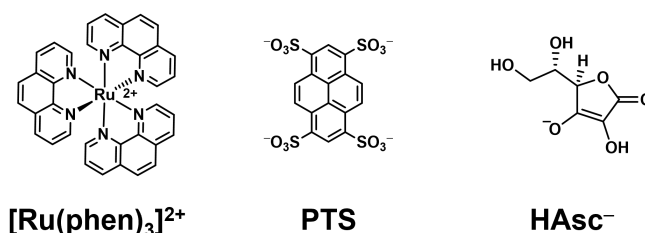


Figure 19: Compounds and abbreviations employed for the green light driven TTET and ET catalytic mechanism (exact mechanism is detailed in Figure 21). $[\text{Ru}(\text{phen})_3]^{2+}$ was chosen as MC, PTS as OC and the sacrificial electron donor is HAsc^- . For more details see reference [36].

Thermodynamic considerations:

The triplet energy of $^3[\text{Ru}(\text{phen})_3]^{2+}$ is sufficiently high for an exergonic TTET to pyrene and its sulfonated derivative PTS ($\Delta E_{\text{TTET}} < 0 \text{ eV}$). Decoration of the OC with sulfonate groups reduces the triplet energy, which increases the energy gap between ^3MC and ^3OC and as a consequence the thermodynamic driving force for the triplet energy transfer from $^3[\text{Ru}(\text{phen})_3]^{2+}$ to PTS. The larger energetic difference between the triplet excited state energies also impede the back energy transfer from ^3PTS to $[\text{Ru}(\text{phen})_3]^{2+}$, which is possible for unsubstituted pyrene (Supporting information of^[36] and molecular dyads in Section 2.3), but largely prohibited with PTS as an energy acceptor.

Similar to the blue-photon driven Ir-based catalytic systems (previously discussed in Section 2.3), HAsc[−] was used as a sacrificial electron donor. HAsc[−] has a sufficiently low reduction potential (0.72 V *vs* NHE)^[219], such that the reduction of both ³[Ru(phen)₃]²⁺ and ³PTS are thermodynamically feasible (Table 6), which was not the case for the previously discussed Ir-based systems (Table 5). This competing reaction has to be considered in the overall analysis of the different pathways in the catalytic mechanism. The reduction potentials for PTS in the ground and excited state were estimated based on several quenching experiments performed within this project and a more detailed discussion is provided in the appendix (Section 6.3).

Table 6: Key photophysical parameters of [Ru(phen)₃]²⁺ as a metal-based sensitizer and pyrene and derived organic chromophores. Listed are the triplet energy (E_T), the triplet lifetime (τ_T), the ground and excited state reduction potential (E_{red}).

chromophore (C, OC or MC)	E_T / eV	τ_T / μ s	E_{red} (C ^{0/•−}) / V <i>vs</i> NHE	E_{red} (³ C/C ^{•−}) / V <i>vs</i> NHE
[Ru(phen) ₃] ²⁺ ^[48]	2.19	1.09	−1.11 ^a	1.08
pyrene ^[48,84]	2.09	180	−1.85 ^a	0.25
PTS ^b	1.8	355	~ −0.8	~1.0
PMS ^[31]	2.06 ^c	477 ^c	-	-

^aMeasured in acetonitrile, calculated from V *vs* SCE by addition of 0.24 V.^[71] ^bThis work, see Table 12. ^cin DMF.

Finally, the efficiency of converting the energy of the input photon is considered. The test reactions were performed using a 525 nm LED corresponding to 2.36 eV. Compared to the redox potential of PTS, the energy conversion is below 50 %, which is comparatively low.⁸ Future developments including PMS might achieve higher efficiencies in this context. The choice for [Ru(phen)₃]²⁺ and PTS was based on optimizing towards high efficiency of each reaction step and cage escape quantum efficiencies close to unity were achieved, thereby making this system highly successful and efficient in various electron transfer test reactions.

Mechanistic investigations on TTET:

The enhanced interaction between [Ru(phen)₃]²⁺ and PTS becomes apparent in combined static and dynamic quenching and was established by two key observations in

⁸Taking into account the triplet energy of ³PTS, sensitization could generally be possible at wavelengths below 525 nm.^[36]

kinetic quenching experiments. Firstly, the kinetic emission traces of $^3[\text{Ru}(\text{phen})_3]^{2+}$ decreased in both lifetime (dynamic quenching, Figure 20 orange arrow) and relative intensity (static quenching, Figure 20 green arrow) upon increasing concentrations of PTS in the solution. The resulting $k_{\text{TTET}} = 2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ is above the diffusion limit for bimolecular quenching in H_2O ($k_{\text{diff}} = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [48]. Secondly, analysis of the isolated formation kinetics of ^3PTS at the isosbestic point, $\lambda_{\text{max}} = 496 \text{ nm}$, (TA spectrum in Figure 21 and reference [36] Figure 3c) revealed an essentially instantaneous signal increase after the laser pulse, which became more pronounced with increasing PTS concentrations. This observation implies an ultrafast process, which is caused by static quenching, therefore independent from the lifetime and can only be resolved indirectly on the ns-timescale [126]. Further rise of the ^3PTS concentration can be resolved on the ns-timescale and corresponds to the concentration-dependent lifetime decrease of $^3[\text{Ru}(\text{phen})_3]^{2+}$ detected *via* the emission kinetics. Hence, besides the abovementioned static quenching, this observation represents the dynamic fraction of the quenching process. A detailed discussion can be found in reference [36]. The fast energy transfer, enabled by combined static and dynamic quenching, paved the way for a highly efficient energy transfer ($\eta_{\text{TTET}} \approx 1$) even at the very low PTS concentration of $120 \mu\text{M}$. In addition to the detailed quenching analysis, the absolute concentration of ^3PTS after static and dynamic processes can be determined with the $\Delta\varepsilon$ of ^3PTS (Supporting Information of reference [36] in Section 6.7). Quantitative measurements with respect to the number of photons absorbed by the sensitizer, the quantum yield of the energy transfer step with $120 \mu\text{M}$ PTS yielded a nearly quantitative $\phi_{\text{TTET}} \sim 1$. [36]

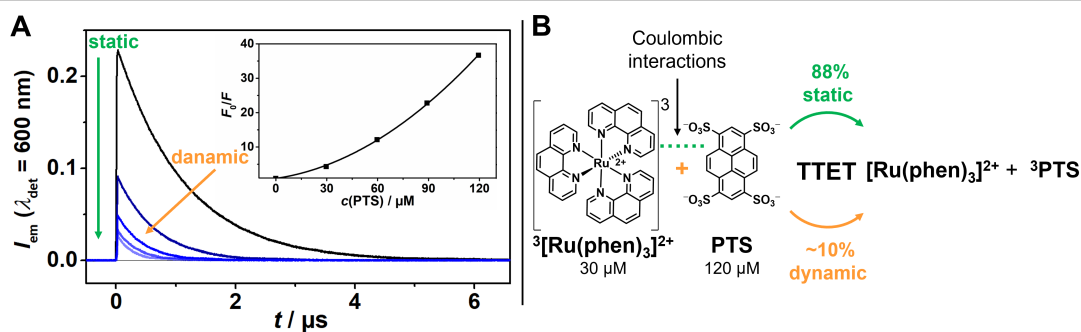


Figure 20: A: Kinetically resolved emission quenching of $^3[\text{Ru}(\text{phen})_3]^{2+}$ with increasing concentrations of PTS. The green arrow indicates the static component and the orange arrow indicates the dynamic component (same color code throughout the figure). The inset shows the Stern–Volmer plot with the expected upward curvature for combined static and dynamic quenching. B: Scheme of the triplet-triplet energy transfer together with the concentrations of $[\text{Ru}(\text{phen})_3]^{2+}$ and PTS, which were employed for further investigations and the respective contributions of static and dynamic quenching. Figure adapted from Figure 3 in reference [36].

Mechanistic investigations on ET:

The next step, following TTET from $^3[\text{Ru}(\text{phen})_3]^{2+}$ to PTS, involves reductive quenching of ^3PTS by the sacrificial electron donor HAsc^- . As discussed previously (in the paragraph Thermodynamic considerations, Table 6),^[5] the reductive quenching of both ^3PTS and $^3[\text{Ru}(\text{phen})_3]^{2+}$ by HAsc^- is thermodynamically feasible thereby making the direct reduction of $^3[\text{Ru}(\text{phen})_3]^{2+}$ a competing step, which extends the catalytic cycle as shown in Figure 21.

Excited state quenching experiments even revealed a quenching rate constant for the electron transfer $k_{\text{ET}2} = 4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for $^3[\text{Ru}(\text{phen})_3]^{2+}$ exceeding that for ^3PTS ($k_{\text{ET}1} = 0.23 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)^[36] by about one order of magnitude (Figure 21 and Table 7). The static quenching between $^3[\text{Ru}(\text{phen})_3]^{2+}$ and PTS, however prevents the electron transfer quenching between $^3[\text{Ru}(\text{phen})_3]^{2+}$ and HAsc^- .

Under the conditions used in model photoreactions, the formation of the radical anion ($\text{PTS}^{\bullet-}$) is about five times more efficient in the system with PTS compared to using only $[\text{Ru}(\text{phen})_3]^{2+}$. Two key features explain this, at first glance counter-intuitive (considering the electron transfer rate constants), finding:⁹ One is the increase in triplet lifetime by over two orders of magnitude for ^3PTS compared to $^3[\text{Ru}(\text{phen})_3]^{2+}$ (Table 6), which makes the reductive quenching at the concentration used for photocatalysis (10 mM HAsc^-) much more efficient ($\eta_{\text{q}2} = 0.86$ and $\eta_{\text{q}1} \sim 1$, Figure 21). This finding establishes experimentally the previously discussed kinetic advantage originating from an increase in lifetime (Section 1.2.5). The second important difference is the significantly higher cage escape efficiency for the electron transfer step, under the chosen conditions, and the $\text{PTS}^{\bullet-}$ formation ($\eta_{\text{CE}1} \sim 1.0$), which is much lower for $[\text{Ru}(\text{phen})_3]^+$ ($\eta_{\text{CE}2} = 0.21$). The heavy atom effect introduced by ruthenium in the MC, which is useful for the fast and quantitative ISC after excitation, makes an unproductive back electron transfer feasible, yielding the overall unproductive return to the photocatalyst ground state, instead of the desired reduced species. The smaller heavy atom effect and overall less effective (b)ISC in PTS compared to ruthenium-based sensitizers is expected to contribute to the higher cage escape in this case (Section 1.2.5).^[92]

⁹Section 1.2.4 provides a more detailed discussion regarding the efficiencies for quenching, product formation and the quantum yield.

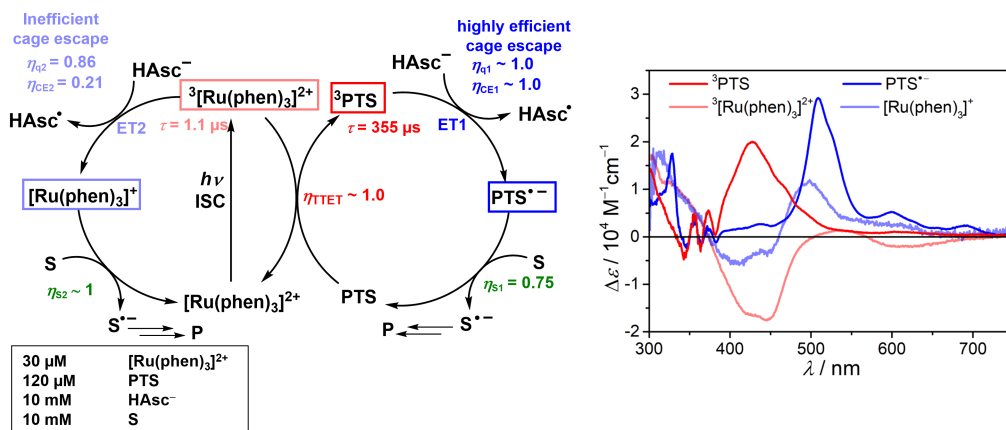


Figure 21: Catalytic cycle for ruthenium-based combined TTET and ET mechanism compared to direct reductive quenching of the sensitizer together with the decisive efficiencies. The concentration of each compound is given below. The right side shows the calibrated TA spectra of all species involved. (Measurements and calculations for the $\Delta\epsilon$ of $^3[\text{Ru}(\text{phen})_3]^{2+}$, ^3PTS and $[\text{Ru}(\text{phen})_3]^+$ and the cage escape efficiencies are described in the Appendix (Section 6.3). Figure adapted from Figure 7 in reference[36]).

Table 7: Quenching rates (k_q), quenching efficiencies (η_q) and cage escape efficiencies (η_{CE}) for the TTET and ET steps of the catalytic cycle shown in Figure 21.

	$k_q / 10^8 \text{ M}^{-1} \text{ s}^{-1}$	η_q	η_{CE}
TTET ^b	250	1	1
ET1	0.23 ^a	1 ^b	0.97 ^b
ET2	4.5 ^b	0.86 ^a	0.21 ^a

^aData and measurements in Section 6.3. ^bData and measurements in reference[36].

The exact analysis of the reaction mechanism and especially the cage escape efficiencies required knowledge of the concentrations of all involved intermediates at the chosen reaction conditions (Figure 21, lower left) and therefore the $\Delta\epsilon$ of every species involved, which was determined using different methods of transient absorption measurements (based on the Beer-Lambert law, Section 1.2.1). For ^3PTS $\Delta\epsilon$ was determined by relative actinometry using $[\text{Ru}(\text{bpy})_3]^{2+}$ as a reference compound, which then allowed to derive the absolute concentration of ^3PTS after sensitization and the efficiency for TTET (Appendix, Section 6.7). An indirect method was chosen for $\Delta\epsilon$ of $[\text{Ru}(\text{phen})_3]^+$. Methylviologen (MV^{2+}) is a highly reactive oxidizing quencher, capa-

ble to accept an electron from $[\text{Ru}(\text{phen})_3]^+$ to recover $[\text{Ru}(\text{phen})_3]^{2+}$. Based on the extinction coefficients for the reduced $\text{MV}^{+ [226]}$ this species was used to determine the extinction coefficient of $[\text{Ru}(\text{phen})_3]^+$. In a following experiment, the corresponding ϕ_{CE} was determined. The detailed calculations are in the Appendix (Section 6.3) and 6.7 as well as in reference [36].

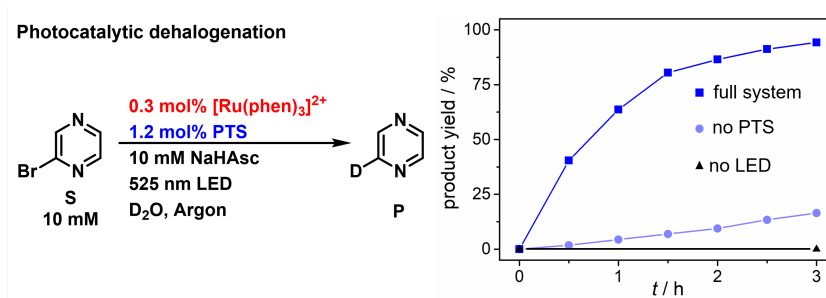


Figure 22: Reaction scheme and conditions for the debromination of bromo-pyrazin (S) under green light LED irradiation. The right side shows the reaction progression comparing the full system (blue) to that without PTS (light blue). Without the LED, no conversion is observed (black). Figure adapted from Figure 7 in reference [36], see below.

To evaluate the system also for photocatalytic applications, an NMR-scale debromination reaction was investigated (Figures 22 and 51). In the full system, the product formation is much faster in the beginning and leads to nearly full conversion after 3 h. In contrast, using only the ruthenium as photoredox catalyst, the product formation is less efficient and after 3 h only $\sim 20\%$ of the product is formed. This is in good agreement with the improvement expected from the ϕ_{CE} for reductive quenching by HAsc^- , and the according data can be found in reference [36].

Reprinted from M. Schmitz, M.-S. Bertrams, A. C. Sell, F. Glaser, C. Kerzig, *J. Am. Chem. Soc.*, **2024**, publication is currently under revision.^[36] The supporting information can be found in Section 6.7.

Author contributions: M.-S. Bertrams determined the $\Delta\varepsilon$ and the ϕ_{CE} for $[\text{Ru}(\text{phen})_3]^+$, the $\Delta\varepsilon$ of ^3PTS , and the k_q for the excited-state quenching of ^3PTS by HAsc^- , results are found in the section above and the corresponding data in the Appendix (Section 6.3). The irradiation reaction with bromopyrazine was performed and analyzed by M.-S. Bertrams (see also Section 6.3). M. Schmitz performed all experiments involving the characterization of the system, investigations related to the ϕ of TTET, the quenching experiments with the substrate and $\Delta\varepsilon$ and ϕ_{CE} for $\text{PTS}^{\bullet-}$. M. Schmitz performed the experiments and spectroscopy for O_2 sensitization and corresponding catalytic applications as well as the irradiation experiments for the pinacol coupling. F. Glaser provided the ruthenium-PMS salt. C. Kerzig conceived the project and provided general guidance.

Efficient Energy and Electron Transfer Photocatalysis with a Coulombic Dyad

Matthias Schmitz^a, Maria-Sophie Bertrams^a, Arne C. Sell^a, Felix Glaser^{a, b},
and Christoph Kerzig^{a*}

^a Department of Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10–14,
55128 Mainz, Germany

^b Present Address: Université catholique de Louvain (UCLouvain), Institute of Condensed Matter and
Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Place Louis Pasteur 1,
bte L4.01.02, 1348 Louvain-la-Neuve, Belgium

* Email: ckertzig@uni-mainz.de

Abstract: Photocatalysis holds great promise for changing the way value-added molecules are currently prepared. However, many photocatalytic reactions suffer from quantum yields well below 10 %, hampering the transition from lab-scale reactions to large-scale or even industrial applications. Molecular dyads can be designed such that the beneficial properties of inorganic and organic chromophores are combined, resulting in milder reaction conditions and improved quantum yields of photocatalytic reactions. We have developed a novel approach for obtaining the advantages of molecular dyads without the time- and resource-consuming synthesis of these tailored photocatalysts. Simply by mixing a cationic ruthenium complex with an anionic pyrene derivative in water a salt bichromophore is produced owing to electrostatic interactions. The long-lived organic triplet state is obtained by static and quantitative energy transfer from the preorganized ruthenium complex. We exploited this so-called Coulombic dyad for energy transfer catalysis with similar reactivity and even higher photostability compared to a molecular dyad and reference photosensitizers in several photooxygenations. In addition, it was shown that this system can also be used to maximize the quantum yield of photoredox reactions. This is due to an intrinsically higher cage escape quantum yield after photoinduced electron transfer for purely organic compounds compared to heavy atom-containing molecules. The combination of laboratory-scale as well as mechanistic irradiation experiments with detailed spectroscopic investigations provided deep mechanistic insights into this easy-to-use photocatalyst class.

Introduction

Catalytic transformations of small molecules via photoredox^{1–4} and energy transfer^{5–7} catalysis represent a rapidly growing research field.^{8,9} Scientists from several disciplines actively contributed to this impressive development and recent breakthroughs in the sub-disciplines mechanism development,^{10–15} reaction engineering^{16–18} and photocatalyst design^{19–26} have been achieved. However, many or even most of the photocatalytic reactions reported so far have to rely on several hours of irradiation using high-power LEDs for transforming milligram quantities of given substrates, which already implies very low overall quantum yields. The reaction quantum yield is frequently overlooked in the design of novel photoreactions but this parameter will likely play a key role in the further development of industrially scalable photoreactions.²⁷ Deep mechanistic investigations using transient absorption (TA) spectroscopy are a powerful tool not only to differentiate between different mechanistic scenarios but also to optimize reaction steps and the overall reaction quantum yield.^{28–32}

Metal complexes having 4d⁶ or 5d⁶ valence electron configurations with corresponding metal-to-ligand charge transfer (MLCT) states are among the most-investigated photocatalysts as a result of their beneficial properties including visible-light absorptivity, quantitative triplet formation and tunability.^{2,33–35} However, their triplet state lifetimes are frequently too short for quantitative quenching via energy transfer (EnT) or electron transfer (ET) with a substrate or additive in a catalytic cycle.^{36,37} Additionally, ET quenching suffers from unproductive in-cage recombination due to the heavy-atom effect and concomitant radical-pair intersystem crossing (ISC).^{38–44} These issues reduce the achievable quantum yields for many photoreactions drastically, given that productive onward reactions of the initial photoinduced ET reaction products can only occur after their escape from the so-called solvent cage.⁴⁵ Tailor-made molecular dyads consisting of a metal complex (MC) unit and a covalently linked organic chromophore (OC)^{46–48} have the potential to solve these efficiency problems owing to the long-lived and heavy-atom free organic triplet being accessible after intramolecular energy transfer (iEnT) from the photoexcited metal complex. Significantly improved quantum yields for EnT and ET key reaction steps in photocatalysis were observed when comparing dyads and parent metal complexes,^{36,38,49–58} but the required multi-step syntheses of these improved bichromophoric photocatalysts hamper their broader usage.

Attractive and repulsive Coulombic interactions are among the most fundamental non-covalent interactions and it comes to no surprise that they have been used extensively to control the outcome of chemical reactions. Exploiting photocatalyst–quencher^{59–70} Coulombic interactions

is a well-established strategy for improving the efficiency of photochemical key steps and the reaction performance accordingly, either by accelerated diffusion between oppositely charged species or by static quenching owing to pre-aggregation. Furthermore, underexplored counterion^{71–75} as well as ion-pairing^{61,76–79} effects received some attention from the photochemistry community in recent years. Herein, we demonstrate that the favorable properties of MC–OC dyads can be obtained by exploiting Coulombic attraction between commercially available ionic chromophores. As we will show, these readily accessible Coulombic dyads clearly outperform the catalytic reactivity of the parent ruthenium(II) and also osmium(II) complexes. Using several spectroscopic techniques and test reactions, we compare all key properties of a molecular and a Coulombic dyad based on a ruthenium-tris(diimine) unit as MC and a pyrene moiety as OC (Figure 1). Despite the ongoing development in preparing photoactive complexes based on Earth-abundant metals and recent breakthroughs in this field,^{20–22,24–26,80,81} precious 4d⁶ and 5d⁶ metal complexes will most likely stay the workhorses for most photoreactions in the near future. Concepts significantly improving the performance of precious photoactive metal complexes that are easy to implement would thus have far-reaching implications.

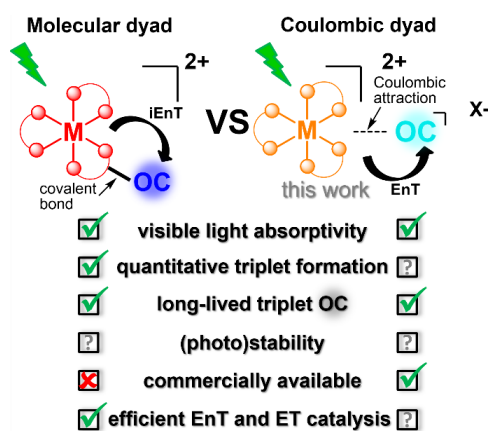


Figure 1 Comparison of key properties of well-known, tailor-made molecular metal complex–organic chromophore (MC–OC) dyads and novel Coulombic dyads prepared by mixing commercially available chromophore-containing salts.

Results and Discussion

Dyad Design

Guided by our recent studies with a water-soluble molecular dyad comprising a ruthenium-tris(phenanthroline) (**Ruphen**) complex and a pyrene moiety,^{36,58} hereafter referred to as **RuphenPy** (see Figure 2), we aimed at mimicking its photophysical and photochemical properties through intermolecular interactions without the necessity of a multi-step synthesis.

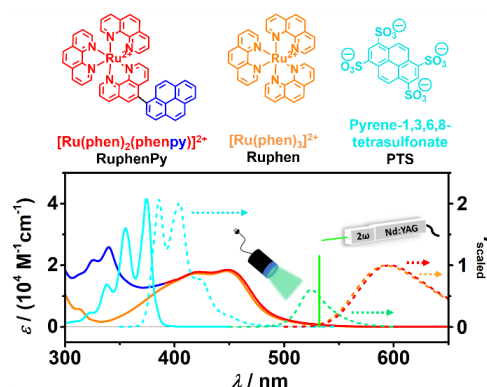


Figure 2 Molecular structures of the main compounds of this study, together with corresponding abbreviations, UV-vis absorption (solid line) and normalized emission spectra (dotted line). The spectra of the metal complexes (as chloride salts) and the pyrene-derivative (as sodium salt) were recorded in water. The excitation wavelength for laser flash photolysis measurements (solid vertical line, $\lambda_{\text{exc}} = 532 \text{ nm}$) and the emission spectrum of the LED used for lab-scale irradiation experiments (dotted green line, $\lambda_{\text{exc,max}} = 525 \text{ nm}$) are highlighted in the spectrum.

Dicationic **Ruphen** is intrinsically suitable for using Coulombic interactions – as numerous photoactive Ru, Ir and Os complexes are – to accelerate diffusion or to form a supramolecular complex with a negatively charged OC salt. Regarding the triplet energy-matched pyrene-based acceptor,^{48,58,64,82–88} the tetrasodium salt of pyrene-1,3,6,8-tetrakisulfonic acid (**PTS**), a low-cost and commercially available compound with four negative charges, emerges as a well-suited aggregation counterpart for **Ruphen**. **PTS** has been used in different fields, including the formation of charge transfer (CT) complexes,⁸⁹ aggregation with enzymes,⁹⁰ integration into 2D metal-organic frameworks,⁹¹ and participation in self-assembling supramolecular systems.⁹² All of these applications exploit the high charge density of **PTS**. In addition, **PTS** is also widely used as a fluorescence probe,^{92,93} along with various other pyrene-based fluorophores.⁹⁴ Considering the typically low pK_a of aromatic sulfonic acids in water,⁹⁵ and the absence of pH-dependent changes in the UV-Vis spectrum of **PTS** (section S2.4), it is very likely that **PTS** is

exclusively present in its fully deprotonated state, maximizing the attractive Coulombic interactions with a positively charged sensitizer. Moreover, the water-soluble chloride salt of the ruthenium complex is commercially available, allowing straightforward preparation of a Coulombic dyad of **Ruphen** and **PTS** by simply dissolving both salts in water.

Steady-State Absorption and Emission Properties

Ruphen exhibits a $^1\text{MLCT}$ absorption band in the visible region along with a $^3\text{MLCT}$ emission peaking at $\lambda_{\text{max}} \sim 594 \text{ nm}$.⁹⁶ In the molecular dyad **RuphenPy**, the MLCT absorption and emission bands exhibit a slight red shift compared to those of **Ruphen**. This shift is due to minor changes in the $^3\text{MLCT}$ state energies caused by the covalently bound chromophore. The **RuphenPy** absorption spectrum is basically a superposition of the **Ruphen** and pyrene ground state absorption bands, confirming the presence of both chromophores (see Figure 2).³⁶ Dissolved **PTS** shows a characteristic fine-structured pyrene $^1(\pi-\pi)^*$ absorption band^{93,97} located at the low-energy end of the UV spectrum. It also exhibits a fluorescence spectrum with a Stokes-shifted fluorescence profile that accurately reflects the absorption features.⁹³ Due to the presence of four sulfonic acid groups, the absorption and emission characteristics of **PTS** show a prominent red shift compared to the spectra of unmodified pyrene, which implies lower excited-state energies for **PTS**. Upon the addition of **PTS** to a solution containing **Ruphen**, a slight spectral broadening and a red shift of the MLCT absorption band become apparent, while solubility issues do not occur for micromolar and lower millimolar concentrations. This initial observation is a first indication of ground state aggregation involving both chromophores, which will be discussed in the next subsection.

Ground State Association and Energy Transfer between Ruphen and PTS

In the molecular dyad **RuphenPy** (see Figure 2 for its structure), the organic triplet state is produced through a sub-nanosecond intramolecular energy transfer from the $^3\text{MLCT}$ state as the energy donor.³⁶ This transfer leads to the formation of a $^3(\pi-\pi)^*$ state almost exclusively localized on the pyrene moiety. To explore whether a similar phenomenon in the **Ruphen–PTS** pair takes place, a classical Stern–Volmer experiment was performed investigating the quenching of the emissive $^3\text{MLCT}$ state upon the addition of **PTS** (see Figure 3 (a)). The experiments reveal a shortening of the $^3\text{MLCT}$ lifetime and a simultaneous decrease in the initial emission intensity. The shorter lifetime of the $^3\text{MLCT}$ state is attributed to dynamic, *i.e.* diffusion-based, quenching between dicationic **Ruphen** and tetraanionic **PTS**. The calculated quenching rate constant, $k_q = 2.5 \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1}$, significantly exceeds the conventional diffusion

limit in an aqueous medium, which is calculated for uncharged reaction partners with identical molecular radii ($6.5 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$)⁹⁷. This pronounced difference is rationalized by Coulombic attraction between **Ruphen** and **PTS**, which effectively accelerates the dynamic quenching process. For entirely diffusion-controlled quenching, the amount of ³MLCT states generated following laser pulses of constant energy would remain constant regardless of the amount of quencher present, leading to identical initial emission amplitudes. However, we observed a decrease in the initial emission amplitude that correlates with the **PTS** concentration, indicating the occurrence of quasi-instantaneous (on a sub-ns timescale) static quenching. In molecular dyads, spatial proximity is ensured through covalent bonds, which enable rapid *intramolecular* energy transfer processes. A similar process with predominantly static quenching is seemingly achieved through strong attractive interactions^{98,99} in the Coulombic dyad, resulting in *ion-pair* energy transfer. Comparative investigations with pyrene monosulfonic acid (**PMS**, monoanionic) and uncharged pyrene (see SI, section S4) showed less pronounced static quenching and the complete absence of static quenching, respectively. These observations indicate that electrostatic interactions are in charge for the prominent static quenching phenomenon.

To provide clear evidence for ion-pairing, an NMR titration^{100,101} experiment (see section S2.1 in the SI) was carried out, which revealed that **Ruphen** and **PTS** aggregate predominantly in a 1:1 ratio. Based on this result and considering that the **Ruphen** molar absorption coefficient is essentially identical in the aggregate at our excitation wavelengths (see also section S2.2 of the SI), we employed the conventional equation for quantifying static quenching⁹⁹ in combination with the initial emission intensity, which leads to an association constant of $K_s = 6.1 \cdot 10^4 \text{ M}^{-1}$. Gratifyingly, both static and dynamic quenching contributions show a linear trend in the Stern–Volmer plot (see inset in Figure 3 (a)). Moreover, a textbook-like quadratic trend is evident when the total emission intensity is used as the basis for the Stern–Volmer plot, as illustrated by the black curve. This result is consistent with the expected behavior for mixed dynamic and static quenching.⁹⁹ The quadratic dependency is also obtained in steady-state emission quenching measurements, as explained in more detail in the SI (section S2.3). However, to separate the effects of static and dynamic quenching, it is mandatory to utilize time-resolved measurements. The high constants for dynamic and static quenching enable almost quantitative quenching (> 95%) of ³**Ruphen** already at **PTS** concentrations as low as 90 μM (88% static quenching, 9% dynamic quenching).

Detailed TA studies with our nanosecond laser flash photolysis (LFP) setup⁷² (see SI for details) were carried out to obtain clear evidence for the underlying quenching mechanism and to exclude undesired reaction pathways. After complete quenching, the TA spectrum exhibit the characteristic features of the **PTS** triplet state (see Figure 3 (b)).^{102–104} The formation of **PTS**-derived radical ions that could result from photoinduced electron transfer quenching can be excluded with the literature-known reference spectra.^{102,103} The same results are obtained for the molecular dyad **RuphenPy**, where the $^3(\pi-\pi)^*$ state is populated with a time constant of 25 ps after selective excitation of the Ru complex unit.³⁶ Figure 3 (c) shows the TA data sets monitored at the isosbestic point of **Ruphen** and its triplet **³Ruphen** (496 nm), allowing the observation of the newly formed species **³PTS** in isolation. Within the instrument response function (~10 ns), an increase in the transient absorption signal of **³PTS** can be detected due to the productive static quenching process. This is followed by a much slower increase in absorption attributed to the **³PTS** formation via dynamic quenching. The relative contributions of dynamic and static quenching to the formation of **³PTS** closely mirror their roles in the overall emission quenching efficiencies (section S8.3), suggesting a highly efficient energy transfer mechanism from **³Ruphen** to **PTS**. Quantitative LFP measurements^{39,105} using the molar absorption coefficients of the excited states indicate that this initial energy transfer process proceeds with a near-quantitative efficiency of 0.94 (corresponding to a quantum yield of 0.91) under our conditions using 120 μM of **PTS** (see sections S7 and S8.1 in the SI). Millimolar concentrations of a pyrene derivative would be required without exploiting attractive electrostatic interactions and the resulting ion-pairing for achieving similar efficiencies.^{64,87}

The pyrene triplet state has an elongated triplet lifetime due to the much lower spin-orbit coupling compared to the ruthenium complex.⁹⁷ For the molecular dyad, a lifetime of the mainly pyrene-localized triplet on the order of 50 μs is achieved (see ref. ³⁶ and Figure 4). However, for **PTS**, an even longer triplet lifetime, of 355 μs is detected (Figure 4). In the molecular dyad, the energy difference between the $^3(\pi-\pi)^*$ and $^3\text{MLCT}$ states is only about 0.1 eV,³⁶ resulting in a thermally activated intramolecular back energy transfer, depopulation the $^3(\pi-\pi)^*$ state on a microsecond timescale. **PTS**, on the other hand, bears four sulfonate groups, significantly lowering its triplet energy as confirmed by 77 K phosphorescence measurements of **PTS**, which gave a triplet energy of 1.80 eV (see SI, section S10.1), and DFT calculations that predict the **PTS** triplet at 1.85 eV (see SI, section S10.2). This leads to an energy difference of almost 0.4 eV between **³Ruphen** and **³PTS**, rendering uphill back energy transfer inefficient under the given conditions (see also section S8.3.2).^{106,107} Consequently, an almost purely pyrene-

localized triplet is present in the Coulombic dyad, while the molecular dyad under study serves as a triplet reservoir.^{36,48} The formation of the pyrene triplets for the molecular or the Coulombic dyad is briefly summarized in Figure 3 (d). After visible-light excitation, the ruthenium complex units undergo quantitative ISC. Subsequently, quenching efficiencies of up to 100% can be achieved either by *intramolecular* energy transfer (**RuphenPy**) or by highly efficient *ion-pair* and additional *intermolecular* dynamic energy transfer processes (Coulombic dyad). Hence, almost every photon harvested by the ruthenium complex leads to the generation of a long-lived organic triplet state, which would not be possible with harmful UV light sources upon direct pyrene excitation owing to inefficient ISC and side reactions.^{97,102,103}

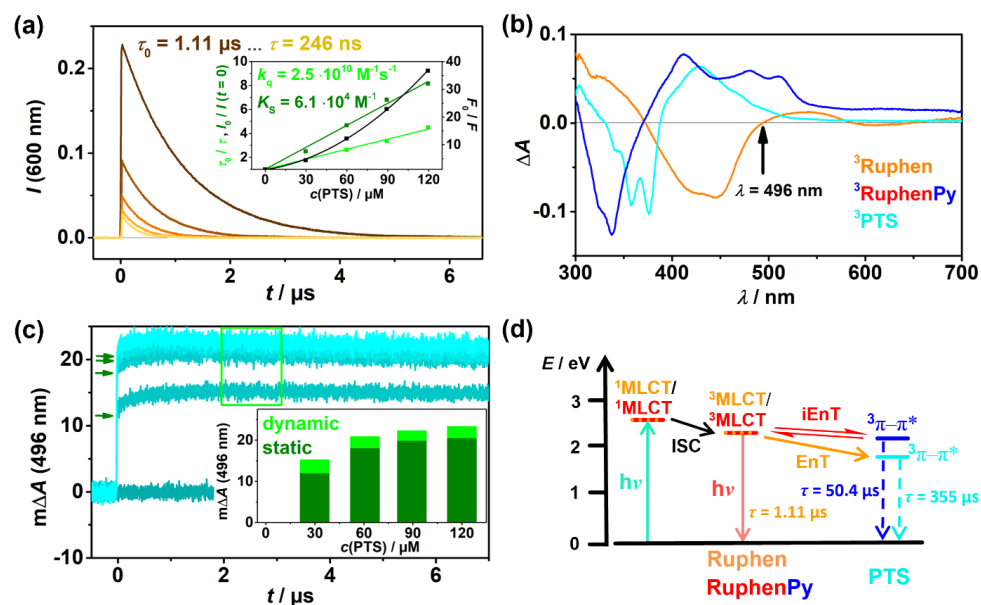


Figure 3 Investigations on the quenching mechanism of the photoexcited metal complex. (a) Main plot: time-resolved emission traces of **Ruphen** (30 μM) with increasing **PTS** concentrations (30 μM steps) in Ar-saturated water with their corresponding lifetimes after laser excitation ($\lambda = 532$ nm, ~ 5 ns pulses, 50 mJ). Inset: Stern–Volmer-plots for static quenching (intensity I at $t = 0$ μs), dynamic quenching (τ) and total emission quenching (F). (b) Transient absorption spectra of $^3\text{Ruphen}$ ($c(\text{Ruphen}) = 30$ μM , orange, delay 50 ns), $^3\text{RuphenPy}$ ($c(\text{RuphenPy}) = 30$ μM , blue, delay 50 ns) and ^3PTS ($c(\text{PTS}) = 30$ μM , $c(\text{Ruphen}) = 30$ μM , cyan, delay 5 μs) after laser excitation ($\lambda = 532$ nm) in Ar-saturated water. (c) Main plot: time-resolved transient absorption traces of the same solutions as in (a) at $\lambda_{\text{det}} = 496$ nm with an indication of sub-ns static energy transfer (dark green arrows). Inset: **PTS** concentration-dependent total transient absorption signals at $\lambda_{\text{det}} = 496$ nm with respective contributions of static quenching (dark green arrows) and dynamic quenching (light green box). See text for further details. (d) Simplified energy diagram demonstrating the formation of long-lived organic triplet states in ruthenium complex-pyrene dyads.

Exploiting the Long ^3PTS Lifetime for Photooxygenations

For excited-state quenching to be efficient, the product of the quenching rate k_q , the unquenched lifetime τ of the excited state and the quencher concentration $[Q]$ should be as high as possible. If τ is already very high, high quenching efficiencies are possible even with relatively small values of k_q or $[Q]$. This is demonstrated by the example of the quencher oxygen in air-saturated water, which is present in a very small concentration (0.27 mM O_2 in neat water at 25°C, see sections S.3.2 and S5.2.4 kinetic simulations)⁹⁷. The relatively short unquenched triplet lifetime of **Ruphen**, 1.1 μs , leads to a maximum oxygen quenching efficiency η on the order of 50% under our conditions.³⁶ In contrast, the dyads, which are characterized by much longer triplet lifetimes, exhibit remarkable quenching efficiencies approaching quantitative values even when non-diffusion controlled quenching processes are considered. The experimentally measured quenching efficiencies in air-saturated water are shown in Figure 4.

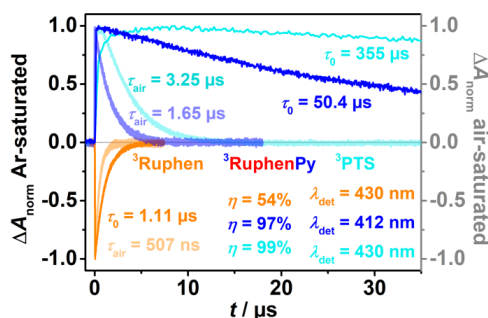


Figure 4 Normalized time-resolved transient absorption traces of the same solutions as in Figure 3 (b) in Ar- or air-saturated water with their corresponding lifetimes and calculated efficiencies for quenching by dissolved oxygen. Complete raw data sets for the long-lived triplets can be found in Figure S62.

Quenching the triplet states of **Ruphen** or pyrene derivatives through Dexter energy transfer with triplet oxygen results in the generation of singlet oxygen ($^1\text{O}_2$),³⁶ an impactful species for chemical synthesis, in medicine or the environment.^{108–114} Due to the very short lifetime and the near-zero phosphorescence quantum yield of $^1\text{O}_2$ in water, it is difficult to detect and quantify this species spectroscopically.¹¹⁵ However, there are multiple techniques available to confirm the presence of singlet oxygen in solution.¹¹⁰ The RNO method, as developed by Kraljić and Mohsni,¹¹⁶ offers a reliable and specific way of detecting $^1\text{O}_2$ in aqueous

environments. Briefly, in this approach a nitrosyl compound (*N,N*-dimethyl-4-nitrosoaniline, RNO) undergoes oxidation to generate the corresponding nitro compound, which is facilitated by imidazole acting as a catalyst. The reduction in the RNO concentration can be quantified through UV-vis spectroscopy and is directly proportional to the rate of $^1\text{O}_2$ formation. Consequently, this method enables a direct comparative analysis between the dyads regarding their $^1\text{O}_2$ production capabilities (see also section S3.1 of the SI). In a recent comparative study, we already investigated **Ruphen** and the molecular dyad **RuphenPy** employing the RNO method³⁶ and observed a threefold $^1\text{O}_2$ quantum yield increase for **RuphenPy**. This quantum yield increase is more pronounced compared to what would be expected from the oxygen quenching efficiencies (Figure 4). This discrepancy is likely a result of the higher redox reactivity of $^3\text{Ruphen}$ ^{58,117} facilitating additional electron transfer quenching pathways with dissolved oxygen that are less favored for a purely pyrene localized triplet. Interestingly, the $^1\text{O}_2$ assay revealed that the Coulombic dyad possesses essentially the same $^1\text{O}_2$ formation efficiency as the molecular dyad **RuphenPy** (SI, section S3.1). These experiments further substantiate that the addition of an oppositely charged organic acceptor to an ionic metal complex sensitizer can lead to superior photochemical properties resembling those of more sophisticated dyads with covalent linkage of the two chromophores.

The outstanding ability of the Coulombic dyad to efficiently produce singlet oxygen in air-saturated water prompted us to perform photooxygenation reactions of the promising platform chemical 5-(hydroxymethyl)furan-2-carbaldehyde (**5-HMF**), which can be obtained from sugars.^{118,119} The **5-HMF** photooxidation yields the potential polymer precursor 5-hydroxy-5-(hydroxymethyl)-furan-2(5H)-one,^{36,120} and the valuable C_1 building block formic acid as a by-product in a 1:1 ratio. For a meaningful comparison with the molecular dyad, **PTS** was used for the Coulombic dyad at the same concentration as **Ruphen** (60 μM), resulting in 92% $^3\text{Ruphen}$ quenching even without a **PTS** excess. It was further shown that a catalyst loading of only 0.2 mol% of the Coulombic dyad gives suitable conversion rates for our comparative experiments, which is discussed in more detail in the SI (section S5.2.1). Using only **Ruphen** (see Figure 5 (a), left panel) at a substrate concentration of 30 mM, a yield of 61% (with the same conversion) is achieved after 5 h of 525 nm LED irradiation. Under identical conditions, the molecular dyad **RuphenPy** exhibits a higher initial product formation rate than **Ruphen**, but this advantage rapidly diminishes. After 5 h of irradiation, the molecular dyad reaches a yield of 58% at a substrate conversion of 65%. The initially increased product formation rate is consistent with previous $^1\text{O}_2$ assay results and is in line with expectations.³⁶ However, the lower performance of the molecular dyad under prolonged irradiation time indicates a limited

photostability of this tailor-made molecule, which is corroborated by comparative UV-vis measurements (SI, section S3.4). In welcome contrast, the Coulombic dyad maintains a high product formation rate such that the reaction approaches complete conversion after just 5 h, yielding a yield of 93% and a corresponding turnover number (TON) of 465. Control experiments conducted in the absence of light or any constituent of the catalytic system, including oxygen, do not yield any product formation. For comparison, traditional organic photocatalysts for singlet oxygen generation, such as rose bengal, methylene blue, and eosin Y,^{121–128} were employed in the experiments. However, their performance was notably lower, with yields below 20% following irradiation under our standardized conditions (yellow, pink and pale blue traces in Figure 5 (b)), despite their considerably higher extinction coefficients in the green spectral region compared to the employed ruthenium complexes. This discrepancy is attributed to the comparatively low (photo)stability of these organic photocatalysts under our conditions (see section S3.4 for details).

Moreover, it was observed that the reaction rate in D₂O, where the lifetime of ¹O₂ is about twenty times longer, is almost identical to that in H₂O (see SI, section S5.2.2).¹²⁹ This observation rules out the [2+2] cycloaddition between ¹O₂ and **5-HMF** as the rate-determining step of the reaction. Alternatively, it seems plausible that the oxygen uptake rate in water serves as a limiting factor for the reaction rate. In this context, LFP was used to estimate the oxygen concentration during the ongoing reaction (see SI, section S5.2.3). An equilibrium oxygen concentration is assumed to be reached, which is primarily influenced by the uptake of oxygen from the atmosphere and its depletion as a result of the photoreaction. This analysis yields an “*in operando*” oxygen concentration of 0.16 mM for the use of the Coulombic dyad and 0.23 mM for **Ruphen**, which is in line with the observed faster conversion rate for the former. At an effective concentration of dissolved oxygen during irradiation as low as 0.16 mM, the quenching efficiency of ³**PTS** still exceeds 90%. Thus, the Coulombic dyad maintains a high performance even at very low quencher concentrations.

Under conditions of much higher substrate concentration (0.33 M instead of 30 mM **5-HMF**), the Coulombic dyad shows an impressive TON of 3000 (Figure 5 (c)). Remarkably, by increasing the concentration of inexpensive **PTS** while keeping all other conditions identical, a TON of 5400 with respect to the ruthenium catalyst was reached, which represents a 4.2-fold increase compared to what was obtained with conventional **Ruphen**. The molecular dyad gives a slightly higher TON (1700) than **Ruphen**, indicating that dyad degradation (likely via ¹O₂) is slower at very high substrate concentrations. Encouraged by this comparison, we successfully

realized the first gram-scale **5-HMF** photooxidation with the Coulombic dyad in neat water, employing only 1.1 mg **Ruphen** per gram of the value-added product.¹³⁰ Moreover, sunlight was used for sensitizer excitation (see SI, section S5.2.5). In this photoreaction, we observed a 2.4-fold increase in the reaction yield (84% vs 35%) when using the Coulombic dyad instead of **Ruphen**, demonstrating that the easy-to-use Coulombic dyad approach is also attractive under reaction conditions with broadband excitation.

A variety of products can be obtained starting from **5-HMF**.¹¹⁹ When the photooxygenation process is carried out under alkaline conditions, it leads to *in situ* ring opening of 5-hydroxy-5-(hydroxymethyl)-furan-2(5H)-one, forming (Z)-5-hydroxy-4-keto-2-pentenoic acid (see SI, section S5.2.8).³⁶ This product has direct potential as a monomeric building block for biopolymers. Interestingly, under alkaline conditions, the Coulombic dyad shows the same performance as under neutral-to-acidic conditions, which implies that the novel dyad approach can be exploited regardless of the pH value of the solution. All these results not only confirm the possibility to mimic the photophysical advantages of a molecular dyad by adding the oppositely charged pyrene **PTS** to **Ruphen** solutions, but they also highlight that achieving much higher reaction rates and TONs in practical applications are feasible by adding an inexpensive additive (**PTS**, less than 0.3 € per mmol¹³¹ as sodium salt) to a precious photocatalyst (**Ruphen**, 32 € per mmol¹³¹ as chloride salt).

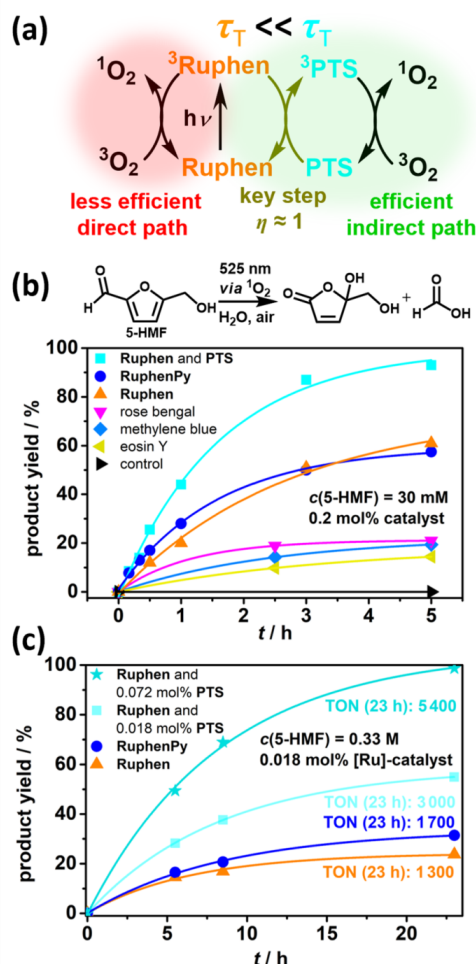


Figure 5 5-HMF photooxygenation in water. (a) Mechanism for conventional, less efficient (left) and improved, efficient (right) generation of singlet oxygen in air-saturated water and (b) reaction equation for the 5-HMF test reaction. Main plot: time-resolved product yield (lactone) during irradiation experiments (LED with $\lambda_{\text{max,exc}} = 525$ nm) with a solution of 5-HMF (30 mM), 0.2 mol% catalyst (orange: **Ruphen**, blue: **RuphenPy**, cyan: **Ruphen** and **PTS**, magenta: rose bengal, pale blue: methylene blue, yellow: eosin Y, black: **PTS**) in air-saturated water at 20 °C. (c) Product yields and the resulting TON after 23 h of irradiation with a higher substrate concentration (0.33 M).

Next, we extended our investigations to the synthesis of a sulfoxide in water. The sulfoxide moiety is a highly important group in organic and medical chemistry.¹³² One elegant and selective way of forming this functional group from the respective thioether is the reaction with $^1\text{O}_2$.¹³³ We selected the photooxygenation of thioanisole (**TAN**) as a test reaction, which cannot be carried out in water at room temperature for solubility reasons,^{134,135} but, as we found, the limited water solubility of **TAN** can be addressed by increasing the temperature of the reaction

mixture to 50 °C. The obtained product shows a better water solubility than **TAN** at room temperature and it can be quantified via ^1H NMR spectroscopy under the chosen conditions (see section S5.3). Temperature variations lead to pronounced changes in the unquenched and oxygen-quenched lifetimes of triplet states, which consequently results in different oxygen quenching efficiencies. Complementary quenching studies at an elevated temperature of 50 °C revealed that the quenching efficiencies of ^3PTS and $^3\text{RuphenPy}$ by O_2 remain remarkably high at 99% and 90%, respectively. In contrast, the quenching efficiency of $^3\text{Ruphen}$ drops to 43% (see SI, section S3.3). In the course of the photooxygenation of **TAN** (Figure 6), a flattening in the reaction progress curve is evident when **Ruphen** and **RuphenPy** are used as photocatalysts, indicating incomplete conversion most likely as a result of catalyst photodegradation. This phenomenon is most pronounced for **Ruphen** and related photoactive metal complexes, for which photodegradation is known to proceed in a thermally activated manner via a metal-centered excited state.^{136–138} In stark contrast, the Coulombic dyad shows a yield exceeding 90% and no discernible signs of degradation within the system. We attribute this resistance to the rapid and quantitative quenching of $^3\text{Ruphen}$ by **PTS**, effectively preventing thermally activated degradation. The improved stability of the catalytic system at higher temperatures is also important for applications on larger scales, when heating can be a side effect of intense photoirradiation. The photooxygenation results at elevated temperatures thus revealed another advantage of Coulombic dyads over conventional metal complexes and molecular dyads.

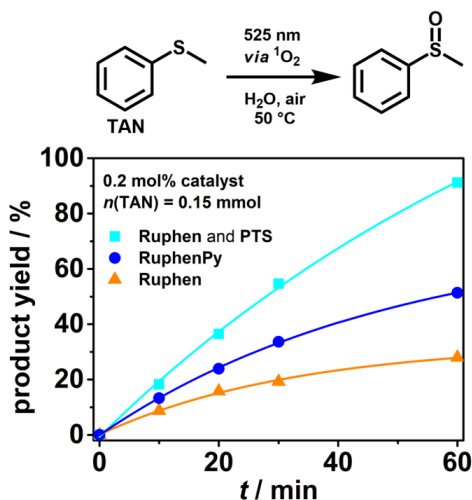


Figure 6 Time-resolved product yields for the formation of methyl phenyl sulfoxide from TAN (30 mM in total) with 0.2 mol% catalyst (orange: **Ruphen**, blue: **RuphenPy**, cyan: **Ruphen** and **PTS**) and LED irradiation ($\lambda_{\text{max,exc}} = 525$ nm) in air-saturated water at 50 °C. See text for details.

Improving the Electron Transfer Reactivity with Coulombic Dyads

Building on the substantial improvements of the photooxygenation efficiencies described in the preceding section and encouraged by reports dealing with improved electron transfer photoreactivity of molecular dyads,^{38,51–53} we explored whether the **Ruphen**–**PTS** pair is a superior catalyst for photoreductions. After excitation of the sensitizer **Ruphen**, the resulting ³MLCT state can be reductively quenched by the ascorbate monoanion **HAsc**[−]. This electron transfer quenching process yields **Ruphen**^{•−} and **HAsc**[•] as a spin-correlated radical pair within the so-called solvent cage, which is born in the same spin state as the photoexcited precursor, *i.e.* in a triplet state.^{38,139–141} Direct geminate recombination is spin-forbidden for a triplet pair, which can enable quantitative cage escape yielding the desired “free” radicals/radical ions that initiate photoreactions.^{40,41,142,143} However, the high spin-orbit coupling caused by the heavy atom ruthenium induces radical-pair ISC, and the singlet pair so obtained undergoes highly efficient in-cage recombination. This mechanism is the reason for the frequently observed very low cage escape quantum yields for photoinduced electron transfer reactions with 4d and 5d metal complexes.^{38,42–44,144} In the case of the reductive quenching of **Ruphen** (see Figure 7 (a)) by **HAsc**[−], **Ruphen**^{•−}^{145,146} is produced with a cage escape quantum yield of 0.21 under our conditions (SI, section S8.2). This means that unproductive back electron transfer within the solvent cage dominates. The cage escape quantum yields were determined using the carefully calibrated absorption spectra of the respective species (see sections S7 and S8 for further explanations), which are displayed in Figure 7 (b). As we found, ³**PTS** generated by

sensitization with **Ruphen** with a nearly quantitative yield can also be effectively reduced by **HAsc⁻** in an aqueous environment, giving rise to **PTS^{•-}**.^{103,147} **PTS^{•-}** exhibits a characteristic absorption maximum at 510 nm with an extinction coefficient of 29000 M⁻¹cm⁻¹ (SI, section S7.5). An outstanding cage-escape quantum yield close to unity (within the experimental error) was determined for this process. In contrast to **Ruphen**, **PTS** lacks a comparable heavy atom, making the rate of radical-pair ISC negligible, thereby ensuring a maximized quantum yield for cage escape.

To test whether the divergent cage escape yields are accompanied by an improved photocatalytic reactivity of the Coulombic dyad, the reductive dehalogenation of 2-bromopyrazine (**2-BP**) was selected as the first benchmark reaction.¹⁴⁸ Under our standardized conditions, we used 10 mM **2-BP** and one equivalent of **NaHAsc**, which is a common electron donor in aqueous photocatalytic cycles.^{105,149–152} The ascorbate monoanion is a reversible electron donor, ensuring that significant **HAsc⁻** decomposition does not occur, and the stable ascorbyl radical undergoes disproportionation partially regenerating **HAsc⁻**.¹⁵³ Hence, an **NaHAsc** excess is not required. Under these specific conditions and in the absence of **PTS**, the triplet state of pure **Ruphen** is reductively quenched with an efficiency of 0.84 ($k_q = 4.5 \cdot 10^8$ M⁻¹s⁻¹, section S6.1). Taking the low cage-escape quantum yield of only 0.21 into account, a theoretical **Ruphen^{•-}** quantum yield of 0.18 is predicted, which is in close agreement with the measured total quantum yield of 0.16, as demonstrated in Figure 7 (d). In stark contrast, when the Coulombic dyad is used through the addition of **PTS**, the quenching of the **³Ruphen** occurs predominantly by an energy transfer to give **³PTS** because dynamic quenching by **HAsc⁻** cannot compete with static quenching by **PTS**. Although **³PTS** is reduced by **HAsc⁻** with a lower rate constant ($k_q = 2.3 \cdot 10^7$ M⁻¹s⁻¹, section S6.2) than **³Ruphen**, quantitative quenching is possible owing to the much longer unquenched triplet lifetime of the organic chromophore. Combined with the high cage escape yield for this step, an overall quantum yield for the formation of **PTS^{•-}** as high as 0.97 (expected relative error below 20%) is achieved. No electron transfer from **PTS^{•-}** to the **Ruphen** ground state was observed, indicating that the reduction potential of **PTS^{•-}** is below that of **Ruphen^{•-}**. The addition of high salt concentrations might attenuate the attractive interactions within the Coulombic dyad due to salt effects.^{64,154} However, under our conditions with moderate salt concentrations ($c(\text{NaHAsc}) = 10$ mM), the static and dynamic quenching of **³Ruphen** by **PTS** is hardly affected such that **PTS^{•-}** quantum yields close to unity are within reach despite the seemingly complicated mechanism (Figure 7 (a)). Additional experiments addressing the effect of external salt additives on the formation efficiencies of both **³PTS** and **PTS^{•-}** were carried out with different NaCl concentrations (section S8.3.3). The

relative efficiency decrease is below 40% even at NaCl concentrations as high as 100 mM, implying that the Coulombic dyad approach is also useful for photocatalytic reactions that have to rely on ionic additives. Next, the reactions between the radical ions **Ruphen**^{•−} or **PTS**^{•−} and the substrate **2-BP** were analyzed. After the **2-BP** reduction by one of those radicals, a very rapid cleavage of the halide and the formation of a pyrazine σ-radical is expected to occur,¹⁴⁸ which in turn abstracts an hydrogen atom from **HAsc**[−] or its oxidized products.¹⁵⁵ **Ruphen**^{•−} reacts with a rate constant of $k_q \sim 3 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$, which corresponds to essentially complete quenching considering the **Ruphen**^{•−} lifetime of about 200 μs at a chosen concentration of $c(\text{2-BP}) = 10 \text{ mM}$. In line with the lower redox potential, **PTS**^{•−} is slowly intercepted by **2-BP** at a rate of $k_q \sim 4 \cdot 10^5 \text{ M}^{-1}\text{s}^{-1}$. Taking its prolonged lifetime exceeding 800 μs, an efficiency of the **2-BP** activation by **PTS**^{•−} of 75% is calculated at the initial **2-BP** concentration (10 mM). When comparing the efficiencies of the individual steps in both catalytic cycles (Figure 7 (a)), the non-quantitative quenching of ³**Ruphen** by **HAsc**[−] and the non-quantitative quenching of **PTS**^{•−} by **2-BP** almost cancel each other out, so that the performance of the two photoredox cycles is mainly determined by the cage escape efficiencies of the photoreduction steps. The time-resolved yields of the lab-scale reaction confirm the trend previously characterized through LFP measurements. In the presence of **Ruphen** only, the dehalogenation of **2-BP** is quite slow, resulting in a yield of 16% after 3 h of irradiation. Gratifyingly, when utilizing the Coulombic dyad, a yield as high as 94% is achieved after the same irradiation duration (Figure 7 (c)). The slightly higher efficiency increase when using **PTS** (compared to what can be estimated from the LFP studies in water) can be explained by the fact that D₂O was used as the solvent for the irradiation experiments, whereas the mechanistic studies were carried out in H₂O. This remarkable reaction quantum yield enhancement clearly demonstrates the advantages of a Coulombic dyad, which are simply achieved through the addition of an inexpensive additive.

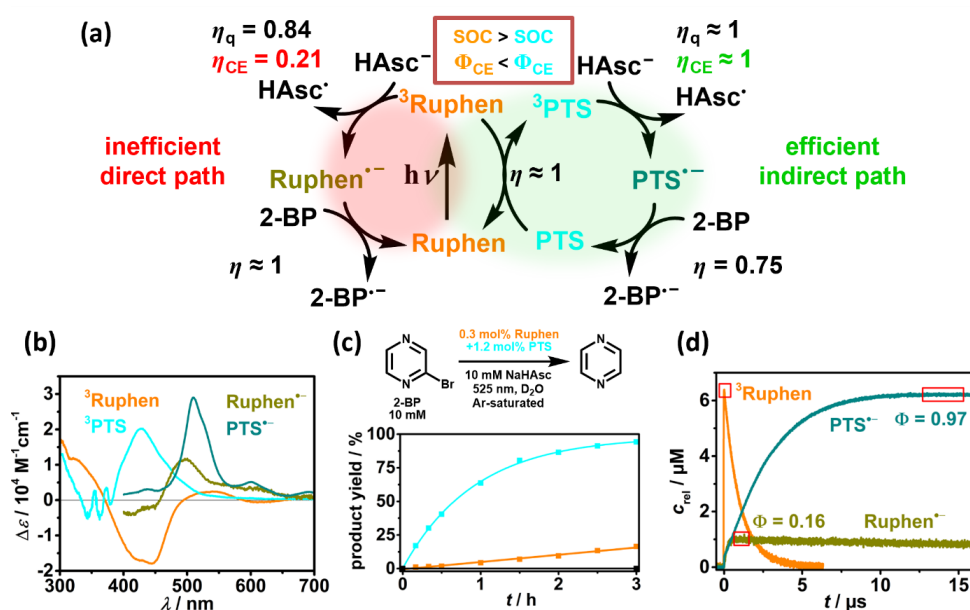


Figure 7 Mechanistic studies and irradiation experiments for a photoredox test reaction. (a) Mechanism for inefficient (left) and efficient (right) reductive dehalogenation of **2-BP**. (b) Calibrated transient absorption spectra of $^3\text{Ruphen}$ (orange), ^3PTS (cyan), $\text{Ruphen}^{\bullet-}$ (ochre) and $\text{PTS}^{\bullet-}$ (petrol) after laser excitation (532 nm) in Ar-saturated water. See SI for details regarding the spectral calibration. (c) Reaction equation with pertinent conditions and time-resolved product yield of the dehalogenation of **2-BP** (10 mM) with 0.3 mol% **Ruphen** (orange)/0.3 mol% **Ruphen** and 1.2 mol% **PTS** (cyan)/1.2 mol% **PTS** (black) upon LED irradiation ($\lambda_{\text{max,exc}} = 525 \text{ nm}$) in Ar-saturated water (D_2O) at 20 °C. (d) Transient absorption traces monitoring the concentrations of key species of solutions containing **Ruphen** (30 μM , $\lambda_{\text{det}} = 455 \text{ nm}$, orange), **Ruphen** and **NaHAsc** (30 μM and 10 mM, respectively, $\lambda_{\text{det}} = 496 \text{ nm}$, ochre), **Ruphen**, **PTS** and **NaHAsc** (30 μM , 120 μM and 10 mM, $\lambda_{\text{det}} = 510 \text{ nm}$, petrol) after the laser pulse ($\lambda_{\text{exc}} = 532 \text{ nm}$). Red boxes indicate the maximum TA values used for quantum yield determinations of $\text{Ruphen}^{\bullet-}$ or $\text{PTS}^{\bullet-}$ formation.

Finally, the Coulombic dyad was employed for pinacol coupling reactions^{156–158} of fluorinated benzaldehyde derivatives. The catalytic cycle of reductive substrate activation is the same as above for the **2-BP** dehalogenation,^{105,159} and the electron transfer from $\text{Ruphen}^{\bullet-}$ or $\text{PTS}^{\bullet-}$ to the model substrate 2-fluorobenzaldehyde (**2-FBA**) exhibits similar efficiency values (see SI, sections S6.5 and S6.6) approaching quantitative quenching. The exclusive presence of the pinacol product produced by dimerization of one-electron reduced substrate molecules is confirmed by both ^1H NMR and ^{19}F NMR analyses after the reaction. **Ruphen** irradiation in the presence of ascorbate led to yields ranging from 25% to 35% for the different derivatives, while the Coulombic dyad gave remarkable results ranging from 70% yield to quantitative conversion.

It is worth mentioning that successful transformations of practically water-insoluble benzaldehyde derivatives bearing a CF₃ group are feasible through the utilization of the promising food additive hydroxypropyl- β -cyclodextrin (**HPCD**), which seemingly does not interfere with the Coulombic dyad and the catalytic cycle. This cyclic sugar possesses the ability to encapsulate hydrophobic substances within its interior, thereby facilitating their solubilization in water.^{159,160} A dynamic equilibrium exists between the encapsulated and “free” forms of the substrates in solution. The reaction of the aldehyde with the activated catalysts **Ruphen**^{•-} or **PTS**^{•-} likely occurs with the non-complexed substrate present in solution. The highly hydrophobic pinacol product is also encapsulated within **HPCD**, which avoids solubility issues throughout the photoreaction. Hence, the Coulombic dyad has been effectively employed for pinacol coupling reactions – even with water-insoluble carbonyl compounds – resulting in significantly enhanced reaction kinetics and a much more efficient use of the precious ruthenium sensitizer.

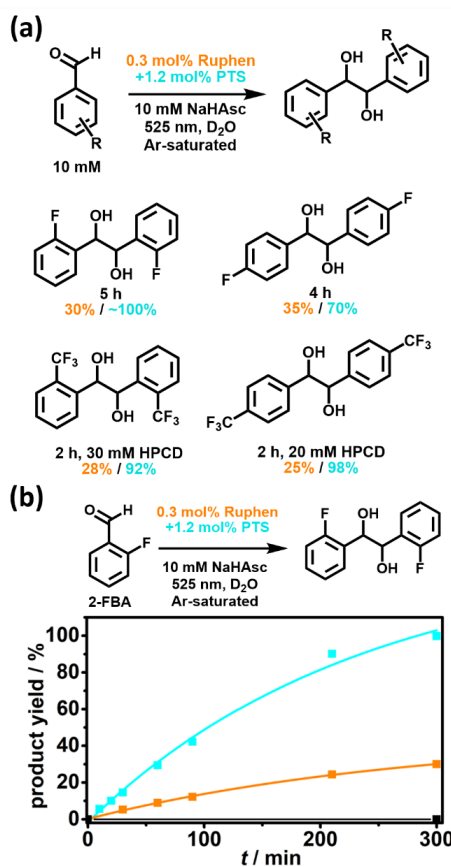


Figure 8 (a) Pinacol coupling of different benzaldehyde derivatives in neat D₂O or D₂O containing **HPCD**. (b) Time-resolved product yield of the pinacol coupling of **2-FBA** (10 mM) with 0.3 mol% **Ruphen** (orange)/0.3 mol% **Ruphen** and 1.2 mol% **PTS** (cyan)/1.2 mol% **PTS** (black) upon LED irradiation ($\lambda_{\text{max,exc}} = 525$ nm) in Ar-saturated D₂O at 20 °C.

It seems natural to assume that a delicate balance between the solvent and both ionic chromophores is essential for realizing dyad properties without a covalent bond. In a recent study in which we focused on upconversion with [Ru(phen)₃]²⁺ and the oppositely charged mediator pyrene-1-sulfonate (**PMS**), we did not observe static (*i.e.* dyad-like) energy transfer in DMF, neither upon mixing commercially available salts nor by using the synthesized salt [Ru(phen)₃](**PMS**)₂ lacking non-chromophoric counterions.⁶⁴ However, when dichloromethane is used as the solvent, that [Ru(phen)₃](**PMS**)₂ salt undergoes highly efficient static formation of long-lived ³**PMS** upon selective excitation of the ruthenium unit in the visible (see SI, section S9.2). These findings unambiguously establish that Coulombic dyads are more than a lab curiosity in aqueous solutions. To demonstrate that the Coulombic dyad concept is not limited to ruthenium sensitizers in combination with pyrene derivatives, initial investigations with a

dicationic osmium sensitizer were carried out. Highly efficient and predominantly static energy transfer quenching was observed with $[\text{Os}(\text{phen})_3]^{2+}$ and the anionic triplet energy-matched perylene-3,4,9,10-tetracarboxylate (section S9.1 of the SI). An impressive energy transfer reactivity improvement by as much as a factor of 15 was observed for this Coulombic dyad compared to $[\text{Os}(\text{phen})_3]^{2+}$ alone (SI, Figure S56), which we attribute to the even shorter unquenched lifetime of the photoexcited metal complex in this case. Considering that numerous photoactive metal complexes are cationic in nature, the experiments of this section illustrate the potential of Coulombic dyads for versatile photochemical applications in different solvents.

Conclusions

In summary, we have demonstrated that efficient inorganic-organic hybrid photocatalysts with photochemical properties reminiscent of tailor-made bichromophores are formed simply by mixing commercially available salts in aqueous solution. As a result of Coulombic attraction, the organic triplet is produced with efficiencies close to unity upon visible-light excitation of a photoactive metal complex and a subsequent Dexter-type energy transfer. Compared to the triplet-excited metal complex, the organic triplet so obtained undergoes highly efficient energy and electron transfer key reaction steps owing to its longer lifetime and inherently more efficient cage escape yields. Both lab-scale irradiation experiments and detailed spectroscopic investigations highlight the beneficial properties of Coulombic dyads as easy-to-prepare catalysts with improved reaction quantum yields. Initial studies with other chromophore combinations and in other solvents imply that Coulombic dyads can be developed into a versatile catalyst class for efficient applications in the greater context of photochemical energy conversion.

Supporting Information

The Supporting Information is available free of charge at ...:

Experimental details, additional steady-state and time-resolved spectroscopic results, raw data sets, quantum-mechanical calculations and details about the irradiation experiments.

Data Availability

All experimental data have been provided in the main text and the SI. The data sets shown in the main paper and DFT output files will be uploaded via the JGU library “Gutenberg Open Science” after acceptance of the manuscript.

Notes

The authors declare no competing financial interest.

Acknowledgements

We acknowledge generous financial support from the JGU Mainz and the German Research Foundation (DFG, grant number KE 2313/7-1). M.S. is grateful to the Chemical Industry Funds for a Kekulé fellowship. We thank David Pauly for carrying out first experiments with **PTS** in combination with sodium ascorbate. We thank Ernesto Llamas from Sketching-Science for drawing and allowing us to use the chemist displayed in the table of contents graphic. DFT calculations were conducted using the supercomputer Elwetritsch and advisory services offered by the University of Kaiserslautern-Landau (<https://hpc.rz.rptu.de>), which is a member of the AHRP and the Gauss Alliance e. V.

References

- (1) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. Photoredox Catalysis in Organic Chemistry. *J. Org. Chem.* **2016**, *81* (16), 6898–6926. <https://doi.org/10.1021/acs.joc.6b01449>.
- (2) Arias-Rotondo, D. M.; McCusker, J. K. The Photophysics of Photoredox Catalysis: A Roadmap for Catalyst Design. *Chem. Soc. Rev.* **2016**, *45* (21), 5803–5820. <https://doi.org/10.1039/C6CS00526H>.
- (3) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116* (17), 10075–10166. <https://doi.org/10.1021/acs.chemrev.6b00057>.
- (4) Narayanam, J. M. R.; Stephenson, C. R. J. Visible Light Photoredox Catalysis: Applications in Organic Synthesis. *Chem. Soc. Rev.* **2011**, *40* (1), 102–113. <https://doi.org/10.1039/B913880N>.
- (5) Großkopf, J.; Kratz, T.; Rigotti, T.; Bach, T. Enantioselective Photochemical Reactions Enabled by Triplet Energy Transfer. *Chem. Rev.* **2022**, *122* (2), 1626–1653. <https://doi.org/10.1021/acs.chemrev.1c00272>.
- (6) Dutta, S.; Erchinger, J. E.; Strieth-Kalthoff, F.; Kleinmans, R.; Glorius, F. Energy Transfer Photocatalysis: Exciting Modes of Reactivity. *Chem. Soc. Rev.* **2024**, *53* (3), 1068–1089. <https://doi.org/10.1039/D3CS00190C>.
- (7) Nevesely, T.; Wienhold, M.; Molloy, J. J.; Gilmour, R. Advances in the *E* → *Z* Isomerization of Alkenes Using Small Molecule Photocatalysts. *Chem. Rev.* **2022**, *122* (2), 2650–2694. <https://doi.org/10.1021/acs.chemrev.1c00324>.
- (8) Noël, T.; Zysman-Colman, E. The Promise and Pitfalls of Photocatalysis for Organic Synthesis. *Chem Catal.* **2022**, *2* (3), 468–476. <https://doi.org/10.1016/j.checat.2021.12.015>.

- (9) Crisenza, G. E. M.; Melchiorre, P. Chemistry Glows Green with Photoredox Catalysis. *Nat. Commun.* **2020**, *11* (1), 803. <https://doi.org/10.1038/s41467-019-13887-8>.
- (10) Ravetz, B. D.; Pun, A. B.; Churchill, E. M.; Congreve, D. N.; Rovis, T.; Campos, L. M. Photoredox Catalysis Using Infrared Light via Triplet Fusion Upconversion. *Nature* **2019**, *565* (7739), 343–346. <https://doi.org/10.1038/s41586-018-0835-2>.
- (11) MacKenzie, I. A.; Wang, L.; Onuska, N. P. R.; Williams, O. F.; Begam, K.; Moran, A. M.; Dunietz, B. D.; Nicewicz, D. A. Discovery and Characterization of an Acridine Radical Photoreductant. *Nature* **2020**, *580* (7801), 76–80. <https://doi.org/10.1038/s41586-020-2131-1>.
- (12) Glaser, F.; Kerzig, C.; Wenger, O. S. Multi-Photon Excitation in Photoredox Catalysis: Concepts, Applications, Methods. *Angew. Chem. Int. Ed.* **2020**, *59* (26), 10266–10284. <https://doi.org/10.1002/anie.201915762>.
- (13) Schreier, M. R.; Guo, X.; Pfund, B.; Okamoto, Y.; Ward, T. R.; Kerzig, C.; Wenger, O. S. Water-Soluble Tris(cyclometalated) Iridium(III) Complexes for Aqueous Electron and Energy Transfer Photochemistry. *Acc. Chem. Res.* **2022**, *55* (9), 1290–1300. <https://doi.org/10.1021/acs.accounts.2c00075>.
- (14) Marzo, L.; Pagire, S. K.; Reiser, O.; König, B. Visible-Light Photocatalysis: Does It Make a Difference in Organic Synthesis? *Angew. Chem. Int. Ed.* **2018**, *57* (32), 10034–10072. <https://doi.org/10.1002/anie.201709766>.
- (15) Barham, J. P.; König, B. Synthetic Photoelectrochemistry. *Angew. Chem. Int. Ed.* **2020**, *59* (29), 11732–11747. <https://doi.org/10.1002/anie.201913767>.
- (16) Ravetz, B. D.; Tay, N. E. S.; Joe, C. L.; Sezen-Edmonds, M.; Schmidt, M. A.; Tan, Y.; Janey, J. M.; Eastgate, M. D.; Rovis, T. Development of a Platform for Near-Infrared Photoredox Catalysis. *ACS Cent. Sci.* **2020**, *6* (11), 2053–2059. <https://doi.org/10.1021/acscentsci.0c00948>.
- (17) Ziegenbalg, D.; Pannwitz, A.; Rau, S.; Dietzek-Ivanšić, B.; Streb, C. Comparative Evaluation of Light-Driven Catalysis: A Framework for Standardized Reporting of Data**. *Angew. Chem. Int. Ed.* **2022**, *61* (28), e202114106. <https://doi.org/10.1002/anie.202114106>.
- (18) Cambié, D.; Bottecchia, C.; Straathof, N. J. W.; Hessel, V.; Noël, T. Applications of Continuous-Flow Photochemistry in Organic Synthesis, Material Science, and Water Treatment. *Chem. Rev.* **2016**, *116* (17), 10276–10341. <https://doi.org/10.1021/acs.chemrev.5b00707>.
- (19) Speckmeier, E.; Fischer, T. G.; Zeitler, K. A Toolbox Approach To Construct Broadly Applicable Metal-Free Catalysts for Photoredox Chemistry: Deliberate Tuning of Redox Potentials and Importance of Halogens in Donor–Acceptor Cyanoarenes. *J. Am. Chem. Soc.* **2018**, *140* (45), 15353–15365. <https://doi.org/10.1021/jacs.8b08933>.
- (20) Wenger, O. S. Photoactive Complexes with Earth-Abundant Metals. *J. Am. Chem. Soc.* **2018**, *140* (42), 13522–13533. <https://doi.org/10.1021/jacs.8b08822>.
- (21) Kitzmann, W. R.; Heinze, K. Charge-Transfer and Spin-Flip States: Thriving as Complements. *Angew. Chem. Int. Ed.* **2023**, *62* (15), e202213207. <https://doi.org/10.1002/anie.202213207>.
- (22) Zhang, Y.; Lee, T. S.; Favale, J. M.; Leary, D. C.; Petersen, J. L.; Scholes, G. D.; Castellano, F. N.; Milsmann, C. Delayed Fluorescence from a Zirconium(IV) Photosensitizer with Ligand-to-Metal Charge-Transfer Excited States. *Nat. Chem.* **2020**. <https://doi.org/10.1038/s41557-020-0430-7>.
- (23) Bryden, M. A.; Zysman-Colman, E. Organic Thermally Activated Delayed Fluorescence (TADF) Compounds Used in Photocatalysis. *Chem. Soc. Rev.* **2021**, *50* (13), 7587–7680. <https://doi.org/10.1039/D1CS00198A>.
- (24) Chan, A. Y.; Ghosh, A.; Yarranton, J. T.; Twilton, J.; Jin, J.; Arias-Rotondo, D. M.; Sakai, H. A.; McCusker, J. K.; MacMillan, D. W. C. Exploiting the Marcus Inverted Region for First-Row Transition Metal–Based Photoredox Catalysis. *Science* **2023**, *382* (6667), 191–197. <https://doi.org/10.1126/science.adj0612>.
- (25) De Groot, L. H. M.; Ilic, A.; Schwarz, J.; Wärnmark, K. Iron Photoredox Catalysis—Past, Present, and Future. *J. Am. Chem. Soc.* **2023**, *145* (17), 9369–9388. <https://doi.org/10.1021/jacs.3c01000>.
- (26) Kim, D.; Dang, V. Q.; Teets, T. S. Improved Transition Metal Photosensitizers to Drive Advances in Photocatalysis. *Chem. Sci.* **2024**, *15* (1), 77–94. <https://doi.org/10.1039/D3SC04580C>.
- (27) Swierk, J. R. The Cost of Quantum Yield. *Org. Process Res. Dev.* **2023**, *27* (7), 1411–1419. <https://doi.org/10.1021/acs.oprd.3c00167>.

- (28) Buzzetti, L.; Crisenza, G. E. M.; Melchiorre, P. Mechanistic Studies in Photocatalysis. *Angew. Chem. Int. Ed.* **2019**, *58* (12), 3730–3747. <https://doi.org/10.1002/anie.201809984>.
- (29) Wang, C.; Malinoski, A. Perspective: Mechanistic Investigations of Photocatalytic Processes with Time-Resolved Optical Spectroscopy. *J. Chem. Phys.* **2022**, *157* (16), 160901. <https://doi.org/10.1063/5.0111162>.
- (30) Marchini, M.; Bergamini, G.; Cozzi, P. G.; Ceroni, P.; Balzani, V. Photoredox Catalysis: The Need to Elucidate the Photochemical Mechanism. *Angew. Chem. Int. Ed.* **2017**, *56* (42), 12820–12821. <https://doi.org/10.1002/anie.201706217>.
- (31) De Kreijger, S.; Gillard, M.; Elias, B.; Troian-Gautier, L. Spectroscopic Techniques to Unravel Mechanistic Details in Light-Induced Transformations and Photoredox Catalysis. *ChemCatChem* **2024**, *16* (1), e202301100. <https://doi.org/10.1002/cctc.202301100>.
- (32) Talbott, E. D.; Burnett, N. L.; Swierk, J. R. Mechanistic and Kinetic Studies of Visible Light Photoredox Reactions. *Chem. Phys. Rev.* **2023**, *4* (3), 031312. <https://doi.org/10.1063/5.0156850>.
- (33) Koike, T.; Akita, M. Visible-Light Radical Reaction Designed by Ru- and Ir-Based Photoredox Catalysis. *Inorg. Chem. Front.* **2014**, *1* (8), 562–576. <https://doi.org/10.1039/C4QI00053F>.
- (34) Teegardin, K.; Day, J. I.; Chan, J.; Weaver, J. Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations. *Org. Process Res. Dev.* **2016**, *20* (7), 1156–1163. <https://doi.org/10.1021/acs.oprd.6b00101>.
- (35) Goldschmid, S. L.; Bednářová, E.; Beck, L. R.; Xie, K.; Tay, N. E. S.; Ravetz, B. D.; Li, J.; Joe, C. L.; Rovis, T. Tuning the Electrochemical and Photophysical Properties of Osmium-Based Photoredox Catalysts. *Synlett* **2022**, *33* (03), 247–258. <https://doi.org/10.1055/s-0041-1737792>.
- (36) Sell, A. C.; Wetzel, J. C.; Schmitz, M.; Maijenburg, A. W.; Woltersdorf, G.; Naumann, R.; Kerzig, C. Water-Soluble Ruthenium Complex-Pyrene Dyads with Extended Triplet Lifetimes for Efficient Energy Transfer Applications. *Dalton Trans.* **2022**, *51* (28), 10799–10808. <https://doi.org/10.1039/D2DT01157C>.
- (37) Wehlin, S. A. M.; Troian-Gautier, L.; Maurer, A. B.; Brennaman, M. K.; Meyer, G. J. Photophysical Characterization of New Osmium (II) Photocatalysts for Hydrohalic Acid Splitting. *J. Chem. Phys.* **2020**, *153* (5), 054307. <https://doi.org/10.1063/5.0014269>.
- (38) Neumann, S.; Wenger, O. S.; Kerzig, C. Controlling Spin-Correlated Radical Pairs with Donor–Acceptor Dyads: A New Concept to Generate Reduced Metal Complexes for More Efficient Photocatalysis. *Chem. – Eur. J.* **2021**, *27* (12), 4115–4123. <https://doi.org/10.1002/chem.202004638>.
- (39) Sittel, S.; Sell, A. C.; Hofmann, K.; Wiedemann, C.; Nau, J. P.; Kerzig, C.; Manolikakes, G.; Heinze, K. Visible-Light Induced Fixation of SO₂ into Organic Molecules with Polypyridine Chromium(III) Complexes. *ChemCatChem* **2023**, *15* (6), e202201562. <https://doi.org/10.1002/cctc.202201562>.
- (40) Bürgin, T. H.; Glaser, F.; Wenger, O. S. Shedding Light on the Oxidizing Properties of Spin-Flip Excited States in a Cr^{III} Polypyridine Complex and Their Use in Photoredox Catalysis. *J. Am. Chem. Soc.* **2022**, *144* (31), 14181–14194. <https://doi.org/10.1021/jacs.2c04465>.
- (41) Ripak, A.; De Kreijger, S.; Sampaio, R. N.; Vincent, C. A.; Cauët, É.; Jabin, I.; Tambar, U. K.; Elias, B.; Troian-Gautier, L. Photosensitized Activation of Diazonium Derivatives for C–B Bond Formation. *Chem Catal.* **2023**, *3* (2), 100490. <https://doi.org/10.1016/j.checat.2022.100490>.
- (42) Ozawa, K.; Tamaki, Y.; Kamogawa, K.; Koike, K.; Ishitani, O. Factors Determining Formation Efficiencies of One-Electron-Reduced Species of Redox Photosensitizers. *J. Chem. Phys.* **2020**, *153* (15), 154302. <https://doi.org/10.1063/5.0023593>.
- (43) Miedlar, K.; Das, P. K. Tris(2,2'-Bipyridine)Ruthenium(II)-Sensitized Photooxidation of Phenols. Environmental Effects on Electron Transfer Yields and Kinetics. *J. Am. Chem. Soc.* **1982**, *104* (26), 7462–7469. <https://doi.org/10.1021/ja00390a012>.
- (44) Adams, R. E.; Schmehl, R. H. Micellar Effects on Photoinduced Electron Transfer in Aqueous Solutions Revisited: Dramatic Enhancement of Cage Escape Yields in Surfactant Ru(II) Diimine Complex/[Ru(NH₃)₆]²⁺ Systems. *Langmuir* **2016**, *32* (34), 8598–8607. <https://doi.org/10.1021/acs.langmuir.6b02193>.
- (45) Wang, C.; Li, H.; Bürgin, T. H.; Wenger, O. S. Cage Escape Governs Photoredox Reaction Rates and Quantum Yields. *Nat. Chem.* **2024**. <https://doi.org/10.1038/s41557-024-01482-4>.
- (46) Castellano, F. N. Altering Molecular Photophysics by Merging Organic and Inorganic Chromophores. *Acc. Chem. Res.* **2015**, *48* (3), 828–839. <https://doi.org/10.1021/ar500385e>.

- (47) Castellano, F. N. Transition Metal Complexes Meet the Rylenes. *Dalton Trans.* **2012**, 41 (28), 8493–8501. <https://doi.org/10.1039/c2dt30765k>.
- (48) Howarth, A. J.; Majewski, M. B.; Wolf, M. O. Photophysical Properties and Applications of Coordination Complexes Incorporating Pyrene. *Coord. Chem. Rev.* **2015**, 282–283, 139–149. <https://doi.org/10.1016/j.ccr.2014.03.024>.
- (49) Schmid, M.; Brückmann, J.; Bösking, J.; Nauroozi, D.; Karnahl, M.; Rau, S.; Tschierlei, S. Merging of a Perylene Moiety Enables a Ru^{II} Photosensitizer with Long-Lived Excited States and the Efficient Production of Singlet Oxygen. *Chem. – Eur. J.* **2022**, 28, e202103609. <https://doi.org/10.1002/chem.202103609>.
- (50) Kerzig, C.; Wenger, O. S. Sensitized Triplet–Triplet Annihilation Upconversion in Water and Its Application to Photochemical Transformations. *Chem. Sci.* **2018**, 9 (32), 6670–6678. <https://doi.org/10.1039/C8SC01829D>.
- (51) Wilson, G. J.; Launikonis, A.; Sasse, W. H. F.; Mau, A. W.-H. Chromophore-Specific Quenching of Ruthenium Trisbipyridine–Arene Bichromophores by Methyl Viologen. *J. Phys. Chem. A* **1998**, 102 (26), 5150–5156. <https://doi.org/10.1021/jp973248s>.
- (52) Weinheimer, C.; Choi, Y.; Caldwell, T.; Gresham, P.; Olmsted, J. Effect of a Steric Spacer on Chromophoric Interactions of Ruthenium Complexes Containing Covalently Bound Anthracene. *J. Photochem. Photobiol. Chem.* **1994**, 78 (2), 119–126. [https://doi.org/10.1016/1010-6030\(93\)03723-T](https://doi.org/10.1016/1010-6030(93)03723-T).
- (53) Ma, L.; Wang, P.; Wang, J.-Z.; Guo, S.; Zhang, Z.-M.; Zeng, X.-S.; Lu, T.-B. Bidirectional Sensitization in Ruthenium(II)-Antenna Dyad beyond Energy Flow of Biological Model for Efficient Photosynthesis. *Dyes Pigm.* **2021**, 196, 109811. <https://doi.org/10.1016/j.dyepig.2021.109811>.
- (54) Guo, S.; Chen, K.-K.; Dong, R.; Zhang, Z.-M.; Zhao, J.; Lu, T.-B. Robust and Long-Lived Excited State Ru(II) Polyimine Photosensitizers Boost Hydrogen Production. *ACS Catal.* **2018**, 8 (9), 8659–8670. <https://doi.org/10.1021/acscatal.8b02226>.
- (55) Deng, F.; Lazorski, M. S.; Castellano, F. N. Photon Upconversion Sensitized by a Ru(II)-Pyrenyl Chromophore. *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.* **2015**, 373 (2044), 20140322. <https://doi.org/10.1098/rsta.2014.0322>.
- (56) Lu, Y.; Wang, J.; McGoldrick, N.; Cui, X.; Zhao, J.; Caverly, C.; Twamley, B.; Ó Máille, G. M.; Irwin, B.; Conway-Kenny, R.; Draper, S. M. Iridium(III) Complexes Bearing Pyrene-Functionalized 1,10-Phenanthroline Ligands as Highly Efficient Sensitizers for Triplet-Triplet Annihilation Upconversion. *Angew. Chem. Int. Ed.* **2016**, 55 (47), 14688–14692. <https://doi.org/10.1002/anie.201608442>.
- (57) Wang, P.; Guo, S.; Wang, H.-J.; Chen, K.-K.; Zhang, N.; Zhang, Z.-M.; Lu, T.-B. A Broadband and Strong Visible-Light-Absorbing Photosensitizer Boosts Hydrogen Evolution. *Nat. Commun.* **2019**, 10 (1), 3155. <https://doi.org/10.1038/s41467-019-11099-8>.
- (58) Bertrams, M.-S.; Hermainski, K.; Mörsdorf, J.-M.; Ballmann, J.; Kerzig, C. Triplet Quenching Pathway Control with Molecular Dyads Enables the Identification of a Highly Oxidizing Annihilator Class. *Chem. Sci.* **2023**, 14 (32), 8583–8591. <https://doi.org/10.1039/D3SC01725G>.
- (59) Potocny, A. M.; Phelan, B. T.; Sprague-Klein, E. A.; Mara, M. W.; Tiede, D. M.; Chen, L. X.; Mulfort, K. L. Harnessing Intermolecular Interactions to Promote Long-Lived Photoinduced Charge Separation from Copper Phenanthroline Chromophores. *Inorg. Chem.* **2022**, 61 (48), 19119–19133. <https://doi.org/10.1021/acs.inorgchem.2c02648>.
- (60) Tsuji, Y.; Yamamoto, K.; Yamauchi, K.; Sakai, K. Near-Infrared Light-Driven Hydrogen Evolution from Water Using a Polypyridyl Triruthenium Photosensitizer. *Angew. Chem. Int. Ed.* **2018**, 57 (1), 208–212. <https://doi.org/10.1002/anie.201708996>.
- (61) Li, G.; Swords, W. B.; Meyer, G. J. Bromide Photo-Oxidation Sensitized to Visible Light in Consecutive Ion Pairs. *J. Am. Chem. Soc.* **2017**, 139 (42), 14983–14991. <https://doi.org/10.1021/jacs.7b06735>.
- (62) Deetz, A. M.; Goodwin, M. J.; Kober, E. A.; Meyer, G. J. Nanosecond Intra-Ionic Chloride Photo-Oxidation. *Inorg. Chem.* **2023**, 62 (29), 11414–11425. <https://doi.org/10.1021/acs.inorgchem.3c00970>.
- (63) Freys, J. C.; Wenger, O. S. Supramolecular and Intramolecular Energy Transfer with Ruthenium-Anthracene Donor-Acceptor Couples: Salt Bridge versus Covalent Bond. *Eur. J. Inorg. Chem.* **2010**, 2010 (35), 5509–5516. <https://doi.org/10.1002/ejic.201000815>.

- (64) Glaser, F.; Schmitz, M.; Kerzig, C. Coulomb Interactions for Mediator-Enhanced Sensitized Triplet–Triplet Annihilation Upconversion in Solution. *Nanoscale* **2024**, *16* (1), 123–137. <https://doi.org/10.1039/D3NR05265F>.
- (65) Balzani, V.; Sabbatini, N.; Scandola, F. “Second-Sphere” Photochemistry and Photophysics of Coordination Compounds. *Chem. Rev.* **1986**, *86* (2), 319–337. <https://doi.org/10.1021/cr00072a002>.
- (66) Vogler, A.; Kunkely, H. Photochemistry of Transition Metal Complexes Induced by Outer-Sphere Charge Transfer Excitation. In *Photoinduced Electron Transfer II*; Mattay, J., Ed.; Dewar, M. J. S., Dunitz, J. D., Hafner, K., Itô, S., Lehn, J.-M., Niedenzu, K., Raymond, K. N., Rees, C. W., Vögtle, F., Series Eds.; Topics in Current Chemistry; Springer Berlin Heidelberg: Berlin, Heidelberg, 1990; Vol. 158, pp 1–30. https://doi.org/10.1007/3-540-52568-8_1.
- (67) Billing, R. Optical and Photoinduced Electron Transfer in Ion Pairs of Coordination Compounds. *Coord. Chem. Rev.* **1997**, *159*, 257–270. [https://doi.org/10.1016/S0010-8545\(96\)01288-X](https://doi.org/10.1016/S0010-8545(96)01288-X).
- (68) Knighton, R. C.; Beames, J. M.; Pope, S. J. A. Polycationic Ru(II) Luminophores: Syntheses, Photophysics, and Application in Electrostatically Driven Sensitization of Lanthanide Luminescence. *Inorg. Chem.* **2023**, *62* (48), 19446–19456. <https://doi.org/10.1021/acs.inorgchem.3c02352>.
- (69) Uraguchi, D.; Kimura, Y.; Ueoka, F.; Ooi, T. Urea as a Redox-Active Directing Group under Asymmetric Photocatalysis of Iridium-Chiral Borate Ion Pairs. *J. Am. Chem. Soc.* **2020**, *142* (46), 19462–19467. <https://doi.org/10.1021/jacs.0c09468>.
- (70) Guerrero, I.; Viñas, C.; Fontrodona, X.; Romero, I.; Teixidor, F. Aqueous Persistent Noncovalent Ion-Pair Cooperative Coupling in a Ruthenium Cobaltabis(dicarbollide) System as a Highly Efficient Photoredox Oxidation Catalyst. *Inorg. Chem.* **2021**, *60* (12), 8898–8907. <https://doi.org/10.1021/acs.inorgchem.1c00751>.
- (71) Farney, E. P.; Chapman, S. J.; Swords, W. B.; Torelli, M. D.; Hamers, R. J.; Yoon, T. P. Discovery and Elucidation of Counteranion Dependence in Photoredox Catalysis. *J. Am. Chem. Soc.* **2019**, *141* (15), 6385–6391. <https://doi.org/10.1021/jacs.9b01885>.
- (72) Sau, S. C.; Schmitz, M.; Burdinski, C.; Baumert, M.; Antoni, P. W.; Kerzig, C.; Hansmann, M. M. Dicationic Acridinium/Carbene Hybrids as Strongly Oxidizing Photocatalysts. *J. Am. Chem. Soc.* **2024**, *146* (5), 3416–3426. <https://doi.org/10.1021/jacs.3c12766>.
- (73) Earley, J. D.; Zieleniewska, A.; Ripberger, H. H.; Shin, N. Y.; Lazorski, M. S.; Mast, Z. J.; Sayre, H. J.; McCusker, J. K.; Scholes, G. D.; Knowles, R. R.; Reid, O. G.; Rumbles, G. Ion-Pair Reorganization Regulates Reactivity in Photoredox Catalysts. *Nat. Chem.* **2022**, *14* (7), 746–753. <https://doi.org/10.1038/s41557-022-00911-6>.
- (74) Das, S.; Zhu, C.; Demirbas, D.; Bill, E.; De, C. K.; List, B. Asymmetric Counteranion-Directed Photoredox Catalysis. *Science* **2023**, *379* (6631), 494–499. <https://doi.org/10.1126/science.ade8190>.
- (75) Ohmura, S.; Katagiri, K.; Kato, H.; Horibe, T.; Miyakawa, S.; Hasegawa, J.; Ishihara, K. Highly Enantioselective Radical Cation [2 + 2] and [4 + 2] Cycloadditions by Chiral Iron(III) Photoredox Catalysis. *J. Am. Chem. Soc.* **2023**, *145* (28), 15054–15060. <https://doi.org/10.1021/jacs.3c04010>.
- (76) Takizawa, S.; Okuyama, T.; Yamazaki, S.; Sato, K.; Masai, H.; Iwai, T.; Murata, S.; Terao, J. Ion Pairing of Cationic and Anionic Ir(III) Photosensitizers for Photocatalytic CO₂ Reduction at Lipid–Membrane Surfaces. *J. Am. Chem. Soc.* **2023**, *145* (28), 15049–15053. <https://doi.org/10.1021/jacs.3c03625>.
- (77) Schulte, A. M.; Alachouzos, G.; Szymanski, W.; Feringa, B. L. The Fate of the Contact Ion Pair Determines the Photochemistry of Coumarin-Based Photocleavable Protecting Groups. *Chem. Sci.* **2024**, *15* (6), 2062–2073. <https://doi.org/10.1039/D3SC05725A>.
- (78) Schirmer, T. E.; König, B. Ion-Pairing Catalysis in Stereoselective, Light-Induced Transformations. *J. Am. Chem. Soc.* **2022**, *144* (42), 19207–19218. <https://doi.org/10.1021/jacs.2c04759>.
- (79) Morack, T.; Mück-Lichtenfeld, C.; Gilmour, R. Bioinspired Radical Stetter Reaction: Radical Umpolung Enabled by Ion-Pair Photocatalysis. *Angew. Chem. Int. Ed.* **2019**, *58* (4), 1208–1212. <https://doi.org/10.1002/anie.201809601>.

- (80) Herr, P.; Kerzig, C.; Larsen, C. B.; Häussinger, D.; Wenger, O. S. Manganese(I) Complexes with Metal-to-Ligand Charge Transfer Luminescence and Photoreactivity. *Nat. Chem.* **2021**, *13* (10), 956–962. <https://doi.org/10.1038/s41557-021-00744-9>.
- (81) East, N. R.; Naumann, R.; Förster, C.; Ramanan, C.; Diezemann, G.; Heinze, K. Oxidative Two-State Photoreactivity of a Manganese(IV) Complex Using near-Infrared Light. *Nat. Chem.* **2024**. <https://doi.org/10.1038/s41557-024-01446-8>.
- (82) Ford, W. E.; Rodgers, M. A. J. Reversible Triplet-Triplet Energy Transfer within a Covalently Linked Bichromophoric Molecule. *J. Phys. Chem.* **1992**, *96* (7), 2917–2920. <https://doi.org/10.1021/j100186a026>.
- (83) Tyson, D. S.; Bialecki, J.; Castellano, F. N. Ruthenium(II) Complex with a Notably Long Excited State Lifetime. *Chem. Commun.* **2000**, (23), 2355–2356. <https://doi.org/10.1039/b007336i>.
- (84) Tyson, D. S.; Henbest, K. B.; Bialecki, J.; Castellano, F. N. Excited State Processes in Ruthenium(II)/Pyrenyl Complexes Displaying Extended Lifetimes. *J. Phys. Chem. A* **2001**, *105* (35), 8154–8161. <https://doi.org/10.1021/jp011770f>.
- (85) Kerzig, C.; Goez, M. Combining Energy and Electron Transfer in a Supramolecular Environment for the “Green” Generation and Utilization of Hydrated Electrons through Photoredox Catalysis. *Chem. Sci.* **2016**, *7* (6), 3862–3868. <https://doi.org/10.1039/C5SC04800A>.
- (86) Deng, F.; Lazorski, M. S.; Castellano, F. N. Photon Upconversion Sensitized by a Ru(II)-Pyrenyl Chromophore. *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.* **2015**, *373* (2044), 20140322. <https://doi.org/10.1098/rsta.2014.0322>.
- (87) Ghosh, I.; Shaikh, R. S.; König, B. Sensitization-Initiated Electron Transfer for Photoredox Catalysis. *Angew. Chem. Int. Ed.* **2017**, *56* (29), 8544–8549. <https://doi.org/10.1002/anie.201703004>.
- (88) Coles, M. S.; Quach, G.; Beves, J. E.; Moore, E. G. A Photophysical Study of Sensitization-Initiated Electron Transfer: Insights into the Mechanism of Photoredox Activity. *Angew. Chem. Int. Ed.* **2020**, *59* (24), 9522–9526. <https://doi.org/10.1002/anie.201916359>.
- (89) Yu, W.; Wang, X.-Y.; Li, J.; Li, Z.-T.; Yan, Y.-K.; Wang, W.; Pei, J. A Photoconductive Charge-Transfer Crystal with Mixed-Stacking Donor–Acceptor Heterojunctions within the Lattice. *Chem Commun.* **2013**, *49* (1), 54–56. <https://doi.org/10.1039/C2CC37655E>.
- (90) Mallon, M.; Dutt, S.; Schrader, T.; Crowley, P. B. Protein Camouflage: Supramolecular Anion Recognition by Ubiquitin. *ChemBioChem* **2016**, *17* (8), 774–783. <https://doi.org/10.1002/cbic.201500477>.
- (91) Karakostas, N.; Mavridis, I. M.; Seintis, K.; Fakis, M.; Koini, E. N.; Petsalakis, I. D.; Pistolis, G. Highly Efficient and Unidirectional Energy Transfer within a Tightly Self-Assembled Host–Guest Multichromophoric Array. *Chem. Commun.* **2014**, *50* (11), 1362–1365. <https://doi.org/10.1039/C3CC48076C>.
- (92) Rambabu, D.; Pradeep, C. P.; Dhir, A. Nickel–Sodium Pyrene Tetrasulfonic Acid Based Co-Ordination Polymer as Fluorescent Template for Recognition of Azo Dyes. *Sens. Actuators B Chem.* **2016**, *225*, 586–592. <https://doi.org/10.1016/j.snb.2015.11.055>.
- (93) Hasegawa, M.; Yamasaki, Y.; Sonta, N.; Shindo, Y.; Sugimura, T.; Kitahara, A. Clustering of Aerosol OT Reversed Micelles As Studied by Nonradiative Energy Transfer of Solubilized Probes. *J. Phys. Chem.* **1996**, *100* (38), 15575–15580. <https://doi.org/10.1021/jp961528m>.
- (94) Feng, X.; Wang, X.; Redshaw, C.; Tang, B. Z. Aggregation Behaviour of Pyrene-Based Luminescent Materials, from Molecular Design and Optical Properties to Application. *Chem. Soc. Rev.* **2023**, *52* (19), 6715–6753. <https://doi.org/10.1039/D3CS00251A>.
- (95) Guthrie, J. P. Hydrolysis of Esters of Oxy Acids: pK_a Values for Strong Acids; Brønsted Relationship for Attack of Water at Methyl; Free Energies of Hydrolysis of Esters of Oxy Acids; and a Linear Relationship between Free Energy of Hydrolysis and pK_a Holding over a Range of 20 pK Units. *Can. J. Chem.* **1978**, *56* (17), 2342–2354. <https://doi.org/10.1139/v78-385>.
- (96) Balzani, V.; Campagna, S. *Photochemistry and Photophysics of Coordination Compounds I*; Topics in Current Chemistry; Springer Berlin Heidelberg Springer e-books: Berlin, Heidelberg, 2007.
- (97) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; CRC Press, 2006. <https://doi.org/10.1201/9781420015195>.

- (98) Tanwar, A. S.; Parui, R.; Garai, R.; Chanu, M. A.; Iyer, P. K. Dual “Static and Dynamic” Fluorescence Quenching Mechanisms Based Detection of TNT via a Cationic Conjugated Polymer. *ACS Meas. Sci. Au* **2022**, *2* (1), 23–30. <https://doi.org/10.1021/acsmesuresciau.1c00023>.
- (99) Genovese, D.; Cingolani, M.; Rampazzo, E.; Prodi, L.; Zaccheroni, N. Static Quenching upon Adduct Formation: A Treatment without Shortcuts and Approximations. *Chem. Soc. Rev.* **2021**, *50* (15), 8414–8427. <https://doi.org/10.1039/D1CS00422K>.
- (100) Thordarson, P. Determining Association Constants from Titration Experiments in Supramolecular Chemistry. *Chem. Soc. Rev.* **2011**, *40* (3), 1305–1323. <https://doi.org/10.1039/C0CS00062K>.
- (101) Brynn Hibbert, D.; Thordarson, P. The Death of the Job Plot, Transparency, Open Science and Online Tools, Uncertainty Estimation Methods and Other Developments in Supramolecular Chemistry Data Analysis. *Chem. Commun.* **2016**, *52* (87), 12792–12805. <https://doi.org/10.1039/C6CC03888C>.
- (102) Bohne, C.; Abuin, E. B.; Scaiano, J. C. Characterization of the Triplet-Triplet Annihilation Process of Pyrene and Several Derivatives under Laser Excitation. *J. Am. Chem. Soc.* **1990**, *112* (11), 4226–4231. <https://doi.org/10.1021/ja00167a018>.
- (103) Mori, Y.; Shinoda, H.; Nakano, T.; Kitagawa, T. Formation and Decay Behaviors of Laser-Induced Transient Species from Pyrene Derivatives 1. Spectral Discrimination and Decay Mechanisms in Aqueous Solution. *J. Phys. Chem. A* **2002**, *106* (48), 11743–11749. <https://doi.org/10.1021/jp020332l>.
- (104) Mori, Y.; Shinoda, H.; Nakano, T.; Kitagawa, T. Formation and Decay Behaviors of Laser-Induced Transient Species from Pyrene Derivatives 2. Micellar Effects. *J. Phys. Chem. A* **2002**, *106* (48), 11750–11759. <https://doi.org/10.1021/jp020333d>.
- (105) Bertrams, M.-S.; Kerzig, C. Converting *p*-Terphenyl into a Novel Organo-Catalyst for LED-Driven Energy and Electron Transfer Photoreactions in Water. *Chem. Commun.* **2021**, *57* (55), 6752–6755. <https://doi.org/10.1039/D1CC01947C>.
- (106) Strieth-Kalthoff, F.; Henkel, C.; Teders, M.; Kahnt, A.; Knolle, W.; Gómez-Suárez, A.; Dirian, K.; Alex, W.; Bergander, K.; Daniliuc, C. G.; Abel, B.; Guldi, D. M.; Glorius, F. Discovery of Unforeseen Energy-Transfer-Based Transformations Using a Combined Screening Approach. *Chem* **2019**, *5* (8), 2183–2194. <https://doi.org/10.1016/j.chempr.2019.06.004>.
- (107) Sandros, K.; Haglid, F.; Ryhage, R.; Ryhage, R.; Stevens, R. Transfer of Triplet State Energy in Fluid Solutions. III. Reversible Energy Transfer. *Acta Chem. Scand.* **1964**, *18*, 2355–2374. <https://doi.org/10.3891/acta.chem.scand.18-2355>.
- (108) Wasserman, H. H.; Ives, J. L. Singlet Oxygen in Organic Synthesis. *Tetrahedron* **1981**, *37* (10), 1825–1852. [https://doi.org/10.1016/S0040-4020\(01\)97932-3](https://doi.org/10.1016/S0040-4020(01)97932-3).
- (109) DeRosa, M. Photosensitized Singlet Oxygen and Its Applications. *Coord. Chem. Rev.* **2002**, *233–234*, 351–371. [https://doi.org/10.1016/S0010-8545\(02\)00034-6](https://doi.org/10.1016/S0010-8545(02)00034-6).
- (110) Ogilby, P. R. Singlet Oxygen: There Is Indeed Something New under the Sun. *Chem. Soc. Rev.* **2010**, *39* (8), 3181–3209. <https://doi.org/10.1039/b926014p>.
- (111) Pibiri, I.; Buscemi, S.; Palumbo Piccionello, A.; Pace, A. Photochemically Produced Singlet Oxygen: Applications and Perspectives. *ChemPhotoChem* **2018**, *2* (7), 535–547. <https://doi.org/10.1002/cptc.201800076>.
- (112) Ghogare, A. A.; Greer, A. Using Singlet Oxygen to Synthesize Natural Products and Drugs. *Chem. Rev.* **2016**, *116* (17), 9994–10034. <https://doi.org/10.1021/acs.chemrev.5b00726>.
- (113) Wang, Y.; Lin, Y.; He, S.; Wu, S.; Yang, C. Singlet Oxygen: Properties, Generation, Detection, and Environmental Applications. *J. Hazard. Mater.* **2024**, *461*, 132538. <https://doi.org/10.1016/j.jhazmat.2023.132538>.
- (114) McNeill, K.; Canonica, S. Triplet State Dissolved Organic Matter in Aquatic Photochemistry: Reaction Mechanisms, Substrate Scope, and Photophysical Properties. *Environ. Sci. Process. Impacts* **2016**, *18* (11), 1381–1399. <https://doi.org/10.1039/C6EM00408C>.
- (115) Losev, A. P.; Byteva, I. M.; Gurinovich, G. P. Singlet Oxygen Luminescence Quantum Yields in Organic Solvents and Water. *Chem. Phys. Lett.* **1988**, *143* (2), 127–129. [https://doi.org/10.1016/0009-2614\(88\)87025-8](https://doi.org/10.1016/0009-2614(88)87025-8).

- (116) Kraljić, I.; Mohsni, S. E. A New Method for the Detection of Singlet Oxygen in Aqueous Solutions. *Photochem. Photobiol.* **1978**, 28 (4–5), 577–581. <https://doi.org/10.1111/j.1751-1097.1978.tb06972.x>.
- (117) García-Fresnadillo, D.; Georgiadou, Y.; Orellana, G.; Braun, A. M.; Oliveros, E. Singlet-Oxygen ($^1\Delta_g$) Production by Ruthenium(II) Complexes Containing Polyazaheterocyclic Ligands in Methanol and in Water. *Helv. Chim. Acta* **1996**, 79 (4), 1222–1238. <https://doi.org/10.1002/hlca.19960790428>.
- (118) Galkin, K. I.; Ananikov, V. P. When Will 5-Hydroxymethylfurfural, the “Sleeping Giant” of Sustainable Chemistry, Awaken? *ChemSusChem* **2019**, 12 (13), 2976–2982. <https://doi.org/10.1002/cssc.201900592>.
- (119) Hu, L.; Lin, L.; Wu, Z.; Zhou, S.; Liu, S. Recent Advances in Catalytic Transformation of Biomass-Derived 5-Hydroxymethylfurfural into the Innovative Fuels and Chemicals. *Renew. Sustain. Energy Rev.* **2017**, 74, 230–257. <https://doi.org/10.1016/j.rser.2017.02.042>.
- (120) Heugebaert, T. S. A.; Stevens, C. V.; Kappe, C. O. Singlet-Oxygen Oxidation of 5-Hydroxymethylfurfural in Continuous Flow. *ChemSusChem* **2015**, 8 (10), 1648–1651. <https://doi.org/10.1002/cssc.201403182>.
- (121) Nsubuga, A.; Mandl, G. A.; Capobianco, J. A. Investigating the Reactive Oxygen Species Production of Rose Bengal and Merocyanine 540-Loaded Radioluminescent Nanoparticles. *Nanoscale Adv.* **2021**, 3 (5), 1375–1381. <https://doi.org/10.1039/D0NA00964D>.
- (122) Saito, I.; Inoue, K.; Matsuura, T. Occurrence of the Singlet-Oxygen Mechanism in Photodynamic Oxidations of Guanosine*. *Photochem. Photobiol.* **1975**, 21 (1), 27–30. <https://doi.org/10.1111/j.1751-1097.1975.tb06625.x>.
- (123) Fernandez, J. M.; Bilgin, M. D.; Grossweiner, L. I. Singlet Oxygen Generation by Photodynamic Agents. *J. Photochem. Photobiol. B* **1997**, 37 (1–2), 131–140. [https://doi.org/10.1016/S1011-1344\(96\)07349-6](https://doi.org/10.1016/S1011-1344(96)07349-6).
- (124) Xu, J.; Pelluau, T.; Monnereau, C.; Guari, Y.; Bonneviot, L.; Rodríguez-Pizarro, M.; Albela, B. Incorporation of Methylene Blue into Mesoporous Silica Nanoparticles for Singlet Oxygen Generation. *New J. Chem.* **2023**, 47 (4), 1861–1871. <https://doi.org/10.1039/D2NJ04835C>.
- (125) Guerra Díaz, D.; Mariño-Ocampo, N.; Kabanov, V.; Heyne, B.; Andrade-Villalobos, F.; Fierro, A.; Fuentealba, D. Extraordinary Control of Photosensitized Singlet Oxygen Generation by Acyclic Cucurbituril-like Containers. *J. Phys. Chem. B* **2023**, 127 (15), 3443–3451. <https://doi.org/10.1021/acs.jpcc.3c00583>.
- (126) Usui, Y. Determination of Quantum Yield of Singlet Oxygen Formation by Photosensitization. *Chem. Lett.* **1973**, 2 (7), 743–744. <https://doi.org/10.1246/cl.1973.743>.
- (127) Amat-Guerri, F.; López-González, M. M. C.; Martínez-Utrilla, R.; Sastre, R. Singlet Oxygen Photogeneration by Ionized and Un-Ionized Derivatives of Rose Bengal and Eosin Y in Diluted Solutions. *J. Photochem. Photobiol. Chem.* **1990**, 53 (2), 199–210. [https://doi.org/10.1016/1010-6030\(90\)87124-T](https://doi.org/10.1016/1010-6030(90)87124-T).
- (128) Zhang, Y.; Ye, C.; Li, S.; Ding, A.; Gu, G.; Guo, H. Eosin Y-Catalyzed Photooxidation of Triarylphosphines under Visible Light Irradiation and Aerobic Conditions. *RSC Adv.* **2017**, 7 (22), 13240–13243. <https://doi.org/10.1039/C6RA25469A>.
- (129) Wilkinson, F.; Helman, W. P.; Ross, A. B. Rate Constants for the Decay and Reactions of the Lowest Electronically Excited Singlet State of Molecular Oxygen in Solution. An Expanded and Revised Compilation. *J. Phys. Chem. Ref. Data* **1995**, 24 (2), 663–677. <https://doi.org/10.1063/1.555965>.
- (130) Zhang, Q.; Gu, B.; Fang, W. Sunlight-Driven Photocatalytic Conversion of Furfural and Its Derivatives. *Green Chem.* **2024**, 10.1039.D4GC00140K. <https://doi.org/10.1039/D4GC00140K>.
- (131) Calculated with the Price from “BLDpharm”, Accessed March 08, 2024.
- (132) Skolia, E.; Gkizis, P. L.; Nikitas, N. F.; Kokotos, C. G. Photochemical Aerobic Oxidation of Sulfides to Sulfoxides: The Crucial Role of Wavelength Irradiation. *Green Chem.* **2022**, 24 (10), 4108–4118. <https://doi.org/10.1039/D2GC00799A>.
- (133) Jensen, F.; Greer, A.; Clennan, E. L. Reaction of Organic Sulfides with Singlet Oxygen. A Revised Mechanism. *J. Am. Chem. Soc.* **1998**, 120 (18), 4439–4449. <https://doi.org/10.1021/ja973782d>.

- (134) Biswas, S.; Kumar, M.; Levine, A. M.; Jimenez, I.; Ulijn, R. V.; Braunschweig, A. B. Visible-Light Photooxidation in Water by $^1\text{O}_2$ -Generating Supramolecular Hydrogels. *Chem. Sci.* **2020**, *11* (16), 4239–4245. <https://doi.org/10.1039/C9SC06481H>.
- (135) Skolia, E.; Gkizis, P. L.; Kokotos, C. G. Aerobic Photocatalysis: Oxidation of Sulfides to Sulfoxides. *ChemPlusChem* **2022**, *87* (4), e202200008. <https://doi.org/10.1002/cplu.202200008>.
- (136) Adamson, A. W.; Waltz, W. L.; Zinato, Edoardo.; Watts, D. W.; Fleischauer, P. D.; Lindholm, R. D. Photochemistry of Transition-Metal Coordination Compounds. *Chem. Rev.* **1968**, *68* (5), 541–585. <https://doi.org/10.1021/cr60255a002>.
- (137) Endicott, J. F.; Ramasami, T.; Tamilarasan, R.; Lessard, R. B.; Ryu, C. K.; Brubaker, G. R. Structure and Reactivity of the Metal-Centered Transition Metal Excited States. *Coord. Chem. Rev.* **1987**, *77*, 1–87. [https://doi.org/10.1016/0010-8545\(87\)85032-4](https://doi.org/10.1016/0010-8545(87)85032-4).
- (138) Soupart, A.; Alary, F.; Heully, J.-L.; Elliott, P. I. P.; Dixon, I. M. Theoretical Study of the Full Photosolvolytic Mechanism of $[\text{Ru}(\text{Bpy})_3]^{2+}$: Providing a General Mechanistic Roadmap for the Photochemistry of $[\text{Ru}(\text{N}^{\wedge}\text{N})_3]^{2+}$ -Type Complexes toward Both Cis and Trans Photoproducts. *Inorg. Chem.* **2020**, *59* (20), 14679–14695. <https://doi.org/10.1021/acs.inorgchem.0c01843>.
- (139) Kavarnos, G. J.; Turro, N. J. Photosensitization by Reversible Electron Transfer: Theories, Experimental Evidence, and Examples. *Chem. Rev.* **1986**, *86* (2), 401–449. <https://doi.org/10.1021/cr00072a005>.
- (140) Goetz, M. In *Annual Reports on NMR Spectroscopy*; Elsevier: Amsterdam, 2009; pp 77–147.
- (141) McLauchlan, K. A.; Steiner, U. E. Invited Article: The Spin-Correlated Radical Pair as a Reaction Intermediate. *Mol. Phys.* **1991**, *73* (2), 241–263. <https://doi.org/10.1080/00268979100101181>.
- (142) Haselbach, E.; Vauthey, E.; Suppan, P. Comparison of Photoinduced Electron Transfer Reactions of Aromatic Carbonyl vs. Cyano Compounds with Electron Donors in Condensed Phase: The Importance. *Tetrahedron* **1988**, *44* (24), 7335–7344. [https://doi.org/10.1016/S0040-4020\(01\)86228-1](https://doi.org/10.1016/S0040-4020(01)86228-1).
- (143) Olmsted, John.; Meyer, T. J. Factors Affecting Cage Escape Yields Following Electron-Transfer Quenching. *J. Phys. Chem.* **1987**, *91* (6), 1649–1655. <https://doi.org/10.1021/j100290a071>.
- (144) Troian-Gautier, L.; Turlington, M. D.; Wehlin, S. A. M.; Maurer, A. B.; Brady, M. D.; Swords, W. B.; Meyer, G. J. Halide Photoredox Chemistry. *Chem. Rev.* **2019**, *119* (7), 4628–4683. <https://doi.org/10.1021/acs.chemrev.8b00732>.
- (145) Venturi, M.; Emmi, S.; Fucchi, P. G.; Mulazzani, Q. G. Nucleophilic Addition of .Alpha.-Hydroxyalkyl Radicals to Polypyridyl Complexes of Chromium(III), Cobalt(III), Rhodium(III), and Ruthenium(II) in Aqueous Solution. *J. Phys. Chem.* **1980**, *84* (17), 2160–2166. <https://doi.org/10.1021/j100454a011>.
- (146) Ohno, Takeshi.; Yoshimura, Akio.; Mataga, Noboru. Bell-Shaped Energy-Gap Dependence of Backward Electron Transfer Occurring within Geminant Radical Pairs Produced by Quenching of Ruthenium(II) Polypyridine Complexes by Aromatic Amines. *J. Phys. Chem.* **1990**, *94* (12), 4871–4876. <https://doi.org/10.1021/j100375a023>.
- (147) Hai-Xia, Y.; Hu-Xiang, P.; Yan-Lin, W.; Jian-Feng, Z.; Wen-Bo, D.; 复旦大学环境科学与工程系, 上海 200433; Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, P. R. China; 海军医学研究所, 上海 200433, Institute of Naval Medicine, Shanghai 200433, P. R. China. Laser Flash Photolysis Mechanism of Pyrenetetrasulfonate in Aqueous Solution. *Acta Phys.-Chim. Sin.* **2012**, *28* (04), 957–962. <https://doi.org/10.3866/PKU.WHXB201202203>.
- (148) Kitzmann, W. R.; Bertrams, M.-S.; Boden, P.; Fischer, A. C.; Klauer, R.; Sutter, J.; Naumann, R.; Förster, C.; Niedner-Schatteburg, G.; Bings, N. H.; Hunger, J.; Kerzig, C.; Heinze, K. Stable Molybdenum(0) Carbonyl Complex for Upconversion and Photoredox Catalysis. *J. Am. Chem. Soc.* **2023**, *145* (30), 16597–16609. <https://doi.org/10.1021/jacs.3c03832>.
- (149) Pellegrin, Y.; Odobel, F. Sacrificial Electron Donor Reagents for Solar Fuel Production. *C. R. Chim.* **2017**, *20* (3), 283–295. <https://doi.org/10.1016/j.crci.2015.11.026>.
- (150) Kerzig, C.; Guo, X.; Wenger, O. S. Unexpected Hydrated Electron Source for Preparative Visible-Light Driven Photoredox Catalysis. *J. Am. Chem. Soc.* **2019**, *141* (5), 2122–2127. <https://doi.org/10.1021/jacs.8b12223>.
- (151) Khnayzer, R. S.; Thoi, V. S.; Nippe, M.; King, A. E.; Jurss, J. W.; El Roz, K. A.; Long, J. R.; Chang, C. J.; Castellano, F. N. Towards a Comprehensive Understanding of Visible-Light

- Photogeneration of Hydrogen from Water Using Cobalt(II) Polypyridyl Catalysts. *Energy Env. Sci.* **2014**, 7 (4), 1477–1488. <https://doi.org/10.1039/C3EE43982H>.
- (152) Giedyk, M.; Narobe, R.; Weiß, S.; Touraud, D.; Kunz, W.; König, B. Photocatalytic Activation of Alkyl Chlorides by Assembly-Promoted Single Electron Transfer in Microheterogeneous Solutions. *Nat. Catal.* **2019**, 3 (1), 40–47. <https://doi.org/10.1038/s41929-019-0369-5>.
- (153) Guttentag, M.; Rodenberg, A.; Kopelent, R.; Probst, B.; Buchwalder, C.; Brandstätter, M.; Hamm, P.; Alberto, R. Photocatalytic H₂ Production with a Rhenium/Cobalt System in Water under Acidic Conditions. *Eur. J. Inorg. Chem.* **2012**, 2012 (1), 59–64. <https://doi.org/10.1002/ejic.201100883>.
- (154) Logan, S. R. Effects of Ionic Strength on the Rates of Reaction between Ions in Solution. *Trans. Faraday Soc.* **1967**, 63, 3004. <https://doi.org/10.1039/tf9676303004>.
- (155) Davies, M. B.; Austin, J.; Partridge, D. A. *Vitamin C: Its Chemistry and Biochemistry*; Royal society of chemistry paperbacks; The Royal society of chemistry: Cambridge, 1991.
- (156) Bryden, M. A.; Millward, F.; Matulaitis, T.; Chen, D.; Villa, M.; Fermi, A.; Cetin, S.; Ceroni, P.; Zysman-Colman, E. Moving Beyond Cyanoarene Thermally Activated Delayed Fluorescence Compounds as Photocatalysts: An Assessment of the Performance of a Pyrimidyl Sulfone Photocatalyst in Comparison to 4CzIPN. *J. Org. Chem.* **2023**, 88 (10), 6364–6373. <https://doi.org/10.1021/acs.joc.2c01137>.
- (157) Nakajima, M.; Fava, E.; Loescher, S.; Jiang, Z.; Rueping, M. Photoredox-Catalyzed Reductive Coupling of Aldehydes, Ketones, and Imines with Visible Light. *Angew. Chem. Int. Ed.* **2015**, 54 (30), 8828–8832. <https://doi.org/10.1002/anie.201501556>.
- (158) Huh, H. H.; Lee, Y. J.; Anita, Y.; Woo, S. K. Visible-Light-Photocatalyzed Pinacol Coupling in Water. *Asian J. Org. Chem.* **2024**, e202300591. <https://doi.org/10.1002/ajoc.202300591>.
- (159) Naumann, R.; Goez, M. How the Sustainable Solvent Water Unleashes the Photoredox Catalytic Potential of Ruthenium Polypyridyl Complexes for Pinacol Couplings. *Green Chem.* **2019**, 21 (16), 4470–4474. <https://doi.org/10.1039/C9GC02069A>.
- (160) Bai, C.; Tian, B.; Zhao, T.; Huang, Q.; Wang, Z. Cyclodextrin-Catalyzed Organic Synthesis: Reactions, Mechanisms, and Applications. *Molecules* **2017**, 22 (9), 1475. <https://doi.org/10.3390/molecules22091475>.

2.2 Organic photo(redox) catalyst with triplet-mediated energy and electron transfer reactivity

This section presents:

Converting *p*-terphenyl into a novel organo-catalyst for LED-driven energy and electron transfer photoreactions in water

Maria-Sophie Bertrams, Christoph Kerzig, Chem. Commun., 2021, 57, 6752-6755.

Slightly modifying the reaction conditions for the synthesis of TDS (Section 2.1.1) leads to an additional SO₂-bridge within the terphenyl backbone and the compound SO₂TDS was isolated as sodium salt (structure in Figure 23).^[63] Compared to the linear TDS, the SO₂-bridge lowers the symmetry substantially for SO₂TDS, which results in a lowered oscillator strength at the bathochromically shifted E_{00} transition. Those findings rationalize the increase in the fluorescence lifetime (τ_0)^[61] (Section 1.3.3) and therefore a deceleration of the fluorescence rate constant (k_F), enabling further photophysical relaxation processes such as the population of the triplet excited state. In addition, DFT calculations revealed orbital contributions of the heteroatom containing SO₂-bridge to the LUMO as well as spin density located on the terphenyl backbone and the bridge in the triplet excited state. Transient absorption spectroscopy revealed a long-lived species after direct excitation of SO₂TDS at 355 nm, which is identified as the corresponding ³SO₂TDS based on DFT calculations and TTET quenching experiments. The useful properties of ³SO₂TDS were further explored spectroscopically for energy and electron transfer reactivity and successfully employed in laboratory scaled TTET and ET photocatalytic reactions (catalytic cycles in Figure 23). For the latter, the ascorbate monoanion, Vitamin C, was used as a sacrificial electron donor. Every key intermediate of both reaction mechanisms was observed spectroscopically allowing the proposal of a reaction mechanism substantiated by the spectroscopic data. Finally, the organic photocatalyst can sensitize stilbene-derivatives regardless of their charge and furthermore is active for both energy and electron transfer in micellar environments.

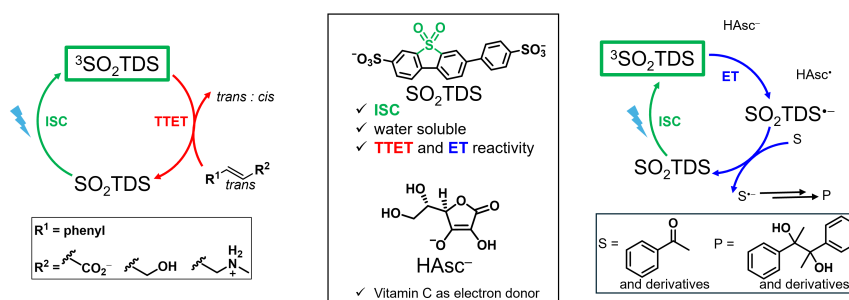


Figure 23: Key aspects of the water-soluble organic triplet chromophore SO_2TDS , together with all relevant chemical structures for photocatalysis and the two catalytic mechanisms for energy and electron transfer.

The symmetry lowering and heteroatom-containing SO_2 -bridge enabled ISC in SO_2TDS . This purely organic photo(redox) catalyst offered the possibility to perform light-driven reactions involving a triplet-excited state aqueous environments.

Reproduced from reference: M.-S. Bertrams, C. Kerzig, *Chem. Comm.*, **2021**, 57, 6752-6755 with permission from the Royal Society of Chemistry.

The reference can be found in the following pages and under reference [63]. The article is licensed under CC BY-NC 3.0 (<https://creativecommons.org/licenses/by-nc/3.0/>). The supporting information can be found in Section 6.8.

Author contributions: M.-S. Bertrams performed the synthesis, optical spectroscopy measurements and irradiation reactions. M.-S. Bertrams provided the graphs for the main paper and prepared the initial draft of the supporting information document. C. Kerzig conceived the project and provided general guidance.

Cite this: *Chem. Commun.*, 2021, 57, 6752Received 12th April 2021,
Accepted 8th June 2021

DOI: 10.1039/d1cc01947c

rsc.li/chemcomm

Converting *p*-terphenyl into a novel organo-catalyst for LED-driven energy and electron transfer photoreactions in water†‡

Maria-Sophie Bertrams  and Christoph Kerzig  *

p-Terphenyl is a potent photoredox catalyst under UV-irradiation. Aiming for more sustainable reaction conditions, we added two sulfonate groups to this key structure to achieve water solubility and incorporated an SO₂-bridge thereby shifting the absorption spectrum towards the visible. The resulting photocatalyst shows unexpected triplet reactivity in several test reactions.

Owing to the rapid development of photo(redox) catalysis with low-energy photons in recent years, numerous light-driven reactions became feasible under particularly mild conditions, which keeps fascinating many scientists.^{1–5} Despite fulfilling several sustainable chemistry criteria,^{6,7} most of these photo-reactions do not have the potential of being the ideal example in a green chemistry textbook. The two main drawbacks of a great many photocatalytic applications are the extensive usage of catalysts derived from precious metals and/or their incompatibility with green solvents such as water, either due to solubility or (photo-)stability issues. Addressing the former, several researchers focused on developing organo-catalysts,^{8–16} which frequently compete with their inorganic congeners.

p-Terphenyl belongs to the most highly reactive organo-photocatalysts even able to activate carbon dioxide for versatile organic transformations,^{17–19} but this reactivity comes at a price: excitation of *p*-terphenyl unavoidably requires hazardous UVB/C-light (see spectra in Fig. 1), usually provided by mercury-based light sources or by employing high-power Xe arc lamps that convert electricity to UV-light below 320 nm with a lousy efficiency. Commercial ready-to-use LEDs are not available with intense UVB/C output.²⁰ Considering that, shifting the absorption spectrum of *p*-terphenyl towards the UVA or even the visible range, where environmentally friendly LEDs efficiently emit, is highly desirable. As we will show, double sulfonation of

p-terphenyl and the addition of an SO₂ (sulfone)-unit to bridge two adjacent phenyl rings results in a highly interesting derivative (hereafter abbreviated as SO₂TDS, see Fig. 1 for the structure), which is readily accessible from inexpensive starting materials in a single synthetic step (synthetic protocols can be found in the ESI†).²¹ Not only does SO₂TDS strongly absorb in the near UV region, but it is also highly water-soluble (as opposed to *p*-terphenyl) laying the grounds for LED-driven photocatalysis in the “greenest” solvent.^{22–24} What is more, the sulfone-bridge converts *p*-terphenyl into a triplet chromophore opening up additional electron²⁵ and energy²⁶ transfer pathways that are unavailable for the parent compound.²⁷ Based on these findings, we have successfully employed SO₂TDS as a

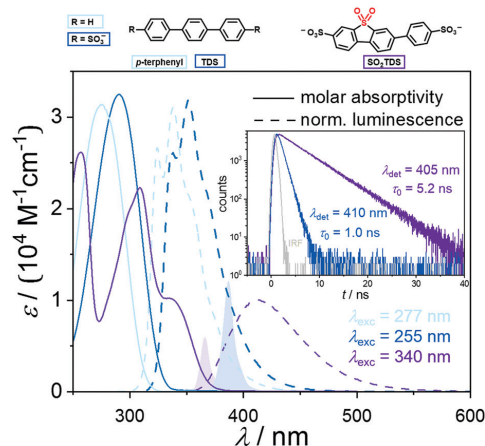


Fig. 1 Color-coded structures of *p*-terphenyl and the water-soluble derivatives (sodium salts) used in this study (top), calibrated absorption and normalized emission spectra, together with LED (390 nm and 370 nm) output spectra (main plot), as well as fluorescence lifetime measurements (inset; excitation occurred at 313 nm). For details, see text and ESI.†

Department of Chemistry, Johannes Gutenberg University Mainz,

Duesbergweg 10–14, 55128 Mainz, Germany. E-mail: ckerzig@uni-mainz.de

† Dedicated to Professor Martin Goez on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Experimental details, energetic and mechanistic considerations, DFT calculations, additional spectroscopic results and irradiation experiments. See DOI: 10.1039/d1cc01947c

Communication

novel organo-catalyst for pinacol coupling,^{22,28–30} isomerization^{11,26,31} and dechlorination³² photoreactions.

Fig. 1 enlarges on the ground-state absorption and fluorescence properties of **SO₂TDS** in comparison to two reference compounds, conventional *p*-terphenyl as well as *p*-terphenyl-4,4''-disulfonate (TDS). Except for showing moderately red-shifted (~15 nm) spectra, the water-soluble TDS behaves almost identically as its lipophilic role model. Both compounds are essentially pure singlet-state chromophores with fluorescence quantum yields close to unity and emission lifetimes on the order of 1 ns (Table 1). The sulfone bridge in **SO₂TDS**, however, completely changes the photophysical properties as our comparative study reveals: the absorption spectrum of **SO₂TDS** exhibits a band in the UVA with an onset at about 390 nm, blue fluorescence with a five-fold longer lifetime was detected and the emission quantum yield is half of that determined for the reference terphenyls (Table 1). Interestingly, the excited-singlet state energy of **SO₂TDS** is reduced by about 0.6 eV (and the computed HOMO–LUMO gap accordingly)²¹ compared to that of *p*-terphenyl while the DFT-calculated triplet energies remain almost unmodified (Table 1).

The observed fluorescence lifetime elongation for **SO₂TDS** seems surprising at first glance, but this can be rationalized in the framework of the well-known Strickler–Berg equation.^{33,34} According to the simplified work form of this equation, the radiative decay rate constant k_f depends on the intensity of the long-wavelength absorption band times the squared energy of the excited singlet state ($E_{0,0}$). Lowering the symmetry by introducing the sulfone bridge results in a substantial decrease of the oscillator strength f of the HOMO–LUMO transition, as indicated by the much lower molar absorption coefficients of **SO₂TDS** at the long-wavelength band (Fig. 1), which is also in line with our DFT²¹ calculations. The substantial f decrease and the reduced $E_{0,0}$ for **SO₂TDS** compared to TDS thus combine to decelerate k_f drastically. With the experimental fluorescence quantum yields and emission lifetimes from Table 1, k_f values of $9.8 \times 10^8 \text{ s}^{-1}$ (TDS) and $9.2 \times 10^7 \text{ s}^{-1}$ (**SO₂TDS**) are obtained for the water-soluble terphenyl derivatives. This deceleration of k_f opens up the possibility of other photophysical processes than fluorescence for singlet-excited **SO₂TDS**.

Assuming that radiationless deactivation directly to the ground state does not contribute to the excited-singlet state decay, we estimate an upper limit for the intersystem crossing ISC quantum yield of TDS as low as 2% ($\phi_{\text{ISC}} = 1 - \phi_F$), with a concomitant k_{ISC} being slower than $2 \times 10^7 \text{ s}^{-1}$. Hence, the

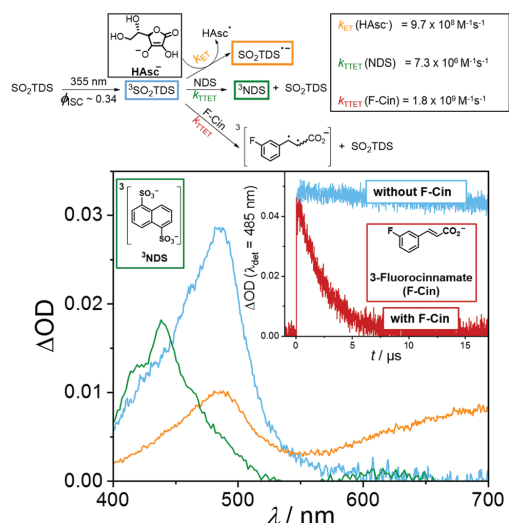


Fig. 2 Top: Schematic representation of the triplet state formation of **SO₂TDS** as well as the electron (ET) and energy (TTET) transfer reactions with ³**SO₂TDS** that have been studied in detail. Bottom: Transient absorption spectra of long-lived intermediates accessible upon pulsed (355 nm) excitation (and subsequent triplet quenching) of **SO₂TDS** (main plot). Shown are color-coded spectra of ³**SO₂TDS** (blue), the radical anion **SO₂TDS**^{•–} (orange) and the triplet of 1,5-naphthalenedisulfonate (³NDS, green). Representative decay traces of ³**SO₂TDS** without (blue) and with 0.2 mM of 3-fluorocinnamate (red) are displayed in the inset.²¹

hetero/heavy atoms of the terminal sulfonate groups do not promote ISC. Our DFT calculations,²¹ however, predict substantial orbital coefficients (LUMO) and spin densities on the sulfone bridge of **SO₂TDS**, which might be beneficial for triplet formation. Indeed, a long-lived species (see Fig. 2, blue data sets) with a transient absorption spectrum resembling that of the *p*-terphenyl triplet³⁵ was clearly observed upon direct **SO₂TDS** excitation. This **SO₂TDS**-derived species reacts with a fluorocinnamate (F-Cin in Fig. 2; triplet energy, ~2.4 eV)³⁶ in a diffusion controlled fashion and it is quenched by a well-characterized water-soluble naphthalene (NDS, triplet energy, 2.58 eV)³⁶ thereby producing ³NDS (Fig. 2, green spectrum). These results provide clear evidence for the formation of ³**SO₂TDS** after **SO₂TDS** excitation, and the observed triplet–triplet energy transfer TTET kinetics support the DFT-calculated triplet energy (2.47 eV, see Table 1).²¹ Quantitative laser flash photolysis (LFP) experiments using ruthenium(tris)bipyridine and NDS³⁶ as standards revealed an ISC quantum yield on the order of 35%, corresponding to a k_{ISC} of $7 \times 10^7 \text{ s}^{-1}$. All these findings highlight the importance of the sulfone bridge for the conversion of *p*-terphenyl into a chromophore with a readily available triplet state.

Having observed TTET donor reactivity, we now turn to exploring electron transfer ET processes with ³**SO₂TDS** as the key species. The *p*-terphenyl radical anion produced by excited-singlet state reduction with amines was exploited for photoreactions in

Table 1 Pertinent photophysical parameters for the terphenyl derivatives under study. For further explanations, see ESI

	<i>p</i> -Terphenyl	TDS	SO₂TDS
Exc.-singlet energy ($E_{0,0}$)/eV	3.99 ^a	3.75 ^b	3.37 ^b
Fluorescence quantum yield (ϕ_F)	0.94 ²⁷	0.98	0.48
Fluorescence lifetime (τ_F)/ns	0.9 ²⁷	1.0	5.2
ISC quantum yield (ϕ_{ISC})	≤ 0.06	≤ 0.02	$\sim 0.34^c$
Triplet energy (E_T)/eV	2.53 ²⁷	2.60	2.47

^a In cyclohexane. ^b In water. ^c Triplet lifetime, >100 μs .²¹

organic solvents,¹⁷ but a triplet-state photoreduction would have inherent efficiency advantages.^{25,37} In the presence of the potent electron donor ascorbate HAsc[−] (vitamin C) in neutral solution, we detected rapid ³SO₂TDS quenching to yield a new species with an additional band in the red/NIR³⁸ (Fig. 2, orange spectrum). This species can be assigned to the radical anion SO₂TDS^{•−}, and its reduction potential, which is hardly accessible in water, is estimated to amount to −1.75 V vs. NHE, corresponding to ∼−2 V vs. SCE.²¹

Guided by recent photocatalytic pinacol couplings in the context of sustainable chemistry, either carried out in organic solvents (ACN or DMF) with organo-catalysts^{28,29} or in the green solvent water²² with Ru catalysts, we aimed to combine the best of both approaches by employing our water-soluble SO₂TDS as catalyst. LFP studies with acetophenone ACP as model substrate and our SO₂TDS/HAsc[−] system allowed us to directly monitor the first step of the desired reaction, namely the acetophenone radical anion³⁹ formation by the reaction with SO₂TDS^{•−}.²¹ These mechanistic investigations prompted us to study the photocatalytic ACP pinacol coupling in NMR-scale experiments using an inexpensive 390 nm LED. Gratifyingly, SO₂TDS (2 mol%) in combination with HAsc[−] as a cheap sacrificial donor (1.33 equiv.) gave excellent results (92% yield). Control experiments corroborate the need for our complete catalytic system and light (see Fig. 3). Further mechanistic investigations demonstrate that reductive singlet-state quenching of excited SO₂TDS by HAsc[−] is unimportant under our reaction conditions,²¹ so pinpoint ³SO₂TDS as key species.

Next, we replaced ACP by the substrate anisaldehyde. However, we observed solubility problems, slow substrate consumption upon LED irradiation and the undesired formation of the monomeric alcohol (resulting from the low local radical concentration). As we found, anionic SO₂TDS is strongly bound to the surface of cationic DTAC micelles,²¹ and HAsc[−] is known to allow fast reactions at the water-micelle interface.⁴⁰ These observations pave

the way for the combination of micellar catalysis^{22,41–44} with organo-photocatalysis. Irradiating anisaldehyde with our catalytic system under micellar conditions gave the desired pinacol in a good yield (83% with 10 mol% SO₂TDS, Fig. 3). Furthermore, the micellar approach with SDS as anionic surfactant was highly beneficial for the photochemical pinacol coupling of an almost water-insoluble acetophenone derivative (lower right part of Fig. 3). In this case, SDS micelles do not interact with our catalytic system,^{21,40} but they serve as an efficient reservoir for hydrophobic substances in our reaction mixture.

To carry out photoreactions that unavoidably require triplet-excited catalysts, we turned to double bond isomerizations.^{26,31,36,44} We have chosen the cinnamate F-Cin as initial substrate, since we have already detected TTET quenching with this olefinic compound via LFP (see inset of Fig. 2). Our NMR-scale studies indicate the existence of a photostationary state (71% *cis* isomer) upon 2 h of photo-irradiation in the presence of 2 mol% SO₂TDS (Fig. 4). Neither TDS (0% *cis*) nor a water-soluble benzophenone^{9,30} derivative (27% *cis*) catalyze this test reaction efficiently (Fig. 4), highlighting the importance of both triplet formation and sufficient catalyst absorption in the near UV. Given that previous F-Cin isomerization reactions had to rely on tailor-made Ir catalysts,^{32,36} the SO₂TDS-catalyzed reaction represents an elegant organo-photocatalytic alternative. Similar results with the *cis* isomers as main products were obtained for a cationic as well as a neutral olefin under our standard conditions (Fig. 4, bottom). Therefore, we conclude that charged and uncharged substrates can be converted similarly without detrimental aggregation phenomena, which implies a versatile usage of our water-soluble catalyst. Quantitative NMR experiments show side product formation only in the case of the neutral cinnamyl alcohol. Again, the addition of DTAC has proven successful for suppressing side reactions such that the absolute yield of the *cis* isomer was increased significantly (35% vs. 51%).²¹

To improve the reaction rate we employed a 370 nm instead of a 390 nm LED (compare, spectral overlap in Fig. 1) for the F-Cin isomerization with a catalyst loading of 1% only. We

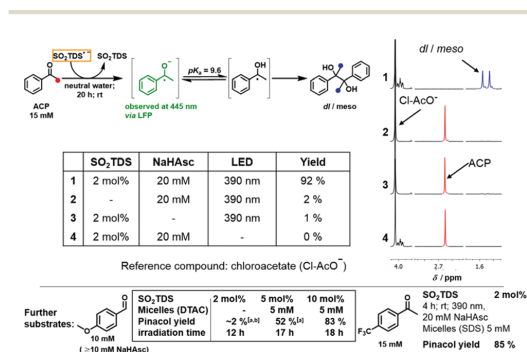


Fig. 3 Reaction scheme with conditions, key intermediate (ketyl radical anion) and control experiments for the LED-induced (390 nm) pinacol coupling with the photoredox catalyst SO₂TDS in neutral Ar-saturated water. Shown are yields obtained by quantitative NMR experiments. ACP was irradiated in neat water, whereas for the other substrates the beneficial effects of micelles have been investigated and exploited.²¹ [a] Side product formation. [b] Incomplete conversion.

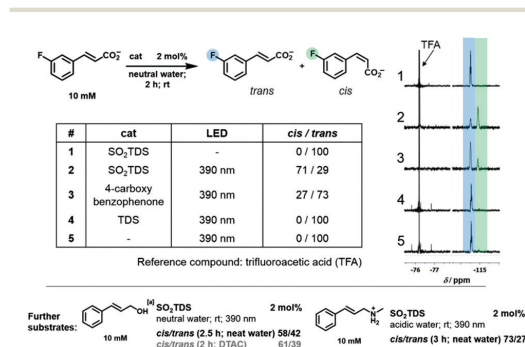


Fig. 4 *cis-trans* Isomerization with olefinic substrates using the LED-driven photocatalytic system (SO₂TDS) in Ar-saturated water.²¹ Several control experiments are displayed for the substrate *trans*-3-fluorocinnamate. [a] Side product formation.

Communication

found a *cis* isomer yield of 63% after 30 minutes of photo-irradiation (0% without catalyst).²¹ Highly attractive reaction durations with **SO₂TDS** are thus within easy reach, while maintaining acceptable product yields. Moreover, this experiment substantiates the high photostability of our novel organo-catalyst with achievable turnover numbers approaching those observed with photoactive metal complexes. Finally, we selected an additional olefin, *trans*-3-(4-pyridyl)acrylic acid, as well as a water-soluble benzyl chloride³² and tested the photocatalytic performance of **SO₂TDS** in comparison to five commercial photocatalysts that are sufficiently soluble under our conditions and known for triplet reactivity (see ESI,† Section 6.6). To our delight, **SO₂TDS** is the only compound catalyzing both the isomerization and the dechlorination efficiently owing to its unique photophysical, photochemical and redox properties presented herein.

In summary, we have identified and characterized an inexpensive photocatalyst being capable of transforming several substrates in a very sustainable manner. Sustainability is addressed in our study (i) by avoiding mercury-based UV light sources, (ii) by relying on catalytic mechanisms with a catalyst lacking precious metals and (iii) by using water as the “greenest” solvent, either without additives or in the presence of micelles to improve the substrate’s solubility and the reaction’s selectivity. Our study might thus contribute to the ongoing rethinking of using more environmentally friendly reaction conditions. The combination of meaningful spectroscopic techniques with preparative as well as mechanistic irradiation experiments revealed the importance of the triplet-excited catalyst and allowed us to distinguish between different catalytic mechanisms. Moreover, based on our photophysical results, incorporating SO₂-units into other organic chromophores seems to be a promising strategy to facilitate intersystem crossing of otherwise triplet-inactive molecules.

We acknowledge generous financial support from the JGU Mainz and we wish to thank Professor Oliver S. Wenger, not only for the use of his equipment for time-resolved spectroscopy but also for his continuous support. C. K. is grateful to the Chemical Industry Funds for a Liebig fellowship.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- J. C. Tellis, D. N. Primer and G. A. Molander, *Science*, 2014, **345**, 433–436.
- L. Marzo, S. K. Pagire, O. Reiser and B. König, *Angew. Chem., Int. Ed.*, 2018, **57**, 10034–10072.
- M. H. Shaw, J. Twilton and D. W. C. MacMillan, *J. Org. Chem.*, 2016, **81**, 6898–6926.
- T. R. Blum, Z. D. Miller, D. M. Bates, I. A. Guzei and T. P. Yoon, *Science*, 2016, **354**, 1391–1395.
- R. C. McAtee, E. J. McClain and C. R. J. Stephenson, *Trends Chem.*, 2019, **1**, 111–125.
- G. E. M. Crisenza and P. Melchiorre, *Nat. Commun.*, 2020, **11**, 803.
- C. G. Bochet, *Chimia*, 2019, **73**, 720–723.
- Y. Du, R. M. Pearson, C.-H. Lim, S. M. Sartor, M. D. Ryan, H. Yang, N. H. Damrauer and G. M. Miyake, *Chem. – Eur. J.*, 2017, **23**, 10962–10968.
- N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166.
- E. Speckmeier, T. G. Fischer and K. Zeitler, *J. Am. Chem. Soc.*, 2018, **140**, 15353–15365.
- C. Fischer, C. Kerzig, B. Zilate, O. S. Wenger and C. Sparr, *ACS Catal.*, 2020, **10**, 210–215.
- T.-Y. Shang, L.-H. Lu, Z. Cao, Y. Liu, W.-M. He and B. Yu, *Chem. Commun.*, 2019, **55**, 5408–5419.
- D. P. Hari and B. König, *Chem. Commun.*, 2014, **50**, 6688–6699.
- A. Vega-Peñaloza, J. Mateos, X. Companyó, M. Escudero-Casao and L. Dell’Amico, *Angew. Chem., Int. Ed.*, 2021, **60**, 1082–1097.
- Y. Lee and M. S. Kwon, *Eur. J. Org. Chem.*, 2020, 6028–6043.
- A. Graml, T. Nevesely, R. Jan Kutta, R. Cibulka and B. König, *Nat. Commun.*, 2020, **11**, 3174.
- H. Seo, M. H. Katcher and T. F. Jamison, *Nat. Chem.*, 2017, **9**, 453–456.
- S. Matsuoka, T. Kohzuki, C. Pac, A. Ishida, S. Takamuku, M. Kusaba, N. Nakashima and S. Yanagida, *J. Phys. Chem.*, 1992, **96**, 4437–4442.
- H. Seo and T. F. Jamison, *Org. Lett.*, 2019, **21**, 10159–10163.
- S. Horikoshi, D. Yamamoto, K. Hagiwara, A. Tsuchida, I. Matsumoto, Y. Nishiura, Y. Kiyoshima and N. Serpone, *Photochem. Photobiol. Sci.*, 2019, **18**, 328–335.
- See the ESI† for details and further explanations.
- R. Naumann and M. Goez, *Green Chem.*, 2019, **21**, 4470–4474.
- M. Bu, C. Cai, F. Gallou and B. H. Lipshutz, *Green Chem.*, 2018, **20**, 1233–1237.
- N. Noto, Y. Hyodo, M. Yoshizawa, T. Koike and M. Akita, *ACS Catal.*, 2020, **10**, 14283–14289.
- S. Neumann, O. S. Wenger and C. Kerzig, *Chem. – Eur. J.*, 2021, **27**, 4115–4123.
- F. Strieth-Kalthoff and F. Glorius, *Chemistry*, 2020, **6**, 1888–1903.
- M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of photochemistry*, CRC/Taylor & Francis, Boca Raton, 3rd edn, 2006.
- S. Okamoto, K. Kojima, H. Tsujioka and A. Sudo, *Chem. Commun.*, 2016, **52**, 11339–11342.
- A. Gualandri, A. Nenov, M. Marchini, G. Rodeghiero, I. Conti, E. Paltanin, M. Balletti, P. Ceroni, M. Garavelli and P. G. Cozzi, *ChemCatChem*, 2021, **13**, 981–989.
- I. K. Sideri, E. Voutyritsa and C. G. Kokotos, *Org. Biomol. Chem.*, 2018, **16**, 4596–4614.
- J. B. Metternich and R. Gilmour, *J. Am. Chem. Soc.*, 2015, **137**, 11254–11257.
- C. Kerzig and O. S. Wenger, *Chem. Sci.*, 2019, **10**, 11023–11029.
- S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 1962, **37**, 814–822.
- J. Mohanty and W. M. Nau, *Photochem. Photobiol. Sci.*, 2004, **3**, 1026.
- R. Kocia, *Int. J. Chem. Kinet.*, 2019, **51**, 958–964.
- B. Pfund, D. M. Steffen, M. R. Schreier, M.-S. Bertrams, C. Ye, K. Börjesson, O. S. Wenger and C. Kerzig, *J. Am. Chem. Soc.*, 2020, **142**, 10468–10476.
- G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401–449.
- A. M. Funston, S. V. Lyman, B. Saunders-Price, G. Czapski and J. R. Miller, *J. Phys. Chem. B*, 2007, **111**, 6895–6902.
- E. Hayon, T. Ibata, N. N. Lichtin and M. Simic, *J. Phys. Chem.*, 1972, **76**, 2072–2078.
- C. Kerzig, M. Hoffmann and M. Goez, *Chem. – Eur. J.*, 2018, **24**, 3038–3044.
- M. Giedyk, R. Narobe, S. Weiß, D. Touraud, W. Kunz and B. König, *Nat. Catal.*, 2020, **3**, 40–47.
- X. Ge, S. Zhang, X. Chen, X. Liu and C. Qian, *Green Chem.*, 2019, **21**, 2771–2776.
- G. La Sorella, G. Strukul and A. Scarso, *Green Chem.*, 2015, **17**, 644–683.
- L. D. Elliott, S. Kayal, M. W. George and K. Booker-Milburn, *J. Am. Chem. Soc.*, 2020, **142**, 14947–14956.

2.3 Dyads as mechanistic switch between energy and electron transfer

This section highlights the modified excited state (redox) properties in molecular dyads compared to their parent metal complexes, enabling the identification and characterization of a novel annihilator structure. In the first project (Section 2.3.1) the reactivity of ruthenium-based metal complexes is compared to their dyad congeners. The second project (Section 2.3.2) extends the principle of a modified reactivity by exchanging metal complexes for dyad derivatives to iridium-based chromophores.

2.3.1 Ruthenium-based dyads

This section presents:

Triplet quenching pathway control with molecular dyads enables the identification of a highly oxidizing annihilator class

Maria-Sophie Bertrams, Katharina Hermainski, Jean-Marc Mörsdorf, Joachim Ballmann, Christoph Kerzig, Chem. Sci., 2023, 14, 8583-8591.

Two water-soluble ruthenium-complex-pyrene dyads were developed and characterized in the Kerzig group, both extending the lifetime of the original ruthenium complexes by over one order of magnitude, which makes them promising sensitizers for TTET and $^1\text{O}_2$ generation.^[84] The water-soluble chromophores P-H^{2+} and derivatives^[227] do not undergo ISC after direct excitation and sensitization is required to obtain the triplet (chemical structures in Figure 24 A)).

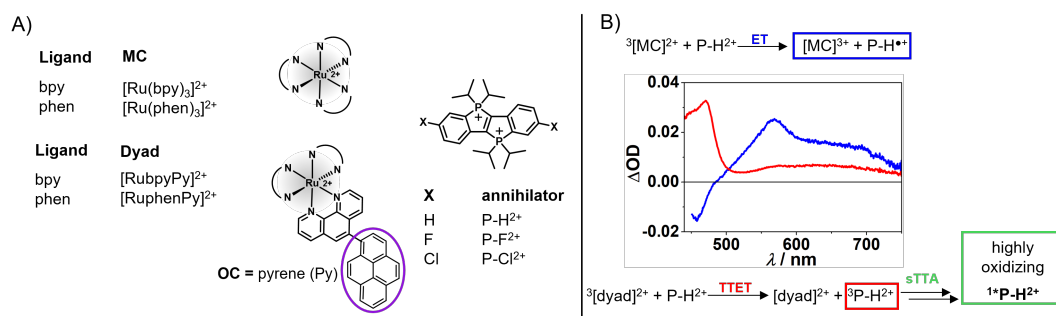


Figure 24: Summary of photosensitizers as mechanistic switch between energy and electron transfer. Part A) presents the structures of metal complexes (MC), the dyads and the annihilators. The general reaction equations for quenching of the triplet excited states of the MCs (ET, blue) and dyads (TTET, red) are shown, together with the corresponding transient absorption spectra.

Using $^3[\text{Ru}(\text{bpy})_3]^{2+}$ and $^3[\text{Ru}(\text{phen})_3]^{2+}$ as photosensitizers results in the ET species and TA spectra show the bleach of the corresponding oxidized $[\text{Ru}]^{3+}$ and the bands of the reduced annihilator species $\text{P-H}^{•+}$. For the dyads, the spin densities in the triplet

excited state are mainly localized on the pyrene ligand. This results in much milder excited-state potentials and in contrast to the metal complexes, ET is thermodynamically unfavorable, which enables a TTET-based sensitization of the annihilators. Time-gated emission spectra of the Ru-dyads and $P-H^{2+}$ showed delayed emission of $^1P-H^{2+}$ originating from an sTTA UC mechanism, which was supported by indicative kinetic and excitation power-dependent measurements (Figure 24, B)). Finally, $P-H^{2+}$ was investigated regarding the oxidative properties of the singlet excited state and comparative quenching studies allowed an estimation of the corresponding highly oxidizing excited state potential. With -2.3 V vs NHE provided by the $^1P-H^{2+}$, even the oxidation of chloride was feasible.^[93,228] Two derivatives of the annihilator core structure, one fluoro- and one chloro-substituted, were explored in the same study and similar findings were made for all three compounds.

Reproduced from reference: M.-S. Bertrams, K. Hermainski, J.-M. Mörsdorf, J. Ballmann, C. Kerzig, *Chem. Sci.*, **2023**, *14*, 8583-8591 with permission from the Royal Society of Chemistry.

The reference and can be found in the following pages and under reference [85]. The article is licensed under CC BY-NC 3.0 (<https://creativecommons.org/licenses/by-nc/3.0/>). The supporting information can be found in Section 6.9.

Author contributions: M.-S. Bertrams performed the optical spectroscopy measurements (absorption, emission and ns-TA), provided the graphs for the main paper and wrote the supporting information. K. Hermainski synthesized the Ru-dyads and within her Bachelor thesis performed additional spectroscopy under the guidance of M.-S. Bertrams. J.-M. Mörsdorf under the supervision of J. Ballmann performed the synthesis and characterization of the three annihilator structures and provided the respective parts for the main paper and supporting information. C. Kerzig provided helpful discussions, conceptualized the study and wrote the main paper.



Cite this: DOI: 10.1039/d3sc01725g

All publication charges for this article have been paid for by the Royal Society of Chemistry

Triplet quenching pathway control with molecular dyads enables the identification of a highly oxidizing annihilator class†

Maria-Sophie Bertrams,^a Katharina Hermainski,^a Jean-Marc Mörsdorf,^b Joachim Ballmann^{b*} and Christoph Kerzig^{a*}

Metal complex – arene dyads typically act as more potent triplet energy donors compared to their parent metal complexes, which is frequently exploited for increasing the efficiencies of energy transfer applications. Using unexplored dicationic phosphonium-bridged ladder stilbenes ($P-X^{2+}$) as quenchers, we exclusively observed photoinduced electron transfer photochemistry with commercial organic photosensitizers and photoactive metal complexes. In contrast, the corresponding pyrene dyads of the tested ruthenium complexes with the very same metal complex units efficiently sensitize the $P-X^{2+}$ triplets. The long-lived and comparatively redox-inert pyrene donor triplet in the dyads thus provides an efficient access to acceptor triplet states that are otherwise very tricky to obtain. This dyad-enabled control over the quenching pathway allowed us to explore the $P-X^{2+}$ photochemistry in detail using laser flash photolysis. The $P-X^{2+}$ triplet undergoes annihilation producing the corresponding excited singlet, which is an extremely strong oxidant (+2.3 V vs. NHE) as demonstrated by halide quenching experiments. This behavior was observed for three P^{2+} derivatives allowing us to add a novel basic structure to the very limited number of annihilators for sensitized triplet–triplet annihilation in neat water.

Received 3rd April 2023
Accepted 15th July 2023

DOI: 10.1039/d3sc01725g
rsc.li/chemical-science

Introduction

The excitation energies and (excited-)state redox properties of photoactive metal complexes can be tuned over wide windows by ligand modifications.^{1–10} This modularity allows the preparation of tailor-made photocatalysts or photosensitizers for a given light-driven application. It seems natural to assume that even more pronounced changes in photoreactivity are within reach when so-called molecular dyads or bichromophores are employed, in which metal complexes are covalently linked with organic chromophores.^{11–14} In such dyads the beneficial properties of both inorganic and organic photoactive compounds are frequently combined, *e.g.* visible-light absorptivity and quantitative intersystem crossing of the former and long-lived triplet states of the latter.^{15–18} Furthermore, the organic chromophores (OC) can possess completely different redox properties than the metal complexes (MC)¹⁹ such that dyads with lowest excited states that are OC-centered offer more

pronounced variations of the photoredox properties than those obtained by conventional ligand modification. This extended photoredox and triplet reactivity control for selective photoreactions with molecular dyads is underexplored, presumably because most studies have focused on inherent photophysical dyad properties.

Most MC-OC dyads known to date are based on ruthenium complexes with covalently connected aromatic hydrocarbons (arenes),^{15,16,20} but there are also many examples with other 4d/5d (ref. 21–23) and even some dyads with non-precious 3d (ref. 24–26) metals. Dyads of the type MC-OC have been successfully employed for increasing the energy transfer (EnT)^{20,27} or electron transfer (ET)^{28–32} reactivity compared to conventional metal complexes (see Fig. 1). The long-lived triplet states of these monometallic dyads have been successfully exploited for sensing³³ and imaging³⁴ applications, photodynamic therapy,³⁵ photon upconversion^{36–40} and, in some cases, for photocatalytic key reaction steps.^{27,28,31,32,41} Despite the popularity of these compounds it seems that relatively easily accessible dyads have a hidden application potential in controlling the quenching pathway and the bimolecular photoreactivity. The above-mentioned triplet lifetime increase that is accessible in well-designed dyads is of particular importance for systems in which the energy or electron acceptor concentration is inherently low. This holds true for annihilators in aqueous photon upconversion (UC) systems. The first bimolecular photoreaction in a sensitized triplet–triplet annihilation upconversion pair is

^aDepartment of Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10–14, 55128 Mainz, Germany. E-mail: ckerzig@uni-mainz.de

^bAnorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 276, 69120 Heidelberg, Germany. E-mail: joachim.ballmann@uni-heidelberg.de

† Electronic supplementary information (ESI) available: Experimental details, synthetic protocols and characterization data, additional spectroscopic results as well as raw data sets, and quantum-mechanical calculations. CCDC 2224633 and 2224634. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3sc01725g>

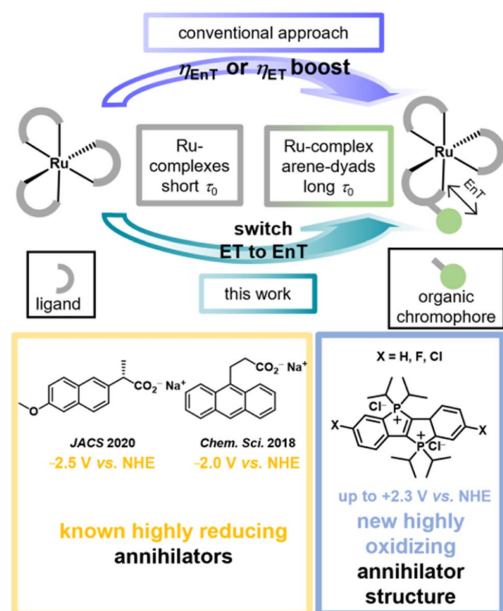


Fig. 1 Triplet lifetime elongation in molecular dyads with covalently connected organic chromophores is well established to increase the efficiency of energy or electron transfer (η_{EnT} or η_{ET}) reactions. In this work, switching of the quenching mechanism when comparing dyad and parent ruthenium complex was observed and exploited for the identification of the first highly oxidizing annihilator in water.

an EnT between the excited sensitizer (usually in a triplet state)⁴² and the annihilator molecule in its ground state. Only a few annihilator structures for UC in neat water have been identified so far.^{27,43–46} In addition to solubility, aggregation or excimer formation issues, one main reason for this situation is that highly polar water as the solvent favors ET over EnT reactions owing to the stabilization of (radical) ions.^{43,45}

As we will show using laser flash photolysis (LFP) as key method, the reduced redox reactivity of arene-localized triplets produced in a water-soluble Ru-containing dyad previously developed in one of our groups enables selective EnT quenching, whereas the parent Ru complexes exclusively operate *via* ET under otherwise identical conditions (Fig. 1). This dyad-induced quenching pathway switch allowed us to identify a novel annihilator class – the recently discovered dicationic phosphonium-bridged ladder stilbenes (P-X^{2+})⁴⁷ – with unmatched properties for aqueous upconversion. This compound class with previously unknown triplet photochemistry is not only sufficiently water-soluble but it has also very high emission quantum yields. These properties are highly beneficial for (aqueous) photon upconversion systems^{48–52} and we speculate that the bulky *iso*-propyl groups prevent the formation of undesired excimers⁵³ during the triplet-triplet annihilation (TTA) step. Two dyads, three reference complexes and three P-X^{2+} derivatives are analyzed in detail to establish

the reactivity switch approach and the novel annihilator class with some generality. While the previously known aqueous annihilators are strong photoreductants (lower part of Fig. 1),^{44,45} initial photoreactivity studies of the singlet-excited P-X^{2+} annihilators show that they are strong photooxidants with excited-state reduction potentials of up to +2.3 V vs. NHE and sufficiently long lifetimes for bimolecular reactions. This unique combination could result in novel photooxidation applications in water.

Results and discussion

The annihilators P-X^{2+} ($\text{X} = \text{H}, \text{Cl}, \text{F}$) were synthesized as described in Fig. 2. Employing appropriately substituted 2,2'-dibromotolanes as starting materials, the corresponding dilitiated intermediates were generated *in situ* *via* bromine-lithium exchange, which proceeds smoothly upon treatment with *n*-BuLi at -20°C . The resulting intermediates were quenched with chloro di(*iso*-propyl)phosphine at -40°C to afford the required diphosphinotolane precursors (*prec*- P-X). For the unsubstituted derivative ($\text{X} = \text{H}$), *prec*- P-X and the target compound P-H^{2+} have been reported previously,⁴⁷ but a significantly more complicated synthesis of P-H^{2+} (starting from *prec*- X-H) has been employed originally. In our first report,⁴⁷ P-H^{2+} was prepared using a three-step approach *via* (i) twofold cyclization of *prec*- P-H followed by (ii) a one-electron oxidation step to afford a radical cation and (iii) a second one-electron oxidation step. Here, it is shown that these three steps can be combined to a one-pot procedure using hexachloroethane (C_2Cl_6) as an oxidant (see Fig. 2). Only tetrachloroethylene (C_2Cl_4) is generated as by-product, while the products (P-X^{2+}) precipitate from the reaction mixture. All three derivatives were characterized comprehensively (see ESI† for details, Sections S2 and S4†), not only NMR spectroscopically in D_2O solution, but also *via* single crystal X-ray diffraction in the solid state. The dicationic core in P-X^{2+} ($\text{X} = \text{H}, \text{Cl}, \text{F}$) is basically isostructural in all three compounds, although a different stacking pattern (see ESI† for additional ORTEP plots) is observed in P-F^{2+} (brick layer stacking) in comparison to P-H^{2+} and P-Cl^{2+} (herringbone stacking), which may be related to the nature of the co-crystallized solvent (P-F^{2+} : MeOH, P-H^{2+} and P-Cl^{2+} : H_2O). Hence, all compounds were finely ground and rigorously dried (*i.e.* the co-crystallized solvents were removed) prior to the photochemical studies.

Initial UV/vis absorption studies in neutral air-saturated water indicated the decomposition of all P-X^{2+} derivatives on a timescale of several hours. However, as we found, P-X^{2+} solutions that are acidified with H_2SO_4 (50 mM) are bench-stable allowing us to reliably investigate their photophysical and photochemical properties. Calibrated UV/vis absorption and normalized emission spectra of the annihilators in this medium are summarized in Fig. 3 (right part). All derivatives have an intense long-wavelength absorption band in the violet/blue spectral region, while they show greenish emission with lifetimes on the order of 15 ns in argon-saturated solution. The energy of the first excited singlet is lower for the halogen-substituted derivatives by 0.10 eV to 0.15 eV compared to the

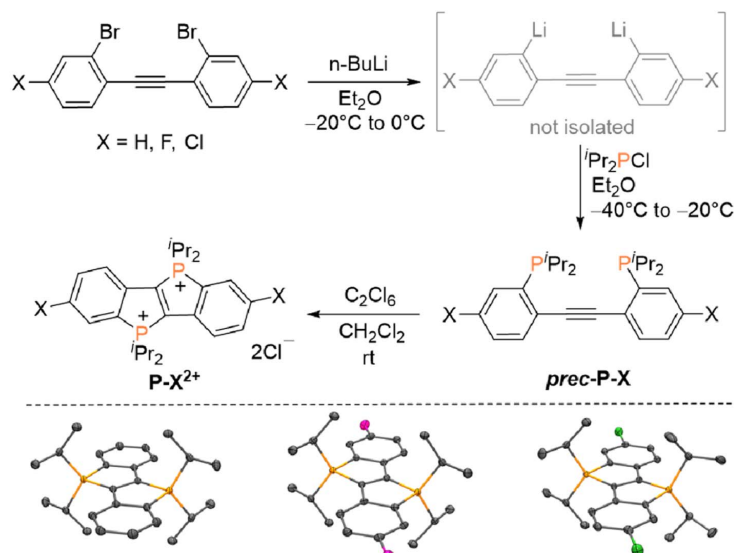


Fig. 2 Top: Synthesis of annihilators $P-H^{2+}$, $P-F^{2+}$ and $P-Cl^{2+}$ ($X = H, F, Cl$). Bottom: ORTEP plots of the dications in $P-H^{2+}$, $P-F^{2+}$ and $P-Cl^{2+}$ (hydrogen atoms, Cl^- counter ions and co-crystallized solvents omitted for clarity, see ESI† for details).

parent compound ($P-H^{2+}$). All derivatives are excellent emitters with fluorescence quantum yields approaching 90%, making them an ideal candidate for a potential annihilator

chromophore. Control experiments with freshly prepared solutions in neat MilliQ water at pH ~ 7 established that H_2SO_4 does not affect the photophysical properties. In welcome

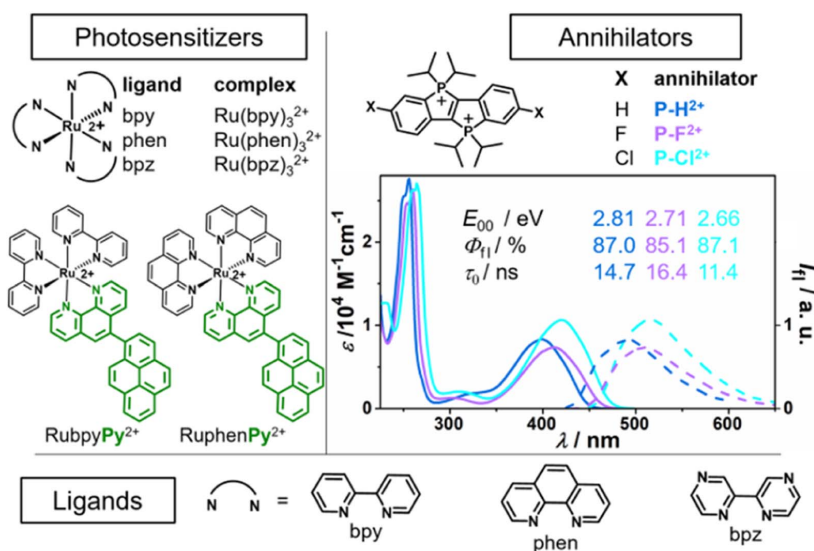


Fig. 3 Left and bottom: Ruthenium complexes and dyads with the respective ligands used as photosensitizers (PS), for more details see ref. 4, 19 and 27. Right: Novel annihilator structure ($P-H^{2+}$)⁴⁷ and derivatives ($P-F^{2+}$, $P-Cl^{2+}$), their calibrated UV/vis absorption and emission spectra and basic photophysical characteristics in Ar-saturated 50 mM H_2SO_4 (see ESI† for details).

contrast, the kinetic salt effect resulting from the H_2SO_4 dissociation products is regarded to accelerate the bimolecular photoreactions between the cationic species in the sTTA mechanism.

The fluorescence quantum yields (Fig. 3, Φ_{fl}) close to unity imply highly inefficient intersystem crossing ISC, and indeed we did not detect any long-lived species with our transient absorption setup (see ESI for details, Section S8.5†) upon direct excitation of P-X^{2+} with 355 nm pulses of ~ 10 ns duration. Previous DFT calculations on the basic structure P-H^{2+} (ref. 47) and additional calculations (see ESI, Section S5†) with a computational method that has been quite useful for the accurate prediction of triplet energies for organic chromophores^{54–57} allowed us to conclude that the P-X^{2+} triplet energy levels are in the range from 1.50 eV to 1.75 eV. With the aim in mind to sensitize the P-X^{2+} triplets with low-energy photons, we selected tris(diimine)ruthenium(II)-based chromophores as they provide a sufficiently high triplet energy and they can be selectively excited with a frequency-doubled Nd:YAG laser (532 nm) in the presence of ground-state P-X^{2+} . The commercially available ruthenium complexes $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{bpz})_3^{2+}$ as well as the recently prepared dyads²⁷ RubpyPy^{2+} and RuphenPy^{2+} were used in this study (see left part of Fig. 3 for the structures).

Comparative Stern–Volmer studies with $\text{Ru}(\text{bpy})_3^{2+}$ and the corresponding dyad RubpyPy^{2+} using P-H^{2+} as the quencher gave linear lifetime-based plots as displayed in Fig. 4 (left part). The Stern–Volmer constant with the latter was higher by a factor of 36, which can be traced to the much longer unquenched triplet lifetime of the dyad (see Table 1 for details). Transient absorption (TA) spectra recorded right after complete quenching of the respective sensitizer triplet are shown in the right part of Fig. 4. These spectra look completely different with

a pronounced bleach below 500 nm and a TA maximum at ~ 570 nm ($\text{Ru}(\text{bpy})_3^{2+}$), or with two maxima at ~ 470 and ~ 630 nm (RubpyPy^{2+}). The characteristic negative band in the former (emission-corrected) spectrum has to be due to a redox reaction of $\text{Ru}(\text{bpy})_3^{2+}$ as both the oxidized and reduced species of this metal complex show negative difference spectra in this region,^{58–60} and the ground state of the quencher P-H^{2+} does not absorb between 500 and 460 nm (see Fig. 3). Owing to (i) the facile reduction of P-H^{2+} in organic solvents,⁴⁷ which is certainly feasible when conventional photoexcited ruthenium complexes such as $\text{Ru}(\text{bpy})_3^{2+}$ or $\text{Ru}(\text{phen})_3^{2+}$ are used, (ii) the characteristic bleach below 500 nm that has also been observed upon chemical oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ (see ESI, Fig. S21†) and (iii) the fact that the remaining absorption features in the visible region are in line with the bands predicted by DFT calculations for P-H^{+} (ESI†), we conclude that P-H^{+} and $\text{Ru}(\text{bpy})_3^{3+}$ are the only primary quenching products. Furthermore, an absorption spectrum of the chemically prepared P-H^{+} in MeOH (where it is sufficiently stable) is in very good agreement with the spectrum of the photoinduced ET product above 500 nm (ESI, Fig. S22†), where the ruthenium complexes do not show clear absorption bands. In contrast, the red spectrum that was recorded right after $^3\text{RubpyPy}^{2+}$ quenching with P-H^{2+} does not show negative signals and both absorption bands decay with wavelength-independent and almost pure first-order kinetics on a time-scale of a few hundreds of microseconds. We assigned this spectrum to the triplet of P-H^{2+} , which is further substantiated by DFT calculations (ESI†) and delayed emission measurements (see below). Time-resolved measurements at selected wavelengths (Fig. 4, central part) clearly demonstrated that both photoproducts are directly formed from the different triplet-excited sensitizers. For the kinetic trace showing the $^3\text{P-H}^{2+}$ formation, a spectral separation had to be carried out because

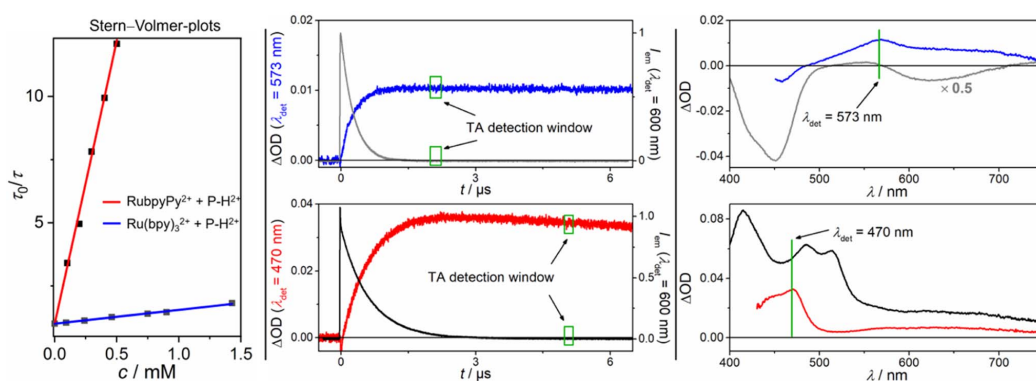


Fig. 4 Left panel: Stern–Volmer plots for the triplet quenching with P-H^{2+} using $^3\text{RubpyPy}^{2+}$ (red fit) and $^3\text{Ru}(\text{bpy})_3^{2+}$ (blue fit) as photosensitizers; Central panel: Kinetic sensitizer emission traces (upper for $^3\text{Ru}(\text{bpy})_3^{2+}$ in gray, concentration $30 \mu\text{M}$, $\lambda_{\text{exc}} = 532$ nm, 42 mJ and lower for $^3\text{RubpyPy}^{2+}$ in black, concentration $31 \mu\text{M}$, $\lambda_{\text{exc}} = 532$ nm, 42 mJ) with P-H^{2+} (2.0 mM with $\text{Ru}(\text{bpy})_3^{2+}$, 0.5 mM with RubpyPy^{2+}), together with the formation kinetics of the quenching products (blue trace corresponds to the one electron reduced P-H^{+} after ET, red trace corresponds to the $^3\text{P-H}^{2+}$ after ET); Right panel: TA spectra of the triplet excited photosensitizer (upper, gray spectrum $^3\text{Ru}(\text{bpy})_3^{2+}$, and lower, black spectrum $^3\text{RubpyPy}^{2+}$) and $^3\text{P-H}^{2+}$ (red, lower graph) after ET or P-H^{+} and $\text{Ru}(\text{bpy})_3^{3+}$ (blue, upper graph) after ET. All measurements were carried out in 50 mM H_2SO_4 . Further explanations are given in the text and ESI†.



Table 1 Key reactivity properties for all ruthenium photosensitizers with the quencher P-H²⁺ in 50 mM H₂SO₄. For more detail, see text and ESI

PS	RuphenPy ²⁺	RubpyPy ²⁺	Ru(bpz) ₃ ²⁺	Ru(phen) ₃ ²⁺	Ru(bpy) ₃ ²⁺
<i>E</i> _T /eV	~2.0 ^a	~2.0 ^a	2.16 ^b	2.19 ^b	2.12 ^b
<i>τ</i> ₀ /μs	43.1 ^c	15.0 ^c	0.55 ^{c,d}	1.09 ^c	0.59 ^c
<i>k</i> _q /10 ⁹ M ⁻¹ s ⁻¹	1.44 ± 0.01 ^e	1.50 ± 0.09 ^e	0.09 ± 0.02 ^{d,e,g}	1.39 ± 0.05 ^f	1.05 ± 0.10 ^f
<i>E</i> [(PS) ³⁺ /3(PS) ²⁺] V vs. NHE	>−0.5	>−0.5	−0.06 ^h	−0.69 ^h	−0.59 ^h

^a Estimated to be slightly lower than for ³pyrene.^{19,27} ^b Taken from ref. 1. ^c Estimated relative error below 5%. ^d In neat water due to protonation of the PS. ^e EnT. ^f ET. ^g Estimated rate constant in 50 mM H₂SO₄, 0.25 × 10⁹ M⁻¹ s⁻¹. ^h Recalculated vs. NHE from values in V vs. SCE^{1,19} see ESI for details.

the sensitizer triplet (which has a triplet pyrene signature)²⁷ absorbs more strongly than ³P-H²⁺ throughout the TA spectrum. Qualitatively identical results have been observed with the phenanthroline-containing dyad and the purely inorganic counterpart Ru(phen)₃²⁺, i.e. P-H²⁺ triplet formation with the dyad and oxidative quenching with the conventional metal complex (ESI†). Second-order rate constants and inherent sensitizer properties under our conditions are summarized in Table 1. The results presented in this paragraph unambiguously establish that a photoexcited dyad can enable a completely different quenching mechanism compared to that observed for the parent metal complex. Clearly, the pyrene-localized triplets in the dyads are less reducing than the MLCT triplet states of the corresponding metal complexes, laying the grounds for the observed effects.

Further evidence for our spectral assignment is provided by experiments with Ru(bpz)₃²⁺. This metal complex is known to be less reducing in its excited state (compare, excited-state oxidation potentials in Table 1), while maintaining a high triplet energy. We clearly observed ³P-H²⁺ (ESI, Fig. S29†) but a very high concentration of the tailor-made annihilator had to be used owing to the short ³Ru(bpz)₃²⁺ lifetime (see also the efficiency discussion in the next paragraph). Moreover, we tested several additional photosensitizers that should have the potential to produce ³P-H²⁺, based on their triplet energies, absorption properties at our laser wavelength (532 nm) and solubility properties. Electron transfer quenching was clearly demonstrated (see ESI for details, Section S7.8†) with four commercially available photosensitizers (two metal complexes and two organic dyes) and a tailor-made ruthenium complex-anthracene dyad. We, therefore, speculate that the P-H²⁺ triplet and its annihilator properties would have been overlooked without the ruthenium complex-pyrene dyads, highlighting their unique energy transfer capability. The second-order rate constants for the EnT reactions are comparable for both dyads (~1.5 × 10⁹ M⁻¹ s⁻¹). For Ru(bpz)₃²⁺, however, that reaction is about six times slower even after salt effect corrections (H₂SO₄ could not be used owing to Ru(bpz)₃²⁺ protonation,^{61,62} see ESI† for details). More pronounced coulombic repulsion between the cationic energy donor Ru(bpz)₃²⁺ and P-H²⁺ might explain these observations.⁴⁴ ET quenching with Ru(bpy)₃²⁺ and Ru(phen)₃²⁺ occurs with diffusion-controlled rates taking coulombic interactions into account.

The efficiencies of the photoreactions employing P-H²⁺ as quencher and the corresponding mechanisms are visualized in

Fig. 5. Using our Stern-Volmer quenching data sets (ESI, Section S7†) and the well-known photokinetic equations,⁶³ we simulated the P-H²⁺ concentration-dependent quenching efficiencies. Owing to the long unquenched triplet lifetimes of the dyads, the P-H²⁺ concentrations required for >90% quenching are below 400 μM. In contrast, the EnT efficiency with Ru(bpz)₃²⁺ is slightly below 25% at the highest experimental P-H²⁺ concentration employed (about 5.5 mM, see Fig. 5). Efficient EnT quenching (>90%) with Ru(bpz)₃²⁺ would require unreasonably high P-H²⁺ concentrations exceeding 0.2 M, which would correspond to P-H²⁺ amounts of almost 100 mg per mL of the chloride salt. The quenching efficiencies with ³Ru(bpy)₃²⁺ and ³Ru(phen)₃²⁺, which transfer a single electron to P-H²⁺ rather than the triplet energy, are in-between the extreme kinetic scenarios of highly efficient and highly inefficient quenching.

Fig. 6 focuses on the triplet of P-H²⁺ and its decay *via* annihilation. Time-gated emission measurements upon 532 nm laser excitation were carried out with RuphenPy²⁺ in the presence of P-H²⁺ (left part of Fig. 6). With an integration window of 150 μs duration starting shortly after the excitation pulse, we clearly detected some unquenched ³RuphenPy²⁺ emission peaking at ~605 nm. In addition, we observed an emission

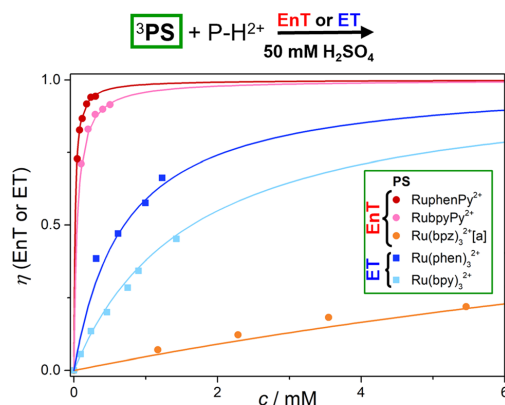


Fig. 5 Comparative quenching efficiency analysis for EnT (color-coded bullets) or ET (color-coded squares) between the excited photosensitizers at a constant concentration of 50 mM H₂SO₄ ([a] in H₂O due to sensitizer protonation in acidic solution).

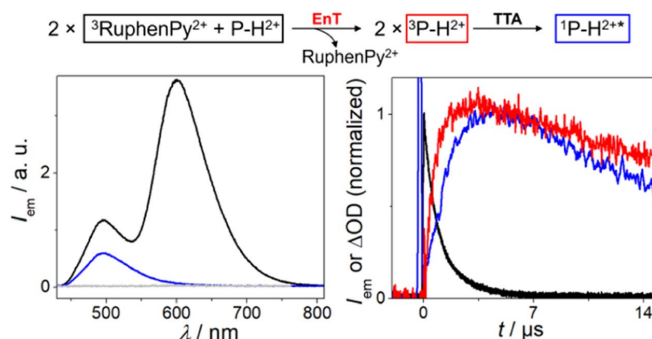


Fig. 6 Reaction scheme (top) of sTTA with RuphenPy²⁺ as PS (30 μ M) and P-H²⁺ (0.5 mM) as annihilator. Left: Time-gated emission spectra (excitation at $\lambda = 532$ nm) of ³RuphenPy²⁺ and ¹P-H²⁺* (black, time delay 300 ns integrated over 150 μ s), the isolated ¹P-H²⁺* spectrum after sTTA (blue, time delay 15 μ s integrated over 150 μ s) and a P-H²⁺ solution without the photosensitizer (gray) as control measurement (time delay 500 ns integrated over 150 μ s). Right: Normalized kinetic traces (excitation at $\lambda = 532$ nm) of ³RuphenPy²⁺ emission with P-H²⁺ (black, $\lambda_{\text{det}} = 600$ nm), formation of ³P-H²⁺ absorption (red, $\lambda_{\text{det}} = 475$ nm, corrected kinetic trace, for details see ESI†) and the formation and decay of ¹P-H²⁺* emission after sTTA (blue, $\lambda_{\text{det}} = 500$ nm).

band with a maximum at ~ 495 nm. This band resembles that of singlet-excited P-H²⁺ in strongly diluted solution taking filter effects into account (see also ESI, Fig. S41†), and it shows the non-linear power dependence being typical for the UC mechanism under study (ESI, Fig. S38†). A time-gated emission measurement with a longer delay between green laser pulse and detection window allowed us to (blue spectrum in Fig. 6) detect the greenish emission in isolation, whereas a control experiment in the absence of the sensitizer did not yield any delayed emission. The fact that a pure annihilator emission spectrum could be obtained without contaminations by the emissive ruthenium complex indicates that back energy transfer from ³P-H²⁺ to the sensitizer ground state does not take place. This observation implies a pronounced triplet energy difference of at least 0.2 eV, allowing us to set an upper limit for the P-H²⁺ triplet energy of 1.8 eV (in line with the DFT calculations mentioned above). More evidence for sensitized TTA was obtained from kinetic absorption and emission measurements monitoring the sensitizer triplet, ³P-H²⁺ and the annihilation product ¹P-H²⁺* under identical conditions (right part of Fig. 6). Both annihilator-derived species reach their maximum intensities at about 4 μ s after the green laser pulse. As a result of the bimolecular nature of the annihilation process, the rise and fall of the singlet emission intensity (blue) are in a quadratic relation to concentration-dependent signals of the precursor ³P-H²⁺ (red), resulting in the characteristic behavior displayed in Fig. 6.^{55,64} All these results unambiguously establish that ³P-H²⁺ acts as annihilator in neat water.

To test whether the dyad quenching pathway control holds also true for the two halogen-substituted annihilators P-X²⁺ (X = Cl, F), comparative experiments with Ru(phen)₃²⁺ and ³RuphenPy²⁺ were carried out (see ESI, Sections S7.5 and S8.4†). In the presence of the conventional metal complex, we clearly observed the signatures of the radical cations P-X^{•+} in the TA spectra (intense band at ~ 590 nm) along with the Ru(phen)₃²⁺

bleach below 500 nm. Employing the dyads as sensitizers, however, a positive TA band could be observed below 500 nm, which we ascribe to ³P-X²⁺. That assignment is again substantiated by delayed annihilator emission for both derivatives ¹P-X²⁺*, which was only detectable in the presence of the dyad. Based on these findings, dicationic phosphonium-bridged ladder stilbenes can be regarded as a new annihilator class. Furthermore, these experiments imply that the quenching pathway control with molecular dyads might well be developed into a versatile method for the generation of triplets and/or radical ions that cannot be formed with well-established sensitizers.

Having established that ¹P-X²⁺* is accessible *via* sTTA with two low-energy photons, we next turned to the photochemical reactivity of this species. The ET quenching observations with the commercial ruthenium complexes with their well-known redox properties indicate that P-X²⁺ is reduced at a potential between -0.6 and -0.1 vs. NHE in water (compare, Table 1). In consequence, the annihilators must be highly oxidizing in their singlet-excited states, taking their S₁ energies of ~ 2.7 eV into account (see Fig. 3). Owing to the observed instability of the chemically prepared P-X^{•+} in water and the inherent difficulties associated with (reductive) cyclic voltammetry in aqueous solvents,⁶⁵ the P-X²⁺ reduction potentials could not be measured directly. Alternatively, we estimated the P-X²⁺ reduction potentials both in the ground states and in the first excited singlet states with several reference reactions and chromophores possessing well-defined potentials in water. The previously identified aqueous annihilators MAMA⁺ (a cationic anthracene derivative) and 1,5-naphthalenedisulfonate are relatively strong oxidants in their excited singlet states with excited-state reduction potentials of $+1.6$ and $+1.9$ V vs. NHE, respectively (see Table 2 for details). As test reactions, we selected the chloride/bromide oxidation to the respective halogen atom.⁶⁶ To study the quenching kinetics in a direct



Table 2 Reactivity studies *via* halide quenching with the new annihilators as well as known annihilator structures and Ru(bpy)₃²⁺ as reference compounds. All quenching rate constants k_q were measured at identical ionic strength (aqueous 50 mM H₂SO₄), except for 1,5-NDS²⁻^a

	Ru(bpy) ₃ ²⁺	MAMA ⁺	1,5-NDS ²⁻	P-Cl ²⁺	P-F ²⁺	P-H ²⁺
$k_q(\text{Cl}^-)/10^8 \text{ M}^{-1} \text{ s}^{-1}$	No quenching	<0.1	No quenching ^a	0.60 ± 0.01	0.45 ± 0.02	5.10 ± 0.18
$k_q(\text{Br}^-)/10^8 \text{ M}^{-1} \text{ s}^{-1}$	No quenching	4.05 ± 0.09	8.06 ± 0.17 (6.68 ± 0.17) ^a	102 ± 2	104 ± 1	122 ± 1
E_{00}/eV	2.12 ^b	3.18 ^c	3.87 ^e	2.66	2.71	2.81
$E(\text{PC}/\text{PC}^{\cdot-})$ V vs. NHE	-1.3 ^b	-1.7 ^d	-1.97 ^e	~ -0.5 ^f	~ -0.5 ^f	~ -0.5 ^f
$E(*\text{PC}/\text{PC}^{\cdot-})$ V vs. NHE	0.8 ^b	1.6	1.9	~ 2.2 ^f	~ 2.2 ^f	~ 2.3 ^f

^a In 50 mM NaOH (in H₂O). ^b Taken from ref. 70. ^c Taken from ref. 44. ^d Estimated from 9-methyl-anthracene.¹⁹ ^e Taken from ref. 45 and 71. ^f Estimated from quenching studies, see text for details. Reference values: $E(\text{Cl}^{\cdot-}) = 2.4 \text{ V vs. NHE}$ ⁶⁷ and $E(\text{Br}^{\cdot-}) = 1.8 \text{ V vs. NHE}$.^{67,68}

manner without potentially disturbing effects on triplet decay rates or annihilation rate constants, we directly produced the emissive singlet states of the annihilator molecules (*i.e.* without sensitizers, see ESI† for details). Averaging several potentials from the literature estimated or determined for aqueous solution,⁶⁷ we took a reference potential of +2.4 V vs. NHE for the chloride oxidation and +1.8 V vs. NHE for bromide (the latter value was also used in a recent study addressing the Br⁻ oxidation in water).⁶⁸ As another test system, we investigated the weakly oxidizing ³Ru(bpy)₃²⁺, which, as we found, does not react with both halide ions under our conditions (Table 2). During the emission quenching studies presented below, high salt or H₂SO₄ concentrations were added to minimize kinetic salt effects on one hand and coulombic effects on the diffusion on the other.

Interestingly, P-H²⁺ is the only compound being able to oxidize chloride in its excited state rapidly with a quenching rate constant of $\sim 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 7). The other excited P-X²⁺

derivatives quench slower by one order of magnitude and the seemingly less oxidizing 1,5-NDS²⁻, whose generation requires one UVB photon or two blue photons,⁴⁵ is not quenched by chloride at all. The less challenging bromide oxidation is diffusion controlled ($\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) for all excited P-X²⁺ derivatives, while quenching with the reference compounds occurs with about 20 times slower rate constants. The observed trends are in perfect accordance with halide oxidation and other potential quenching pathways are thus seen to be unimportant. The well-established relation between the second-order rate constants and the Gibbs energy of photoinduced electron transfer^{69,70} allows us to estimate the excited state reduction potentials of the novel photoactive compounds $E(*\text{PC}/\text{PC}^{\cdot-})$. $E(*\text{PC}/\text{PC}^{\cdot-})$ has to be higher than 2 V due to the rapid bromide and detectable chloride oxidation, and we estimate 2.3 V vs. NHE for the most highly oxidizing ¹P-H²⁺* (see Table 2 for all potentials). The very high potential for ¹P-H²⁺* is further corroborated by kinetic experiments with 1,5-NDS²⁻ acting as quencher. The oxidation of the latter requires 2.03 V vs. NHE⁷¹ and we observed diffusion-controlled quenching (ESI, page S40†), which is in perfect accordance with the annihilator's redox potential estimated *via* halide quenching. This outstanding reactivity for photochemical oxidations is comparable with that observed for the famous acridinium photocatalysts.⁷²⁻⁷⁵

Initial LFP experiments employing Ru(bpy)₃²⁺ as sensitizer and P-H²⁺ as annihilator indicate that green-light driven chloride oxidation is indeed feasible *via* sTTA in water (see ESI for details, Section S9.4†). These results demonstrate that the new annihilator class has the potential to be integrated in up-conversion schemes for challenging oxidative bond activation reactions, even in aqueous solution. This is an important finding considering that most known upconversion-driven photoreactions have to rely on a reductive substrate activation step,^{63,76-78} and the lack of highly oxidizing annihilator molecules likely contributed to this situation.

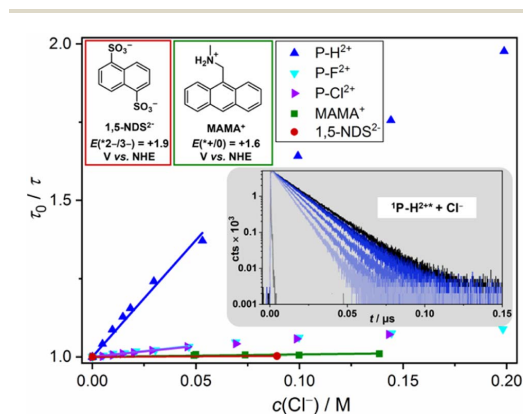


Fig. 7 Main: Color-coded Stern–Volmer (SV) plots for the singlet-state chloride quenching of the new annihilators and two literature-known aqueous annihilators (1,5-NDS²⁻ (ref. 45) and MAMA⁺ (ref. 44), together with the structures and excited-state potentials); inset (gray): selected kinetic traces for ¹P-H²⁺* quenching with increasing concentrations of Cl⁻ (added to the solutions as NaCl, see ESI† for all data sets). The downward curvature of the SV plots at higher quencher concentrations is due to the kinetic salt effect. The linear regions have been used for the kinetic analysis.

Conclusions

As has emerged from this work, molecular dyads that are easily accessible can be exploited for the efficient generation of quencher-derived triplets, while the parent metal complexes and widely used organic photosensitizers exclusively generate electron transfer products. This quenching pathway



manipulation (thermodynamics), in combination with the very long triplet lifetimes (kinetics) of the dyads, paved the way for the identification of a novel annihilator class in water with unmatched photoredox properties. We believe that this extended dyad-induced reactivity switching will find further useful applications in the broad photochemistry field, especially (i) with regard to triplet properties of highly redox-active or charged chromophores, and (ii) for controlling the reaction pathways in photocatalysis. The latter idea would be most promising with metal complexes possessing even higher triplet energies and excited-state oxidation as well as reduction potentials accordingly. Owing to the rather low triplet energy of the dicationic phosphonium-bridged ladder stilbenes (about 1.6 eV), sensitization with lower-energy photons approaching the biological window seems to be within reach. We are currently working on identifying such systems which would have potential applications in red-light driven photocatalysis in water or biochemical applications.

Data availability

All experimental and computational data have been provided in the main text and the ESI.† The data sets shown in the main paper and DFT output files can be found under <http://doi.org/10.25358/openscience-9298>.

Author contributions

M.-S. B. and K. H. designed photochemical studies, carried out spectroscopic experiments and analyzed data. M.-S. B. carried out the DFT calculations. K. H. prepared the dyads. The synthetic and the crystallographic work was carried out by J.-M. M. and J. B. C. K. conceived the project, provided guidance and wrote the initial draft of the manuscript with input from J. B. and M.-S. B. All authors contributed to the writing and editing of the manuscript and the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge generous financial support from the JGU Mainz, SusInnoScience and the German Research Foundation (DFG, grant numbers KE 2313/3-1 and KE 2313/7-1). C. K. is grateful to the Chemical Industry Funds for a Liebig fellowship. J.-M. M. and J. B. thank the Vector foundation for financial support. We thank Arne C. Sell for assistance with the dyad synthesis.

References

- 1 A. A. Vlcek, E. S. Dodsworth, W. J. Pietro and A. B. P. Lever, *Inorg. Chem.*, 1995, **34**, 1906–1913.
- 2 L. Schmid, C. Kerzig, A. Prescimone and O. S. Wenger, *JACS Au*, 2021, **1**, 819–832.
- 3 D. M. Arias-Rotondo and J. K. McCusker, *Chem. Soc. Rev.*, 2016, **45**, 5803–5820.
- 4 K. Teegardin, J. I. Day, J. Chan and J. Weaver, *Org. Process Res. Dev.*, 2016, **20**, 1156–1163.
- 5 C. Sandoval-Pauker, G. Molina-Aguirre and B. Pinter, *Polyhedron*, 2021, **199**, 115105.
- 6 Y. Wu, D. Kim and T. S. Teets, *Synlett*, 2022, **33**, 1154–1179.
- 7 T. Koike and M. Akita, *Inorg. Chem. Front.*, 2014, **1**, 562–576.
- 8 W. R. Kitzmann and K. Heinze, *Angew. Chem., Int. Ed.*, 2023, **62**, e202213207.
- 9 C. B. Larsen and O. S. Wenger, *Chem.-Eur. J.*, 2018, **24**, 2039–2058.
- 10 Z. Mahmood, J. He, S. Cai, Z. Yuan, H. Liang, Q. Chen, Y. Huo, B. König and S. Ji, *Chem.-Eur. J.*, 2023, **29**, e202202677.
- 11 E. A. Medlycott and G. S. Hanan, *Chem. Soc. Rev.*, 2005, **34**, 133–142.
- 12 G. J. Wilson, A. Launikonis, W. H. F. Sasse and A. W.-H. Mau, *J. Phys. Chem. A*, 1997, **101**, 4860–4866.
- 13 W. E. Ford and M. A. J. Rodgers, *J. Phys. Chem.*, 1992, **96**, 2917–2920.
- 14 V. Balzani, P. Ceroni, A. Credi and M. Venturi, *Coord. Chem. Rev.*, 2021, **433**, 213758.
- 15 A. J. Howarth, M. B. Majewski and M. O. Wolf, *Coord. Chem. Rev.*, 2015, **282–283**, 139–149.
- 16 F. N. Castellano, *Acc. Chem. Res.*, 2015, **48**, 828–839.
- 17 S. A. Denisov, S. Yu, J.-L. Pozzo, G. Jonusauskas and N. D. McClenaghan, *ChemPhysChem*, 2016, **17**, 1794–1804.
- 18 J. A. Roque III, H. D. Cole, P. C. Barrett, L. M. Lifshits, R. O. Hodges, S. Kim, G. Deep, A. Francés-Monerris, M. E. Alberto, C. G. Cameron and S. A. McFarland, *J. Am. Chem. Soc.*, 2022, **144**, 8317–8336.
- 19 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of photochemistry*, CRC/Taylor & Francis, Boca Raton, 3rd edn, 2006.
- 20 M. Schmid, J. Brückmann, J. Bösking, D. Nauroozi, M. Karnahl, S. Rau and S. Tschierlei, *Chem.-Eur. J.*, 2022, **28**, e202103609.
- 21 X. Guo, Y. Liu, Q. Chen, D. Zhao and Y. Ma, *Adv. Opt. Mater.*, 2018, **6**, 1700981.
- 22 J. Brückmann, C. Müller, I. Friedländer, A. K. Mengele, K. Peneva, B. Dietzek-Ivancić and S. Rau, *Chem.-Eur. J.*, 2022, **28**, e202201931.
- 23 Y. Sasaki, N. Yanai and N. Kimizuka, *Inorg. Chem.*, 2022, **61**, 5982–5990.
- 24 C. Wegeberg, D. Häussinger and O. S. Wenger, *J. Am. Chem. Soc.*, 2021, **143**, 15800–15811.
- 25 P. Dierks, A. Pöpcke, O. S. Bokareva, B. Altenburger, T. Reuter, K. Heinze, O. Kühn, S. Lochbrunner and M. Bauer, *Inorg. Chem.*, 2020, **59**, 14746–14761.
- 26 M. Sandroni, Y. Pellegrin and F. Odobel, *C. R. Chim.*, 2016, **19**, 79–93.
- 27 A. C. Sell, J. C. Wetzel, M. Schmitz, A. W. Maijenburg, G. Woltersdorf, R. Naumann and C. Kerzig, *Dalton Trans.*, 2022, **51**, 10799–10808.
- 28 S. Neumann, O. S. Wenger and C. Kerzig, *Chem.-Eur. J.*, 2021, **27**, 4115–4123.



- 29 G. J. Wilson, A. Launikonis, W. H. F. Sasse and A. W.-H. Mau, *J. Phys. Chem. A*, 1998, **102**, 5150–5156.
- 30 C. Weinheimer, Y. Choi, T. Caldwell, P. Gresham and J. Olmsted, *J. Photochem. Photobiol., A*, 1994, **78**, 119–126.
- 31 L. Ma, P. Wang, J.-Z. Wang, S. Guo, Z.-M. Zhang, X.-S. Zeng and T.-B. Lu, *Dyes Pigm.*, 2021, **196**, 109811.
- 32 S. Guo, K.-K. Chen, R. Dong, Z.-M. Zhang, J. Zhao and T.-B. Lu, *ACS Catal.*, 2018, **8**, 8659–8670.
- 33 D. Hara, H. Komatsu, A. Son, S. Nishimoto and K. Tanabe, *Bioconjugate Chem.*, 2015, **26**, 645–649.
- 34 H. Komatsu, K. Yoshihara, H. Yamada, Y. Kimura, A. Son, S. Nishimoto and K. Tanabe, *Chem.–Eur. J.*, 2013, **19**, 1971–1977.
- 35 M. Stephenson, C. Reichardt, M. Pinto, M. Wächter, T. Sainuddin, G. Shi, H. Yin, S. Monro, E. Sampson, B. Dietzek and S. A. McFarland, *J. Phys. Chem. A*, 2014, **118**, 10507–10521.
- 36 F. Deng, M. S. Lazorski and F. N. Castellano, *Philos. Trans. R. Soc., A*, 2015, **373**, 20140322.
- 37 K. Chen, M. Hussain, S. S. Razi, Y. Hou, E. A. Yildiz, J. Zhao, H. G. Yaglioglu and M. D. Donato, *Inorg. Chem.*, 2020, **59**, 14731–14745.
- 38 S. Ji, H. Guo, W. Wu, W. Wu and J. Zhao, *Angew. Chem., Int. Ed.*, 2011, **50**, 8283–8286.
- 39 Y. Wei, Y. Li, M. Zheng, X. Zhou, Y. Zou and C. Yang, *Adv. Opt. Mater.*, 2020, **8**, 1902157.
- 40 Y. Lu, J. Wang, N. McGoldrick, X. Cui, J. Zhao, C. Caverly, B. Twamley, G. M. Ó Máille, B. Irwin, R. Conway-Kenny and S. M. Draper, *Angew. Chem., Int. Ed.*, 2016, **55**, 14688–14692.
- 41 P. Wang, S. Guo, H.-J. Wang, K.-K. Chen, N. Zhang, Z.-M. Zhang and T.-B. Lu, *Nat. Commun.*, 2019, **10**, 3155.
- 42 C. Wang, F. Reichenauer, W. R. Kitzmann, C. Kerzig, K. Heinze and U. Resch-Genger, *Angew. Chem., Int. Ed.*, 2022, **61**, e202202238.
- 43 K. A. El Roz and F. N. Castellano, *Chem. Commun.*, 2017, **53**, 11705–11708.
- 44 C. Kerzig and O. S. Wenger, *Chem. Sci.*, 2018, **9**, 6670–6678.
- 45 B. Pfund, D. M. Steffen, M. R. Schreier, M.-S. Bertrams, C. Ye, K. Börjesson, O. S. Wenger and C. Kerzig, *J. Am. Chem. Soc.*, 2020, **142**, 10468–10476.
- 46 Y. Nakadai, S. Tsuchiya, M. Uehara, S. Umezawa, R. Motoki, H. Umezawa, T. Ikoma and T. Yui, *J. Phys. Chem. B*, 2022, **126**, 8245–8250.
- 47 P. Federmann, H. K. Wagner, P. W. Antoni, J.-M. Mörsdorf, J. L. Pérez Lustres, H. Wadepohl, M. Motzkus and J. Ballmann, *Org. Lett.*, 2019, **21**, 2033–2038.
- 48 T. N. Singh-Rachford and F. N. Castellano, *Coord. Chem. Rev.*, 2010, **254**, 2560–2573.
- 49 L. Zeng, L. Huang, J. Han and G. Han, *Acc. Chem. Res.*, 2022, **55**, 2604–2615.
- 50 J. Pedrini and A. Monguzzi, *J. Photonics Energy*, 2017, **8**, 022005.
- 51 V. Gray, K. Moth-Poulsen, B. Albinsson and M. Abrahamsson, *Coord. Chem. Rev.*, 2018, **362**, 54–71.
- 52 J. Zhao, S. Ji and H. Guo, *RSC Adv.*, 2011, **1**, 937–950.
- 53 C. Ye, V. Gray, J. Mårtensson and K. Börjesson, *J. Am. Chem. Soc.*, 2019, **141**, 9578–9584.
- 54 M.-S. Bertrams and C. Kerzig, *Chem. Commun.*, 2021, **57**, 6752–6755.
- 55 T. J. B. Zähringer, J. A. Moghtader, M. Bertrams, B. Roy, M. Uji, N. Yanai and C. Kerzig, *Angew. Chem., Int. Ed.*, 2023, **62**, e202215340.
- 56 T. R. Blum, Z. D. Miller, D. M. Bates, I. A. Guzei and T. P. Yoon, *Science*, 2016, **354**, 1391–1395.
- 57 V. Gray, A. Dreos, P. Erhart, B. Albinsson, K. Moth-Poulsen and M. Abrahamsson, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10931–10939.
- 58 M. Goetz, D. von Ramin-Marro, M. H. Othman Musa and M. Schiewek, *J. Phys. Chem. A*, 2004, **108**, 1090–1100.
- 59 T.-T. Tran, M.-H. Ha-Thi, T. Pino, A. Quaranta, C. Lefumeux, W. Leibl and A. Aukauloo, *J. Phys. Chem. Lett.*, 2018, **9**, 1086–1091.
- 60 B. Shan and R. Schmehl, *J. Phys. Chem. A*, 2014, **118**, 10400–10406.
- 61 O. S. Wenger, *Coord. Chem. Rev.*, 2015, **282–283**, 150–158.
- 62 R. J. Crutchley, N. Kress and A. B. P. Lever, *J. Am. Chem. Soc.*, 1983, **105**, 1170–1178.
- 63 F. Glaser, C. Kerzig and O. S. Wenger, *Angew. Chem., Int. Ed.*, 2020, **59**, 10266–10284.
- 64 Y. Murakami and K. Kamada, *Phys. Chem. Chem. Phys.*, 2021, **23**, 18268–18282.
- 65 N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart and J. L. Dempsey, *J. Chem. Educ.*, 2018, **95**, 197–206.
- 66 L. Troian-Gautier, M. D. Turlington, S. A. M. Wehlin, A. B. Maurer, M. D. Brady, W. B. Swords and G. J. Meyer, *Chem. Rev.*, 2019, **119**, 4628–4683.
- 67 P. Wardman, *J. Phys. Chem. Ref. Data*, 1989, **18**, 1637–1755.
- 68 A. M. Deetz, L. Troian-Gautier, S. A. M. Wehlin, E. J. Piechota and G. J. Meyer, *J. Phys. Chem. A*, 2021, **125**, 9355–9367.
- 69 A. Rosspeintner, G. Angulo and E. Vauthey, *J. Am. Chem. Soc.*, 2014, **136**, 2026–2032.
- 70 R. Naumann and M. Goetz, *Green Chem.*, 2019, **21**, 4470–4474.
- 71 C. Kerzig and M. Goetz, *Phys. Chem. Chem. Phys.*, 2014, **16**, 25342–25349.
- 72 S. Fukuzumi and K. Ohkubo, *Chem. Sci.*, 2013, **4**, 561–574.
- 73 C. Fischer, C. Kerzig, B. Zilate, O. S. Wenger and C. Sparr, *ACS Catal.*, 2020, **10**, 210–215.
- 74 V. A. Pistritto, S. Liu and D. A. Nicewicz, *J. Am. Chem. Soc.*, 2022, **144**, 15118–15131.
- 75 Y.-M. Lee, W. Nam and S. Fukuzumi, *Chem. Sci.*, 2023, **14**, 4205–4218.
- 76 L. Zeng, L. Huang, W. Lin, L.-H. Jiang and G. Han, *Nat. Commun.*, 2023, **14**, 1102.
- 77 R. Pérez-Ruiz, *Top. Curr. Chem.*, 2022, **380**, 23.
- 78 B. D. Ravetz, A. B. Pun, E. M. Churchill, D. N. Congreve, T. Ravis and L. M. Campos, *Nature*, 2019, **565**, 343–346.

2.3.2 Iridium-based dyads

In the previous section, the excited triplet states of ruthenium-based complexes reduce a quencher *via* ET, whereas the dyads sensitize that quencher into its triplet excited state. Compared to the metal complexes congeners, the dyads provided an extended excited triplet state lifetime and caused a change in the excited-state quenching mechanism. In investigations with iridium-based metal complexes and dyads a similar mechanistic switch was investigated aiming at the change between TTET and the oxidation of the quencher.

Two Ir-complexes and dyads containing the same 5-(pyrene-1-yl)1,10-phenanthroline ligand as was used for the Ru-dyads were synthesized and explored in a "proof-of-concept" study (for synthesis and characterization see appendix, Section 6.9). The metal complexes and dyads were isolated as PF₆⁻ salts and for solubility reasons, the following studies are performed mainly in acetonitrile.¹⁰

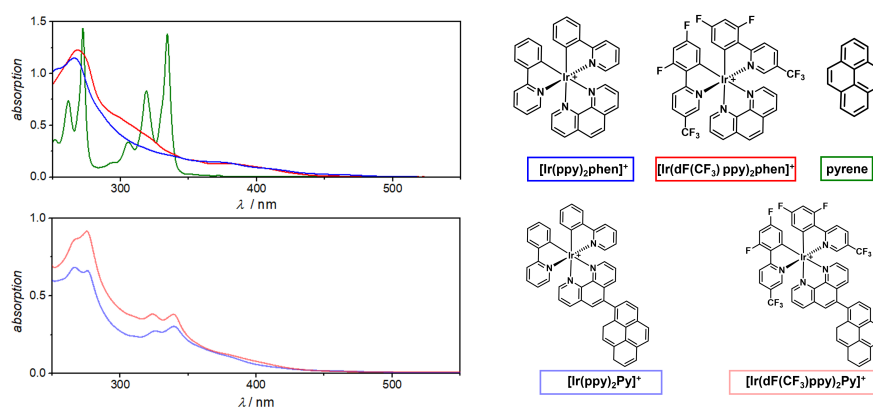


Figure 25: Structures of iridium-based complexes and dyads together with their UV-Vis spectra. All chromophores were dissolved in acetonitrile ([Ir(ppy)₂phen]⁺, 23.7 μM; [Ir(dF(CF₃)ppy)₂phen]⁺, 8.9 μM; [Ir(ppy)₂Py]⁺, 8.9 μM; [Ir(dF(CF₃)ppy)₂Py]⁺, 10 μM).

Similar to the ruthenium-based dyads,^[84] the UV-Vis spectra of the dyads show additional pyrene-derived signals in the UVA spectral region (Figure 25). Similar to the ruthenium-based dyads, the two chromophores can therefore be considered independently in the ground state and the delocalization of the ligand π-system is only very

¹⁰This study is placed in the chapter containing triplet photochemistry in aqueous solution, despite the fact that the main results of this section were achieved in acetonitrile. The concept for a reactivity switch by exchanging metal complex for dyad is derived from findings in aqueous solution in the previous section (Section 2.3.1) and therefore the two sections are thematically in close relation. Furthermore, initial data acquired in aqueous solution and water acetonitrile mixtures indicate that in principle the dyads and metal complexes can be employed using water as a solvent (see Section 6.4.3 in the appendix). An exchange of the counter ion PF₆⁻ to Cl⁻ could provide sufficient water solubility.^[84]

small.^[84] One important difference between the Ru-based and the Ir-based dyads is the difference in triplet energies (ΔE_T , see also Table 8) between the pyrene-substituted ligand and the metal complex, which is significantly higher for the iridium-based dyads ($\Delta E_T \geq 0.4$ eV, Figure 26) compared to ruthenium-based dyads ($\Delta E_T \sim 0.1$ eV). As a consequence, a thermal repopulation of the metal-based triplet state is not possible and no delayed emission based on the so-called reservoir effect is occurring. The choice of the two remaining ligands for the Ir-dyads was based on the different excited state potentials of the literature known Ir-complexes without pyrene substitution,^[229–231] and the expected difference in excited-state potentials between the MC and that of the corresponding dyad.

Simplified energy schemes for dyads

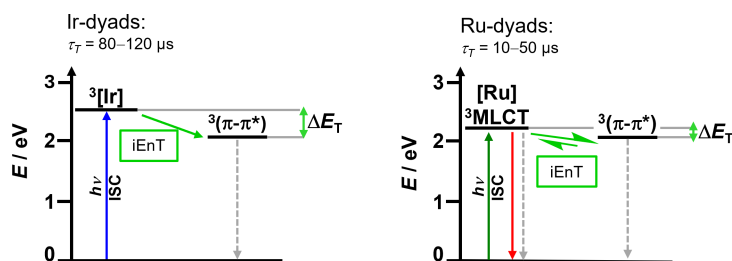


Figure 26: Simplified energy scheme for Ir-dyads (left) compared to Ru-dyads (right)^[84] emphasizing the different ΔE_T between the pyrene-based triplets abbreviated as $^3(\pi - \pi^*)$ and the complex-based triplets.

Transient absorption spectroscopy and analysis of the excited state:

Transient absorption spectroscopy on nano and microsecond time scales of both complexes and dyads reveals a long-lived ($\tau_T = 118 \mu\text{s}$ for $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Py}]^+$ and $\tau_T = 81.3 \mu\text{s}$ for $^3[\text{Ir}(\text{ppy})_2\text{Py}]^+$, Table 8 and Figure 27) non-luminescent triplet state, which is formed immediately after excitation and with bands that highly resemble those of the Ru-dyads. Those findings suggest a fast intramolecular energy transfer from the $^3[\text{Ir}]$ to the pyrene, and due to the lack of thermal repopulation pathway (compare reservoir effect in the Ru-dyads^[84]), delayed emission is eliminated. Hence, the excited-state lifetimes of iridium-based dyads exceed those of the Ru-dyads.

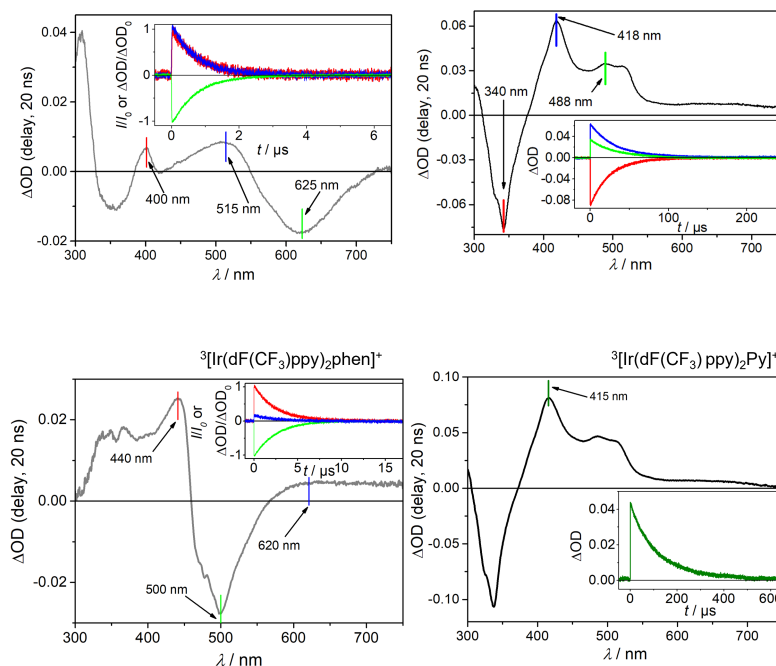


Figure 27: Transient absorption spectra (integrated over 100 ns) and kinetic traces at different detection wavelengths (provided as insets) of the iridium-based metal complexes^[232] and dyads (structures in Figure 25). The different traces of the insets are color-coded in the corresponding panels. All spectra were measured in deaerated acetonitrile (5 min degassed under argon bubbling) and excitation occurred by a pulsed 355 nm laser (10 mJ to 15 mJ).

Spectroscopy and thermodynamic considerations for electron and energy transfer reactivity:

The reactivity change was so far only observed in preliminary measurements using *N,N*-dimethylaniline (DMA, 1.05 V *vs* NHE,^[48,233] calculated from V *vs* SCE, measured in MeCN), methoxyphenol (MeOPhOH, 1.29 V *vs* NHE, calculated from V *vs* SCE, measured in MeCN:AcOH, 8:1^[234,235] or MeCN:MeOH, 7:3^[236]), or *trans*-anethol (1.34 V *vs* NHE,^[234] calculated from V *vs* SCE, measured in MeCN) as electron donors.

For the non-fluorinated iridium-based complex and dyad, the (estimated) potentials differ only by ~ 0.2 V *vs* NHE, compared to the fluorinated version with a difference of ~ 1.0 V *vs* NHE (Table 8). The quenching experiments of the $^3[\text{Ir}(\text{ppy})_2\text{phen}]^+$ with the three electron donors in acetonitrile were unsuccessful, which is confirmed by the weak driving force for the electron transfer reaction ($\Delta G \sim 0$, see Table 8 and potentials for the electron donors). The deprotonated methoxyphenolate is a strong reductant ($E_{\text{red}} = 0.4$ V *vs* NHE, in aqueous solution, pH 13.5)^[219] and was capable of reducing $^3[\text{Ir}(\text{ppy})_2\text{phen}]^+$. Quenching studies with methoxyphenolate resulted in the expected bands for the electron transfer species in the transient absorption spectrum. The compar-

atively low potential of methoxyphenolate indicates that likely both, the non-fluorinated dyad and metal complex are reduced, which is due to the small difference in the excited state potentials (Table 8). Therefore, following experiments focus on the fluorinated metal complex and dyad, with a higher difference in the excited state potentials.

Table 8: Photophysical parameters of iridium-based metal complexes and dyads including the triplet excited state energy (E_T), the lifetime of the triplet excited state (τ_T), the reduction potential ($E_{\text{red}}(\text{C}^{0/\bullet-})$) and the excited state reduction potential ($E_{\text{red}}(^3\text{C}/\text{C}^{\bullet-})$).

chromophore (C, MC or dyad)	E_T / eV	τ_T / μs	$E_{\text{red}}(\text{C}^{0/\bullet-})$ / V vs NHE	$E_{\text{red}}(^3\text{C}/\text{C}^{\bullet-})$ / V vs NHE ^a
$[\text{Ir}(\text{ppy})_2\text{phen}]^+$	2.4 ^{b,c}	0.74	-1.14 ^d	1.26
$[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$	2.6 ^{b,e}	2.59	> -1 ^e	> 1.6
$[\text{Ir}(\text{ppy})_2\text{Py}]^+$	2.0 ^f	81.3	~ -1 ^g	~ 1 ^g
$[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Py}]^+$	2.0 ^f	118	~ -1 ^g	~ 1 ^g

^aCalculated with $E_{\text{red}}(^3\text{C}/\text{C}^{\bullet-}) = E_{\text{red}} + E_T$. ^bFrom 77 K measurements, see Appendix. ^cReferences [106, 230]. ^dLigand reduction in MeCN, reference [106, 229]. ^eReference [230], ligand reduction in MeCN, calculated from V vs SCE by adding 0.24 V^[237]. ^fEstimated to be slightly lower than for ³pyrene.^[48,84] ^gEstimated potentials based on quenching experiments, for details, see Appendix 6.4.5.

N,N-Dimethylaniline quenches the triplet excited $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$, and a transient absorption spectrum detected 4.0 μs after the laser pulse shows the characteristic absorption bands of $\text{DMA}^{\bullet+}$.^[36,238] Furthermore two additional bands arise, which are similar to the structurally related one-electron reduced Ir-complexes^[239] and therefore attributed to the corresponding reduced $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^0$.

Opposite to these findings, the $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Py}]^+$ appears to be mostly unaffected by the presence of the reductive quencher (Figure 28). Further excited state quenching studies with methoxyphenol and *trans*-anethol are presented in the appendix (Section 6.9) confirming those observations: No effect for the $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Py}]^+$ and electron transfer quenching for $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$ and .

The observed quenching and corresponding spectra agree well with literature redox potentials and the triplet energies of the fluorinated iridium-based metal complex. Reduction of the triplet excited $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$ is thermodynamically feasible (Table 8) with a Gibbs free energy of $\Delta G < 0$ (Section 1.2.4 and equation 12) with all of the quenchers (DMA, 1.05 V vs NHE^[48,233]; methoxyphenole, 1.29 V vs NHE^[234–236]; *trans*-anethol 1.34 V vs NHE^[234]). Quenching of $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Py}]^+$ with either of

the three quenchers does not result in the expected one electron oxidized absorption bands for the sacrificial donors (Figure 28, bottom panel and Figures 55 and 56 in the Appendix 6.9). Consequently, the excited state potential of the dyad lies well below that of the unsubstituted metal complex. More details for the calculation of the potential of the dyad can be found in the Appendix (Section 6.9).

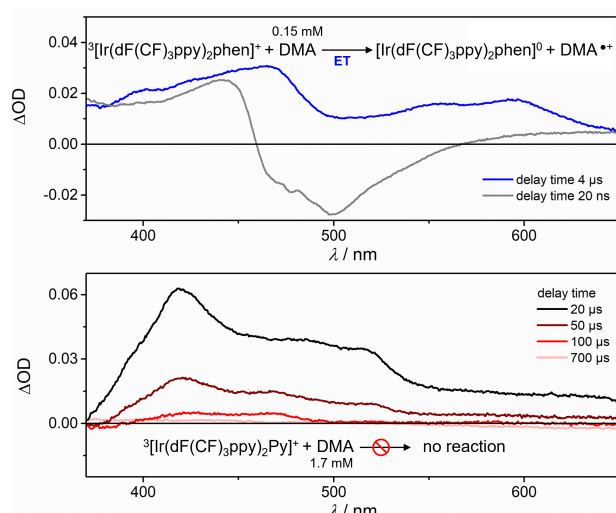


Figure 28: Comparative TA spectra, using 355 nm excitation, for excited state quenching with DMA of $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$ (top) and $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Py}]^+$ (bottom), together with the reaction equations and concentrations of the reductive quencher. The gray spectrum in the top panel displays $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$ without DMA for reference.

This project is still under further investigation. Up to now, the transient absorption data of the fluorinated complex and dyad in acetonitrile confirmed i) the formation of a pyrene-centered, long-lived triplet excited state, and ii) a different reactivity towards excited state quenching *via* electron transfer with DMA, MePhOH and *trans*-anethol between the fluorinated pyrene-decorated and unmodified Ir-complex. These results exemplify that also with iridium-based complexes and dyads, modified reaction mechanism upon changing the sensitizer is possible. Controlling electron transfer reactivity while maintaining high triplet energies and lifetimes might be important in multi-component photocatalytic reactions.

Author contribution: M.-S. Bertrams conceptualized the project and dyad design, chose possible quencher compounds and reactions and performed additional spectroscopy. R. Full performed synthesis and spectroscopy under the supervision of M.-S. Bertrams. C. Kerzig provided general guidance.

2.4 Back electron transfer-induced triplet formation

In this section, further spectroscopic findings of the previously (Section 2.2) investigated P-H^{2+} as a novel, water-soluble annihilator structure^[85] are presented. Opposed to the sensitized triplet formation *via* molecular dyads, this section is based on direct excitation of P-H^{2+} and a triplet formation originating from a recombination mechanism, as presented in Section 1.3.4.

Direct excitation of P-H^{2+} generates the singlet excited state, which decays *via* fluorescence in a high quantum yield ($\phi_F = 87\%$)^[85], and no triplet signatures are observed (Figure 29, gray data). After chloride or bromide quenching of $^1\text{P-H}^{2+}$,¹¹ usually, the spectroscopic signatures of the one-electron reduced $\text{P-H}^{\bullet+}$ are expected. The characteristic transient absorption bands are known from the electron transfer reactions with $^3[\text{Ru}(\text{bpy})_3]^{2+}$ and $^3[\text{Ru}(\text{phen})_3]^{2+}$ (Section 2.3 and reference[85], MCs as sensitizers). However, time-gated transient absorption spectra (Figure 29, green spectra) showed a long-lived species ($\sim 100\ \mu\text{s}$ time range) with absorption bands identical to $^3\text{P-H}^{2+}$, which was observed after sensitization by the Ru-based dyads (Section 2.3 and reference[85]). Moreover, delayed emission was observed in the presence of both of the halogenide quenchers (Figure 29, green spectra in the lower right panel), which hints towards an underlying annihilation process, similar to the sensitization of $^3\text{P-H}^{2+}$ with the ruthenium-based dyads. Only P-H^{2+} in solution, lacking additional halogenides or sensitizers, did not show any signals the delayed transient absorption and emission (gray spectra of the figure). In a more detailed study, the increase in signal intensity of the triplet excited state (derived from time-resolved transient absorption spectroscopy) and the quenching efficiency of the singlet (derived from time-resolved emission quenching) were plotted with respect to the concentration of NaBr (Section 6.5.2 and Figure 60). The two parameters, representing singlet quenching and triplet formation, are almost identical with increasing quencher concentrations indicating a strong correlation.

The above observations strongly suggest that the quenching of $^1\text{P-H}^{2+}$ with Cl^- or Br^- is followed by fast in-cage recombination of the two radical species (Section 1.3.4) yielding the triplet of the chromophore, which is a rare mechanism, especially in highly polar solvents such as water.^[86,90] In initial experiments, the formation of an intermediate $\text{P-H}^{\bullet+}$ is observed (Section 6.5 and Figure 57).

¹¹The notation for the singlet excited state in this section differs from all previous and following sections. Usually, a singlet chromophore is noted as $^1\text{C}^*$. In the case of P-H^{2+} , however, the notation is modified to ^1C (*i. e.* $^1\text{P-H}^{2+}$) for a clear separation of the excited state from the charge.

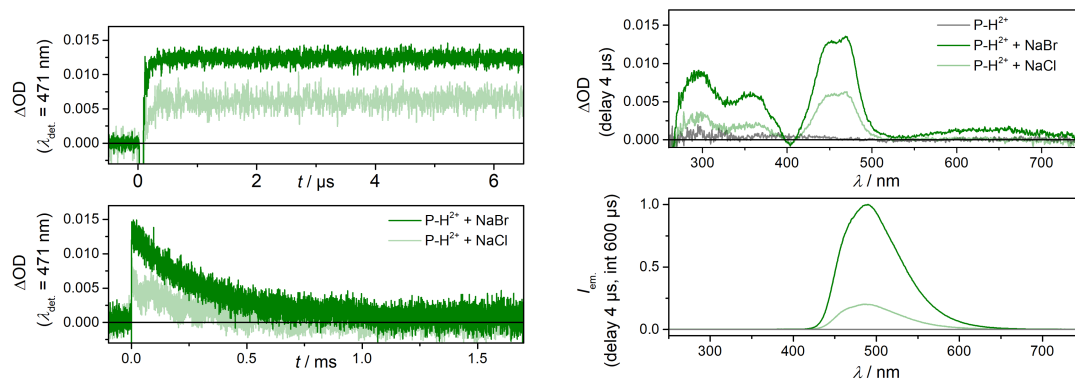


Figure 29: Spectroscopy for chloride (light green) or bromide (green) quenching of $^1\text{P-H}^{2+}$. The concentration of the halogenides was chosen, such that the quenching efficiency is equal for both halogenides ($\eta_{\text{ET}} = 0.45$). The left side shows the kinetic traces detected at 471 nm at a short (upper) and long (lower) timescale. The upper right side shows the TA spectrum after 4.0 μs with either of the halogenides (same color code as kinetic traces) or without a quencher (gray). The lower right spectrum shows the delayed emission spectra of P-H^{2+} with or without quencher, same color code as for the TA spectra.

Thermodynamic and mechanistic considerations:

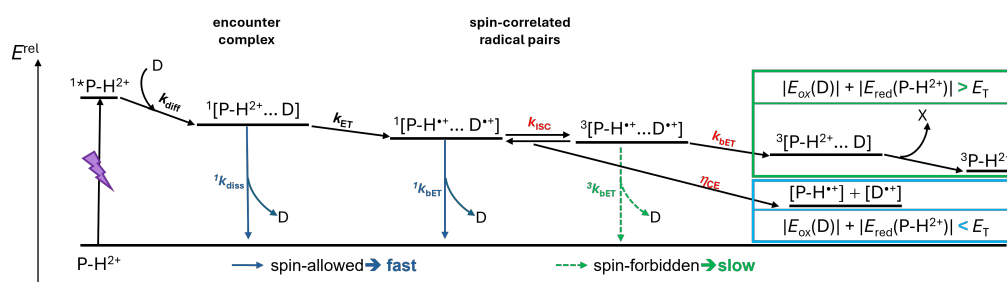


Figure 30: Reaction scheme for quenching of $^1\text{P-H}^{2+}$ by an electron donor (D). For a detailed discussion of the reaction mechanism see Sections 1.2.5 and 1.3.4 and the text. The green and turquoise boxes highlight the possible final quenching products, depending on the ratio of the triplet energy of P-H^{2+} and the combined reduction and oxidation potentials of the two involved molecules.

Figure 30 shows the detailed reaction pathway including the relevant intermediates and reaction steps. The singlet excited $^1\text{P-H}^{2+}$ is quenched by a sacrificial electron donor (D, k_{diff} and k_{ET}) to form the spin-correlated radical pair in a singlet multiplicity (spin conservation). ISC into the triplet multiplicity can take place followed by cage escape of the radical species from both multiplicities (η_{CE} and turquoise box in Figure 30).

A favorable combination of ground state redox potentials and triplet energy allows the population of the $^3\text{P}-\text{H}^{2+}$ (k_{bET} and green box in Figure 30).^[188]

$$|E_{\text{ox}}(\text{D})| + |E_{\text{red}}(\text{P}-\text{H}^{2+})| > E_{\text{T}}(^3\text{P}-\text{H}^{2+}) \quad (15)$$

To test this hypothesis, different quencher molecules (Cl^- , Br^- , I^- , HAsc^- and methanol, see Table 9) with inherently different potentials were employed as sacrificial electron donors (D). According to the calculations in Table 9, only chloride and bromide populate the triplet excited state efficiently, as shown in Figure 29. The ascorbate monoanion selectively produces the one-electron-reduced species $\text{P}-\text{H}^{\bullet+}$, as expected from its potential (Table 9 and Figure 58 in Section 6.5.1). For iodide as an electron donor, the redox potential and triplet energy are very close, which allows no exact prediction for the quenching mechanism. This is also reflected in the spectroscopic findings and the observed bands, which do not allow a clear assignment of the observed species (Section 6.5.1). Finally, from a purely thermodynamic point of view, quenching of $^1\text{P}-\text{H}^{2+}$ with methanol should result in the triplet excited state. However, the corresponding experiments only show signals corresponding to $\text{P}-\text{H}^{\bullet+}$ (Figure 58). In contrast to bromide and chloride, MeOH does not introduce a (pronounced) heavy atom effect. This finding indicates a general contribution of heavy atoms to the ISC in addition to the back electron transfer. As mentioned in Section 1.2.2 the heavy atom effect becomes more effective for higher atomic numbers.^[60,64] Therefore, supporting experiments, on the influence of different concentrations of NaBr on the triplet lifetime or comparative studies with NaCl and CsCl, confirm the absence of a strong external heavy atom effect (spectroscopy and more detailed discussion in the appendix, Section 6.5.3). Hence, the contributions of heavy atoms to the ISC is highly effective within the spin-correlated radical pair and throughout the recombination.

Table 9: Potentials of reductive quenchers (D) and thermodynamic considerations for the feasibility of the recombination-induced triplet formation using P-H^{2+} as a photocatalyst (Figure 30).

D	$E_{\text{ox}}(\text{D})$ / V vs NHE	$ E_{\text{ox}}(\text{D}) + E_{\text{red}}(\text{P-H}^{2+}) $ / V vs NHE ^a	$\Delta G_{\text{ET}}^{\text{b}}$ / eV	expected product ^c
Cl^-	2.40 ^d	2.90	0.01	$^3\text{P-H}^{2+}$
Br^-	1.80 ^d	2.30	-0.51	$^3\text{P-H}^{2+}$
MeOH	$\sim 1.5^{\text{e}}$	~ 2.0	~ -0.8	$\text{P-H}^{\bullet+}$
I^-	1.20 ^d	1.80	-1.01	mixed
HAsc ⁻	0.72 ^f	1.22	-1.59	$\text{P-H}^{\bullet+}$

^a $E_{\text{red}}(\text{P-H}^{2+}) = -0.5$ V vs NHE taken from reference [85]. ^bBased on equation 12 for photon-induced electron transfer with $E_{00} = 2.81$ eV.^[85] ^cBased on equation 15 and $E_{\text{T}}(^3\text{P-H}^{2+}) = 1.7$ eV^[85]. ^dTaken from references [85, 93]. ^eTaken from references [240, 241] and calculated from V vs SCE by addition of 0.24 V. ^fTaken from references [219, 228].

With the previous considerations – thermodynamics and influence of heavy atoms – at hand, the intensities of the spectra and kinetic traces in Figure 29 can be discussed. The concentrations of Cl^- and Br^- were chosen such, that both quench the singlet excited state with an efficiency of $\eta_{\text{q}} = 45\%$. Consequently, a similar signal intensity and concentration of $^3\text{P-H}^{2+}$ is expected. However, the spectra and kinetic traces for the Br^- quenching show a higher signal intensity than for the Cl^- .

One possible explanation is provided when considering heavy atom effects for the triplet formation. The heavy atom effect on ISC is more pronounced for Br^- than for Cl^- , which results in a higher signal intensity for the triplet (*i.e.* higher triplet concentration, Section 1.2.2).^[60,64] A further explanation is provided by the slightly endothermic nature of the chloride oxidation reaction (see Table 9), which could lead to an enhanced dissociation from the encounter complex ($^1k_{\text{diss}}$, Figure 30). This competing mechanism would lead to an overall decreased concentration of $^1[\text{P-H}^{\bullet-} \cdots \text{D}^{\bullet+}]$ and as a result a decreased triplet concentration.

For a complete picture of the mechanism, further transient absorption measurements at shorter timescales (fs-TA) are expected to provide more detailed information. Absorption bands of the short-lived spin-correlated radical pair should be visible on shorter timescales and under optimized conditions.^[90] Time-gated TA spectra, 100 ns and 4 μs after the laser pulse, indicate signals derived from the reduced $\text{P-H}^{\bullet+}$ after quenching of the singlet excited state with Cl^- (Section 6.5 and Figure 57).

To summarize this project, recombination can be considered an unproductive decay

pathway to the photosensitizer and quencher ground state. However, choosing the right conditions and with a detailed understanding of the mechanisms such processes become highly relevant for improving efficiencies of for example solar devices.^[90,185] Furthermore, the results presented in this section contribute to a general understanding of photon-driven pathways to obtain triplet excited states from pure singlet chromophores.

Author contribution: M.-S. Bertrams discovered the unexpected triplet formation, performed the spectroscopy measurements and data analysis. C. Kerzig provided support.

3 Photochemistry of triplet states in organic solvents

The second main chapter of this dissertation comprises cooperative projects, focussing on photochemical systems in organic environments. The three different projects all utilize triplet excited species as main intermediates for their light-driven reactivities. In the first project (Section 3.1) a molybdenum(0) complex with a $^3\text{MLCT}$ is characterized in detail. The complex has a straightforward synthesis and to highlight its versatile usability, the complex is explored to replace noble-metal complexes in an sTTA UC application and an ET reaction. The second project (Section 3.2) explores annihilator structures for sTTA UC to generate photons in the high-energy UVB region. Annihilator structures with the required properties in their excited states were identified by DFT calculations and the predicted properties were in good agreement with the experimental results. In the last project (Section 3.3), platinum(II) complexes, designed to access high triplet energies for blue-light OLED applications, are explored as triplet sensitizers for energy transfer and in a *cis/trans*-isomerization reaction.

3.1 Molybdenum complex as triplet sensitizer for upconversion and as photoredox catalyst

This section presents:

Stable Molybdenum(0) Carbonyl Complex for Upconversion and Photoredox Catalysis

Winald R. Kitzmann, Maria-Sophie Bertrams, Pit Boden, Alexander C. Fischer, René Klauer, Johannes Sutter, Robert Naumann, Christoph Förster, Gereon Niedner-Schatteburg, Nicolas H. Bings, Johannes Hunger, Christoph Kerzig, Katja Heinze, *J. Am. Chem. Soc.*, **2023**, 145, 16597-16609.

The new heteroleptic molybdenum(0) complex prepared in the group of Prof. Heinze features highly interesting photochemical and physical properties in an easily accessible earth-abundant metal complex (structure in Figure 31). After excitation, the complex undergoes efficient ISC and the resulting long-lived $^3\text{MLCT}$ is characterized using time-resolved spectroscopy combined with DFT calculations.^[44]

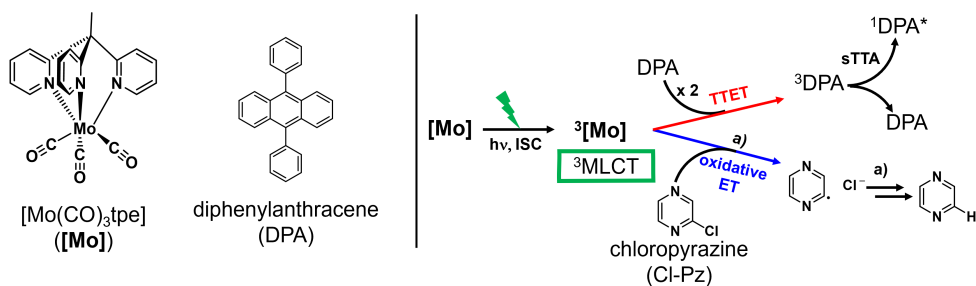


Figure 31: Structures of the molybdenum(0) complex ($[\text{Mo}(\text{CO})_3\text{tpe}]$) under investigation and 9,10-diphenylanthracene (DPA), which functioned as annihilator. The right part of the figure is a schematic illustration of the excited state of the molybdenum(0) complex and the correlated reactivities. The red arrow indicates the energy transfer quenching pathway, established *via* an sTTA UC scheme. The blue arrow represents the oxidative electron transfer quenching pathway using the $^3[\text{Mo}]$ as electron donor, which was implemented in a dehalogenation reaction of chloropyrazine (Cl-Pz). a) For catalyst regeneration and as a hydride donor a benzoimidazoline derivative was used.^[44]

Relative actinometry using $^3[\text{Ru}(\text{bpy})_3]^{2+}$ as a reference compound allowed the calibration of triplet spectrum of $^3[\text{Mo}(\text{CO})_3\text{tpe}]$. The calibrated spectrum, corresponding measurements and a detailed description of the methodology can be found in reference [44] and the supporting information thereof (Section 6.10). Stability measurements in acetonitrile indicated a higher stability by two orders of magnitude under cw-laser irradiation ($\lambda_{\text{exc}} = 514 \text{ nm}$) compared to $[\text{Ru}(\text{bpy})_3]^{2+}$. This finding together with the long $^3\text{MLCT}$ lifetime ($\tau_{\text{T}} = 355 \text{ ns}$ in THF) are promising results for possible photochemical applications, such as sTTA UC.

Energy transfer reactivity of the triplet excited $[\text{Mo}(\text{CO})_3\text{tpe}]$ was established in a green-to-blue sTTA UC system (Figure 31, red arrow). The molybdenum(0) complex replaced a well-established ruthenium complex^[173] as a photosensitizer. After energy transfer to the annihilator (DPA), the corresponding transient absorption spectrum was measured together with characteristic kinetic traces and emission spectra for an annihilation process (Figure 32).^[43,173,242] In addition to the energy transfer reactivity, the molybdenum(0) complex was employed as a reducing electron transfer photocatalyst in a sample dehalogenation reaction of chloropyrazine using a zole derivative as a sacrificial electron donor to regenerate the photocatalyst (Figure 31, blue arrow).

Further data, which was not included in the final publication^[44] is in line with the published results and typical kinetic and spectral features confirm the sTTA UC mechanism (right part of Figure 32).^[33,76,243]

Part a) of Figure 32 illustrates the decreasing emission lifetime of $^3[\text{Mo}(\text{CO})_3\text{tpe}]$ upon addition of the quencher DPA (black trace without DPA and blue trace with DPA, 3 mM).

The green trace corresponds to the newly formed ^3DPA and is representative of its direct formation due to triplet-triplet energy transfer.^[85] The corresponding transient absorption spectra can be found in part b) of the figure.

Formation of $^1\text{DPA}^*$ requires two molecules of ^3DPA , and this correlation is found in typical kinetic traces comparing the formation and decay of the two species (Figure 32 c)). As expected, the upconverted emission of $^1\text{DPA}^*$ (light green trace) has a temporal delay to the formation of the ^3DPA (dark green trace) and both kinetic traces reach their maximum at the same time. In line with the quadratic dependence between the triplet and the singlet excited annihilator (Section 1.3.5 for explanation) the decrease of the upconverted emission is faster compared to the decay of the triplet.^[244] Time-gated emission spectra (part d) of the figure) with different delay times allow to isolate the emission of $^1\text{DPA}^*$ after upconversion. With only the sensitizer present and directly after the laser pulse (black spectrum) the emission originating from the $^3[\text{Mo}(\text{CO})_3\text{tpe}]$ is observed. After a time delay (1 μs) and identical integration time, the spectrum displays only a minor remainder of the emission (gray spectrum), which is in accordance with the unquenched lifetime of the complex (354 ns, THF). Upon the addition of DPA and employing identical measurement conditions (delay 1 μs integration time 10 μs) results in the green spectrum corresponding to the upconverted $^1\text{DPA}^*$ emission. Parts c) and d) of Figure 32 are indicative of an sTTA UC mechanism and similar data sets can be found in upconversion literature.^[33,85,210]

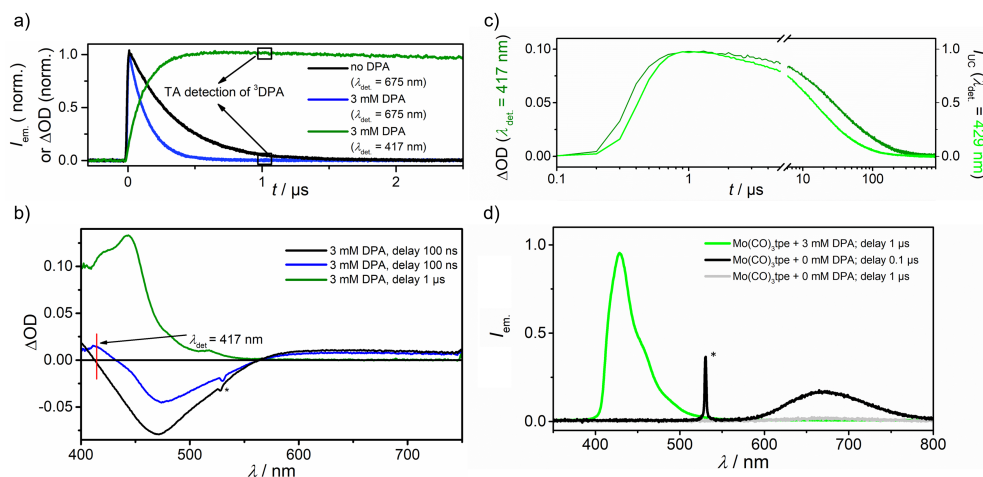


Figure 32: Time-gated spectra and kinetic traces of the sTTA UC system consisting of the Mo(0)-complex as sensitizer and DPA (3 mM) as annihilator (structures in Figure 31). a) Emission traces of the unquenched complex (black) and the shorter lifetime upon DPA addition (blue), together with the absorption trace of the newly formed species 3DPA (green). b) TA spectra of $^3[Mo(CO)_3tpe]$ (black, delay 100 ns) as well as of $^3[Mo(CO)_3tpe]$ with DPA added (blue, delay 100 ns) and the 3DPA (green, delay 1.0 μs). The asterisk marks scattered light from the excitation laser. c) The formation and decay of 3DPA (dark green) and the formation and decay of the upconverted $^1DPA^*$ (light green). d) Spectrum for the delayed emission of $^1DPA^*$ generated via sTTA UC (light green, normalized, delay 1.0 μs) and the emission spectra of a solution without the annihilator directly after the laser pulse (black, peak at 532 nm originates from the scattered excitation laser) and again after 1.0 μs , where almost the entire emission of $^3[Mo(CO)_3tpe]$ has decayed. Figure reproduced and extended from Figures S82 and S83 in the supporting information (Section 6.10) of reference [44].

For electron transfer reactivity, the triplet excited molybdenum(0) complex was employed as photoredox catalyst in a dehalogenation reaction of chloropyrazine (mechanistic scheme in Figure 31). After substrate activation, the oxidized version of the metal complex is reduced to its original form by phenylbenzoimidazoline derivative. A detailed mechanistic analysis is provided in the following publication^[44], including Stern–Volmer emission quenching studies, cyclic voltammetry and photocatalytic irradiation experiments. Additional data from transient absorption spectroscopy support the oxidation of $^3[Mo(CO)_3tpe]$ by electron transfer to chloropyrazine (Figure 64, Section 6.6). After the quenching step the TA spectrum shows a band which corresponds to the $[Mo]^+$ and persists over a longer time scale than the triplet excited state. Overall, the novel molybdenum(0) complex was successfully employed as a photo(redox) catalyst for TTET or ET photochemistry. The earth-abundant metal complex is a promising alternative for ruthenium-based (precious metal) photon-induced processes.

Reprinted with permission from W. R. Kitzmann, M.-S. Bertrams, P. Boden, A. Fischer, R. Klauer, J. Sutter, R. Naumann, C. Förster, G. Niedner-Schatteburg, N. H. Bings, J. Hunger, C. Kerzig, K. Heinze, *J. Am. Chem. Soc.* **2023**, *145*, 30, 16597-16609. Copyright 2023 American Chemical Society.

The reference is attached in the following pages and can be cited corresponding to reference[44] and the supporting information can be found in Section 6.10.

Author contributions: M.-S. Bertrams performed the upconversion and ns-TA measurements. Data analysis and contribution to the manuscript were supervised by C. Kerzig. W. R. Kitzmann conceptualized the study, performed the syntheses, characterization (IR, absorption, luminescence), electrochemical analysis, photostability, photocatalytic irradiation experiments, assisted in upconversion and TA measurements and wrote the manuscript. P. Boden performed step-scan IR experiments, supervised by G. Niedner-Schatteburg. A. Fischer optimized the synthesis and crystallization of the Mo-complex. R. Klauer performed the ICP-MS supervised by N. Bings. J. Sutter and J. Hunger performed the fs-time-resolved vis-pump IR-probe experiments and analyzed the data. R. Naumann performed the fs-TA experiments and analyzed the data. C. Förster solved and refined the crystal structure. K. Heinze supervised the entire study and revised the manuscript.

Stable Molybdenum(0) Carbonyl Complex for Upconversion and Photoredox Catalysis

Winald R. Kitzmann,* Maria-Sophie Bertrams, Pit Boden, Alexander C. Fischer, René Klauer, Johannes Sutter, Robert Naumann, Christoph Förster, Gereon Niedner-Schatteburg, Nicolas H. Bings, Johannes Hunger, Christoph Kerzig, and Katja Heinze*



Cite This: *J. Am. Chem. Soc.* 2023, 145, 16597–16609



Read Online

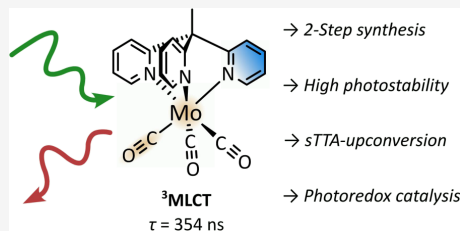
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Photoactive complexes with earth-abundant metals have attracted increasing interest in the recent years fueled by the promise of sustainable photochemistry. However, sophisticated ligands with complicated syntheses are oftentimes required to enable photoactivity with nonprecious metals. Here, we combine a cheap metal with simple ligands to easily access a photoactive complex. Specifically, we synthesize the molybdenum(0) carbonyl complex $\text{Mo}(\text{CO})_3(\text{tpe})$ featuring the tripodal ligand 1,1,1-tris(pyrid-2-yl)ethane (tpe) in two steps with a high overall yield. The complex shows intense deep-red phosphorescence with excited state lifetimes of several hundred nanoseconds. Time-resolved infrared spectroscopy and laser flash photolysis reveal a triplet metal-to-ligand charge-transfer ($^3\text{MLCT}$) state as the lowest excited state. Temperature-dependent luminescence complemented by density functional theory (DFT) calculations suggest thermal deactivation of the $^3\text{MLCT}$ state via higher lying metal-centered states in analogy to the well-known photophysics of $[\text{Ru}(\text{bpy})_3]^{2+}$. Importantly, we found that the title compound is very photostable due to the lack of labilized Mo–CO bonds (as caused by *trans*-coordinated CO) in the facial configuration of the ligands. Finally, we show the versatility of the molybdenum(0) complex in two applications: (1) green-to-blue photon upconversion via a triplet–triplet annihilation mechanism and (2) photoredox catalysis for a green-light-driven dehalogenation reaction. Overall, our results establish tripodal carbonyl complexes as a promising design strategy to access stable photoactive complexes of nonprecious metals avoiding tedious multistep syntheses.



INTRODUCTION

The development of photoactive metal complexes with earth-abundant metals holds great promise to enable sustainable photocatalysis, (solar) energy conversion, and light-emitting diodes (LEDs).^{1–4} Hence, considerable efforts have been undertaken to explore this compound class in the recent years^{5,6} with creative designs utilizing excited states of different characters like metal-to-ligand charge transfer (MLCT),⁷ ligand-to-metal charge transfer (LMCT), ligand-to-ligand charge transfer (LLCT), and metal-centered (MC) states,^{8,9} covering zirconium,^{10–14} vanadium,^{15–18} chromium,^{19–26} iron,^{27–29} manganese,^{30–32} cobalt,^{33,34} copper,^{35–37} molybdenum,^{38–43} and zinc as metal centers^{44,45} among others.

However, elaborate ligand scaffolds are often required to unlock the desired long-lived excited states for photoactivity with earth-abundant metals. While the investigation of these complexes broadens our general understanding of the underlying photophysics, their lengthy syntheses impose a limitation on the sustainability and the overall discovery process of new compounds.⁶

In contrast, complexes of precious metals such as ruthenium(II), iridium(III), or osmium(II) show very favorable optical

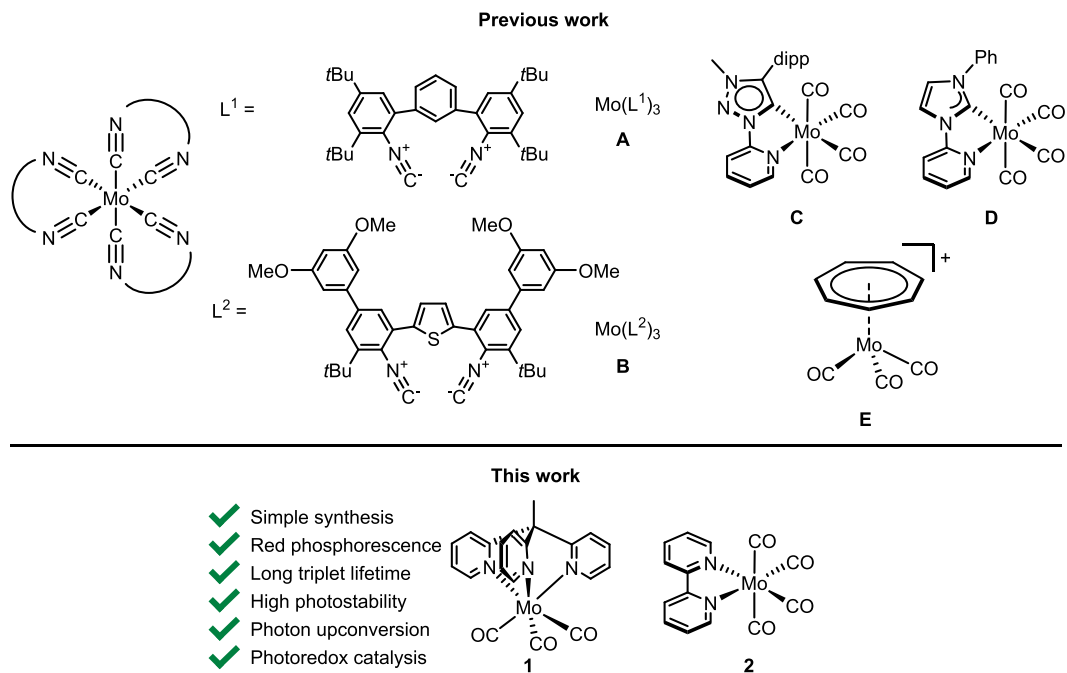
properties even with simple polypyridyl ligands, $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) being the prime example.^{46–50} However, the high cost and limited abundance of these metals discourage widespread applications. As such, photoactive complexes that combine earth-abundant metal centers with simple ligands are highly desirable but generally challenging to design.

Earth-abundant molybdenum(0) shares the $4d^6$ electronic configuration with ruthenium(II), which makes it an attractive substitute for the precious metal ion. Recent studies successfully installed long-lived triplet metal-to-ligand charge-transfer ($^3\text{MLCT}$) states in molybdenum(0) complexes using multidentate isonitrile ligands. For example, complex A (Scheme 1) showed intense green luminescence and also

Received: April 13, 2023
Published: July 21, 2023



Scheme 1. Structures of Representative Examples of Emissive Molybdenum(0) Complexes from the Literature (A–E) and of the Compounds Investigated in This Work (1 and 2)



proved to be a strong photoreductant that can drive demanding redox-neutral photocatalytic transformations.^{39,51}

The excited state energy could be lowered by ligand modification and the resulting complex **B** (Scheme 1) enabled efficient photon upconversion.^{40,43} However, while these multidentate isonitrile complexes possess remarkable properties and provide valuable photophysical insights, they require laborious syntheses of 7–10 steps.^{43,51}

In principle, carbonyl ligands in combination with suitable coligands present a simple alternative to isonitriles as they show similar bonding properties and their complexes are easily accessible from homoleptic metal precursors $M(\text{CO})_n$.⁵² In fact, early studies on molybdenum(0) complexes of the type $\text{Mo}(\text{CO})_4(\text{L}\wedge\text{L})$ with bidentate poly(pyridyl) coligands $\text{L}\wedge\text{L}$ like **2** (Scheme 1) found a weak red phosphorescence from ³MLCT states.^{53,54} Similarly, weak red-to-near infrared (NIR) emission was detected from solid complex **C** (Scheme 1) employing a bidentate mesoionic carbene coligand.^{41,42,55} With a bidentate *N*-heterocyclic carbene coligand (complex **D**, Scheme 1), emission in solution was achieved at 681 nm and the complex could be used as a photoredox catalyst.⁵⁶ However, high-energy blue light was necessary to drive the catalytic reactions,⁵⁶ which likely makes the complex more prone to photodegradation.

A high photostability is generally desirable for photocatalysts and photosensitizers. In this regard, tetracarbonyl complexes with bidentate coligands are disadvantageous as their two *trans*-CO ligands are labilized via the *trans* influence, which facilitates dissociation.⁵⁷ This situation can be avoided with tripodal coligands. However, reports on photoactivity from

these systems are scarce with the tropylium complex **E** (Scheme 1) being one of the few examples. **E** shows yellow ³MLCT phosphorescence and undergoes photoreduction in ethanol.⁵⁸ Other studies using tripodal tris(pyridyl)-type coligands of the type Py_3X with different bridging groups $\text{X} = \text{CH}, \text{P}, \text{Al}, \text{In},$ and Sn have so far focused on structural properties and thermal reactivity.^{59–63}

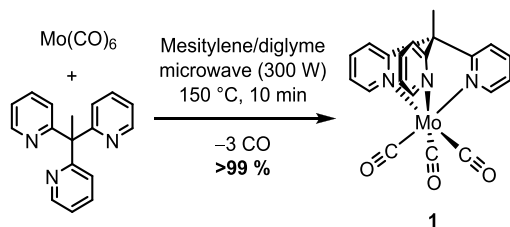
To fill this gap, we herein report the photoactive molybdenum(0) tricarbonyl complex **1** (Scheme 1) featuring the tripodal ligand 1,1,1-tris(pyrid-2-yl)ethane (tpe) and reinvestigate $\text{Mo}(\text{bpy})(\text{CO})_4$ **2** for comparison. Complex **1** is available in two steps from commercial starting materials with a high overall yield (78%). The complex exhibits intense deep-red luminescence with excited state lifetimes of several hundred nanoseconds, which is comparable to $[\text{Ru}(\text{bpy})_3]^{2+}$ and two orders of magnitude longer than the lifetimes of **2**. Remarkably, **1** shows a higher photostability than the benchmark complex $[\text{Ru}(\text{bpy})_3]^{2+}$ under irradiation with green light. Finally, we demonstrate the use of **1** as a sensitizer in green-to-blue photon upconversion with 9,10-diphenylanthracene (DPA) and as a photoreductant in green-light-driven photoredox catalysis as a proof of principle.

RESULTS AND DISCUSSION

Synthesis. The ligand tpe (tpe = 1,1,1-tris(pyrid-2-yl)ethane) was synthesized according to a literature procedure from commercially available 2-fluoropyridine and 2-ethylpyridine (78% yield).⁶⁴ The complex $\text{Mo}(\text{CO})_3(\text{tpe})$ **1** was obtained in a quantitative yield as bright red needles by heating commercial $\text{Mo}(\text{CO})_6$ and tpe in mesitylene/diglyme in a

microwave for 10 min (Scheme 2, Supporting Information (SI) Route A). This procedure guarantees short reaction times and

Scheme 2. Synthetic Route to **1**



avoids sublimation of Mo(CO)_6 that reduces yields when heated under reflux (SI Route B). The identity of the complex was confirmed by ^1H NMR spectroscopy, mass spectrometry, and elemental analysis (see SI Figures S1 and S2). $\text{Mo(bpy)}(\text{CO})_4$ **2** was synthesized according to a published procedure.⁵⁴ While **1** and **2** can be handled under air as solids, the complexes decompose over time in solution under ambient conditions.

IR Spectroscopy, Crystal Structure, and Redox Chemistry. The facial coordination of the tpe ligand in **1** was confirmed by infrared (IR) spectroscopy. Compound **1** shows two intense absorption bands at 1777 and 1898 cm^{-1} (Figure S3), which can be assigned to C–O stretching vibrations of E and A_1 symmetry in the C_{3v} point group.⁶⁵ The IR bands further agree well with literature values for $\text{Mo(CO)}_3(\text{tris(pyrid-2-yl)methane})$.⁵⁹

The solid-state structure of **1** was elucidated using X-ray diffraction. Single crystals were obtained by recrystallization of **1** from hot DMF. Compound **1** crystallizes in the space group Cc (Figure 1 and Table S2 in the SI). The average Mo–C and

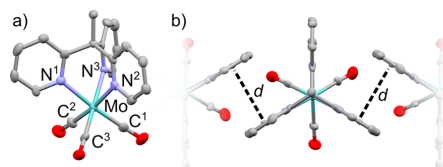


Figure 1. Molecular structure of **1** in the crystal in (a) side view and (b) top view visualizing the π – π interactions between neighboring molecules with the distance between centroids $d = 3.652(9)$ Å. Thermal ellipsoids are displayed at 50% probability. Hydrogen atoms are omitted for clarity.

Mo–N bond lengths were determined to be 1.95 and 2.24 Å, respectively, and agree with an optimized geometry obtained from density functional theory (DFT) calculations (B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN), see SI Tables S2 and S3). In the crystal, each molecule shows strong π – π interactions⁶⁶ to two of its neighbors (centroid distance $d = 3.652(9)$ Å, Figure 1b).

For comparison, literature-known **2** features similar Mo–C and Mo–N bond lengths in the solid state, except for the two *trans* Mo–CO bonds, which are elongated to 2.04 Å due to the *trans* influence.^{57,67} This is also well reproduced by a DFT-optimized geometry of **2** (Figure S4 and Table S4).

In solution, **1** shows a reversible and an irreversible oxidation wave with $E_{1/2} = +0.17$ to $+0.30$ V and $E_{p,1} = +0.82$ to $+1.20$ V vs SCE depending on the solvent (Tables 1

Table 1. Electrochemical Data of **1**, **2**, and **B** with Half-Wave Potentials $E_{1/2}$ and Peak Potentials of Irreversible Waves E_p ^a

complex/solvent	$E_{1/2}/\text{V}$ ($\text{Mo}^{I/0}$)	$E_{p,1}/\text{V}$ ($\text{Mo}^{II/I}$)	$E_{p,2}/\text{V}$	ref
1 /MeCN	+0.17	+0.82		this work
1 /DCM	+0.17	+1.20	+1.36	this work
1 /DMF	+0.25	+1.03		this work
1 /DMSO	+0.30	+1.01		this work
1 /THF	+0.25	+1.04		this work
2 /MeCN	+0.64 ^{b,c}	+1.17 ^b		68
B /THF	+0.10			43

^aAll potentials vs SCE. Electrolyte: 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ if not stated otherwise. ^bElectrolyte: 0.1 M $[\text{nBu}_4\text{N}][\text{BF}_4]$. ^cPeak potential of irreversible waves.

and S1, and Figures S5–S14). The potential of the reversible oxidation of **1** is thus in between the oxidation waves of **B** ($+0.10$ V vs SCE in THF)⁴³ and **2** ($+0.64$ V vs SCE in MeCN, irrev).⁶⁸ The redox events found for **1** are attributed to metal-centered oxidations ($\text{Mo}^{I/0}$ and $\text{Mo}^{II/I}$). The reduction of the pyridine units occurs outside the solvent windows (ca. -1.6 V vs SCE).

We were able to chemically oxidize **1** to I^+ using ferrocenium hexafluorophosphate. The absorption spectrum of I^+ shows excellent agreement with time-dependent DFT (TD-DFT) calculations performed on an optimized geometry of low-spin $[\text{Mo}^I(\text{CO})_3(\text{tpe})]^+$ with an oxidized metal atom (Figure S15). This supports our previous assignment of the reversible oxidation wave found by cyclic voltammetry as being metal-centered ($\text{Mo}^{I/0}$).

Optical Spectroscopy. UV/vis absorption spectra of **1** were recorded in several solvents (Figure 2) and molar absorption coefficients of **1** were determined in DMSO, DMF, THF, DCM, and MeCN with an uncertainty of 3.5% (Table 2, see the SI for details).

The spectra contain up to four absorption bands at around 450, 300, 250, and 220 nm (Table 2). To assign the transitions, TD-DFT calculations (B3LYP/D3BJ/TZVP/

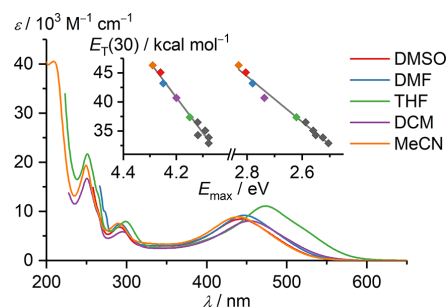


Figure 2. UV/vis absorption spectra of **1** in various solvents at room temperature. Inset: empirical solvent polarity parameter $E_T(30)$ ⁶⁹ plotted against energy at the band maxima of the two lowest-energy MLCT absorptions; gray lines are linear fits. The dark gray points are taken from absorption spectra in other solvents (Figures S23–S28).

Table 2. Absorption Band Maxima λ_{max} and Molar Absorption Coefficients ϵ of **1** and **2** in Different Media at Room Temperature, if not Stated Otherwise, with Assignments Drawn from Charge Transfer Number Analyses⁷⁰ of TD-DFT Calculations

1					
medium	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$)				
	MLCT (Mo→tpe)		MLCT (Mo→CO)		$\pi-\pi^*$
MeCN	439 (8.86)	289 (7.55)	264 (9.99)	249 (19.4)	209 (40.5)
DMSO	442 (8.43)	291 (6.85)	266 (9.15)		
DMF	447 (9.20)	293 (7.44)	273 (9.70)		
DCM	454 (8.06)	295 (5.89)	266 (8.94)	250 (16.7)	
THF	473 (11.1)	299 (7.99)	265 (12.9)	251 (21.7)	
2-MeTHF	479	301	266	250	
2,5-Me ₂ THF	484	303			
benzene	486	301			
toluene	491	304			
xylenes	493				
mesitylene	495	304			
2-MeTHF (77 K)	451				
KBr pellet	450 ^b				

2					
medium	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$)				
	MLCT (Mo→bpy)		$\pi-\pi^*$		$\pi-\pi^*$
MeCN	447 (4.21)	390 (3.72)	294 (25.8)		256 (28.6)
THF	474 (5.24)	390 (3.88)	348 (4.80)	299 (35.6)	259 (34.8)
benzene	494 (5.04)	393 ^c (3.85)	355 (4.85)	301 (33.1)	

^aExperimental uncertainty $\pm 3.5\%$. ^bDetermined from absorbance measurements of **1** (0.0055 w%) diluted in KBr (Figure S16). ^cShoulder.

ZORA/CPCM (MeCN)) were performed on an optimized geometry of **1** and analyzed with regards to the different contributions to each transition using the TheoDOR package (Figures S18, S69, and S70).⁷⁰ The lowest-energy absorption around 450 nm is thus assigned to a ¹MLCT(Mo + CO → tpe) transition. The contribution of carbonyl ligands is attributed to the strong covalency of the Mo–CO bonds. The two absorption bands at 300 and 250 nm correspond to ¹MLCT(Mo→CO) transitions and the high-energy band at 209 nm in MeCN is attributed to ligand-centered ¹($\pi-\pi^*$) transitions.

Complex **2** absorbs strongly in the blue and UV spectral region in MeCN, THF, and benzene (Table 2 and Figures S36–S38). For **2**, the lowest-energy transition at 474–494 nm mostly features (Mo + CO)→bpy character (Figure S69), while the Mo→CO transitions are obscured by intense ligand-centered $\pi-\pi^*$ absorptions (<300 nm).

The ¹MLCT absorption bands of **1** and **2** show strong solvatochromic shifts that can be linearly correlated with the empirical solvent polarity parameter $E_T(30)$ ⁶⁹ (see the inset in Figures 2 and S42). In fact, the solvent sensitivity of the lowest energy ¹MLCT absorption in **1** and **2** is almost identical (Figure S42).⁷¹ Negative solvatochromism indicates a higher polarity of the ground state (GS) compared to the ¹MLCT excited state. The GS is stabilized in a more polar solvent environment, which leads to an increased energy of the electronic transition.⁷² The Mo→CO bands in **1** are more sensitive to the solvent compared to the (Mo + CO)→tpe absorptions, presumably due to a higher change in dipole moments between ground and excited states in this case.

Excitation of **1** in solution with UV/vis light yields a strong red emission peak at 720 nm (Figure 3 and Table 3), which we assign to a ³MLCT state (see below). Excitation spectra follow the corresponding absorption spectra, which underlines that

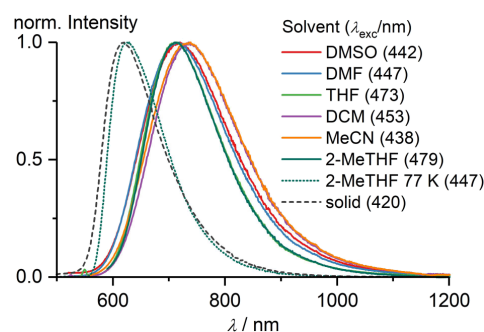


Figure 3. Emission spectra of **1** in various solvents and in the solid state (at 20 °C, if not stated otherwise). Emission spectra in other solvents can be found in the SI, Figures S24–S28.

the emissive lowest excited state is efficiently populated after high-energy excitation (Figures S18–S28).

Complex **2** shows a single emission band in the NIR region at 820–840 nm in MeCN, THF, and benzene solution (Table 3 and Figures S36–S38). This contradicts an earlier study that reported a dual emission at 578 and 773 nm in benzene solution for **2** and for complexes of the type $\text{M}(\text{CO})_4(\text{L}\wedge\text{L})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$) in general.⁵³ These results were rationalized with two emissive ³MLCT states with strongly differing excited state distortions. As we were able to fully reproduce the emission band profile of a suitable organic standard dye with our setup ($\lambda_{\text{max}} = 700 \text{ nm}$, Figure S43),⁷³ we propose a single radiative ³MLCT→¹GS transition for **2** in solution, instead.

Table 3. Luminescence Data of 1 and 2 in Various Media with Emission Maximum λ_{em} , Emission Lifetime τ , Emission Quantum Yield Φ , and Radiative Rate $k_r = \Phi/\tau$

complex	medium	λ_{em}/nm	τ/ns^a	$\Phi/\%^a$	$k_r/10^4 s^{-1a}$
1	MeCN	735	127	0.13 ^b	1.0
1	<i>d</i> ₃ -MeCN		134		
1	DMSO	719	184	0.23 ^b	1.3
1	DMF	715	215	0.26 ^b	1.2
1	DCM	735	146	0.45 ^b	3.1
1	THF	715	355 ^c	0.66 ^b	1.9
1	<i>d</i> ₆ -THF		378		
1	2-MeTHF	712	412	0.79 ^b	1.9
1	2,5-Me ₂ THF	712	460	0.91 ^d	2.2
1	benzene	718	411	1.2 ^d	2.9
1	toluene	712	457	1.2 ^d	2.6
1	xylene	716	478	1.0 ^d	2.1
1	mesitylene	717	471	1.0 ^d	2.1
1	2-MeTHF (77 K)	625	27,600		
1	2-MeTHF (143 K)	712	2900		
1	solid	616	79 ^e	1.0 ^b	13
1	solid (77 K)	634		14 ^b	
2	MeCN	840	0.58 ^f	0.003 ^{b,f}	5.1 ^f
2	THF	820	0.91 ^f	0.009 ^{b,f}	9.9 ^f
2	benzene	820	1.2 ^f	0.012 ^{b,f}	10 ^f

^aEstimated error: $\pm 5\%$. ^bAbsolute values determined using an integrating sphere setup. ^cThe lifetime in THF is unaffected by the presence of the stabilizer dibutylhydroxytoluene (BHT). ^dDetermined relative to [Ru(bpy)₃]Cl₂ in aerated water (see the SI for details). ^eAmplitude-weighted average lifetime obtained from a triexponential fit with $\tau_1 = 23$ ns (63%), $\tau_2 = 115$ ns (31%), and $\tau_3 = 456$ ns (6%). ^fEstimated error: $\pm 10\%$.

In deaerated solutions, **1** displayed monoexponential luminescence decays with long lifetimes of up to 478 ns depending on the solvent (Table 3 and Figure S32), which (in addition to triplet–triplet energy transfer experiments discussed below) warrant an assignment as phosphorescence. Consequently, the luminescence lifetime decreased after opening a sample of **1** in MeCN to air due to dynamic quenching with ³O₂ (Figure S33). In contrast to **1**, the emission of **2** is only short-lived with lifetimes of 0.58–1.2 ns in MeCN, THF, and benzene solution (Table 3 and Figures S39–S41). In the solid state, the luminescence decay of **1** was fitted with three exponential functions with an amplitude-weighted average lifetime of 79 ns (Table 3 and Figure S34).

According to DFT calculations (B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN), see the SI for details), the emissive lowest excited state in **1** is best described as a ³MLCT state with the radical anion localized on one pyridyl moiety (Figure S74). In its fully relaxed geometry, the ³MLCT state is predicted at an energy of 2.01 eV (616 nm) relative to the ¹GS (Figure S73). It features a geometry with elongated Mo^I–CO bonds (two bonds +0.04 Å and one bond +0.09 Å) due to the reduced π -backbonding and a contracted Mo^I–N_{py} bond to the pyridyl radical anion (−0.10 Å) due to the Coulomb attraction (Table S10). The emission energy was calculated as the energy difference between the relaxed ³MLCT state and the ¹GS with ³MLCT geometry (Franck–Condon point for emission, Figure S73) to be 1.67 eV and is in excellent agreement with the emission band maximum in MeCN at 1.69 eV (735 nm, Table 3 and Figure 3). A second excited state of ³MC character (*t*_{2g} → *e*_g excitation) is located at 2.17

eV (572 nm) above the ¹GS (Figure S73). The large contribution of Mo–CO orbitals results in a bent CO coordination with an angle $\angle(\text{Mo–C–O})$ of 135° (Figure S74 and Table S10), suggesting a high covalency of the Mo–CO bond. In **2**, two Mo–CO bonds are already elongated in the ¹GS due to the *trans* influence (+0.07 Å, Table S10). The ³MLCT state energy of **2** (1.87 eV) is lower than that for **1** because the spin density is delocalized over the bpy ligand (Figure S74). The two Mo–CO bonds *trans* to (bpy)^{•−} are elongated (+0.09 Å, Table S10). We were able to optimize a ³MC state of **2** at relatively high energy (2.20 eV) that features two bent Mo–CO bonds (166°, Figure S73). In this state, which we refer to as ³MC₂, there are π -bonding interactions between Mo and the CO ligands *trans* to bpy (Figure S75), which result in relatively short Mo–CO^{trans}_{bpy} bond lengths (2.02 Å, Table S10). Relaxed surface scans with one Mo–CO^{trans}_{CO} bond elongated reveal a change from ³MLCT to ³MC character at distances *d* larger than 2.5 Å. This σ -antibonding ³MC character provides a channel for CO dissociation from the ³MLCT state. Although not a minimum on the triplet potential energy surface, this ³MC₁ state with *d*(Mo–CO) = 2.555 Å (Figure S78) is used in the discussion later on. The energies of high-spin ⁵MC states were calculated at 4.07 and 4.14 eV for **1** and **2**, respectively, which makes them irrelevant for the photophysics following low-energy ¹MLCT excitation (Figures S73 and S74 and Table S10).

In solution, **1** showed a high phosphorescence quantum yield Φ with 1.2% being the highest value obtained in deaerated toluene (Table 3). The quantum yields decreased with increasing polarity of the solvent (Figure S31) reaching 0.13% in MeCN (Table 3). To the best of our knowledge, the phosphorescence lifetimes and quantum yields of **1** are the highest measured for zero-valent molybdenum carbonyl complexes so far^{41,42,53,74} and are comparable to those of **B** ($\Phi = 1.5\%$, $\tau = 56$ ns in deaerated toluene).⁴³ In contrast, the quantum yields of **2** in MeCN, THF, and benzene were found to be very low (0.003–0.012%, Table 3).

Upon cooling of a solution of **1** in 2-MeTHF to 77 K, the ¹MLCT(Mo + CO → tpe) absorption band is blue-shifted from 479 to 451 nm (+1300 cm^{−1}, Figure S23). Similarly, the emission band shifts from 712 to 628 nm (+1900 cm^{−1}) and sharpens (Figure S23). This pronounced shift is known as rigidochromism and commonly observed for MLCT states in carbonyl complexes.^{75,76} The spectral changes are not caused by the lower temperature but the rigidity of the environment as demonstrated by the similarity of the emission bands of solid **1** at room temperature and **1** in frozen 2-MeTHF solution at 77 K (Figure 3). The emission lifetime of **1** dramatically increased to 27.6 μ s in frozen solution at 77 K (Figure S35), which hints to a thermally activated nonradiative decay pathway. An impressive luminescence quantum yield of 14% was determined for solid **1** at 77 K.

The typical deactivation pathway in d⁶ ³MLCT emitters is thermally activated nonradiative relaxation via the ³MC states.^{43,77,78} To investigate this path, we measured the phosphorescence lifetimes of **1** in MeCN, THF, and benzene as well as of **2** in MeCN at different temperatures (Figures S44–S49). The luminescence lifetimes decreased with increasing temperatures due to facilitated thermal population of the detrimental ³MC state. A simple but well-established three parameter model^{43,79,80} was used to fit the data (Figures S47 and S49 and Table S5). For **1**, this approach yielded an

energy barrier ΔE of 1600 cm^{-1} for the $^3\text{MLCT} \rightarrow ^3\text{MC}$ conversion in all three solvents, which is in excellent agreement with the calculated value of 1400 cm^{-1} obtained from a DFT-optimized $^3\text{MLCT} \rightarrow ^3\text{MC}$ transition state ^3TS (Figure S73). The geometry of the ^3TS features a significantly bent Mo–CO bond (146°) and is thus close to the ^3MC geometry (135°). Consequently, the activation energy for repopulating the $^3\text{MLCT}$ state from the ^3MC state in **1** is small ($E(^3\text{TS}) - E(^3\text{MC}) \approx 100 \text{ cm}^{-1}$) and the assumption of a thermal equilibrium between both states made for the model used above is justified.

For **2**, an energy barrier ΔE of 800 cm^{-1} was found experimentally for the $^3\text{MLCT} \rightarrow ^3\text{MC}$ conversion (Figures S48 and S49 and Table S5), which is significantly lower than in **1**. This explains why the excited state lifetimes of **2** are two orders of magnitude shorter than those in **1**. Another reason is the faster deactivation of low-energy excited states according to the energy gap law. The low ΔE also suggests that the $^3\text{MC}_2$ state that was computationally accessible for **2** and lies 2600 cm^{-1} above the $^3\text{MLCT}$ state is unlikely to be responsible for the fast nonradiative deactivation. Unfortunately, we were not able to optimize the geometry of the lower-energy $^3\text{MC}_1$ state as outlined above.

Compared to **1** and **2**, $[\text{Ru}(\text{bpy})_3]^{2+}$ has a significantly higher activation energy of 3600 cm^{-1} for the $^3\text{MLCT} \rightarrow ^3\text{MC}$ conversion, which is qualitatively in line with its higher luminescence quantum yield and lifetime ($\Phi = 9.5\%$, $\tau = 806 \text{ ns}$ in deaerated MeCN).^{7,80–82}

Time-Resolved Spectroscopy. To further investigate the long-lived excited state in **1**, transient absorption (TA) spectra were recorded using laser flash photolysis with 532 nm pulses of $\sim 10 \text{ ns}$ duration in THF (black trace in Figure 4a). The ns-TA spectrum was calibrated using the TA signal of an isoabsorptive $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ solution in water and its differential molar absorption coefficient $\Delta\epsilon(455 \text{ nm}) = -10,100 \text{ M}^{-1} \text{ cm}^{-1}$ (see the SI for details, Figures S50 and S51).^{83–85}

After pulsed laser excitation, **1** shows an intense GS bleach at 476 nm ($\Delta\epsilon = -8400 \text{ M}^{-1} \text{ cm}^{-1}$) and four excited state absorption bands (275, 328, 375, and 700 nm, see Figure 4a) in THF. All TA bands decay monoexponentially with a time constant of $(354 \pm 3) \text{ ns}$ (Figure 4b), which perfectly matches the luminescence lifetime of **1** in THF (355 ns, Table 3). Using femtosecond laser pulses at 480 nm, ultrafast dynamics like the $^1\text{MLCT} \rightarrow ^3\text{MLCT}$ intersystem crossing (ISC) or vibrational cooling could not be resolved (Figure S55) and can therefore be considered faster than the time resolution of the experiment (0.5 ps), similar to the fast and efficient ISC in $[\text{Ru}(\text{bpy})_3]^{2+}$.^{86,87}

By adding the steady state absorption spectrum in THF (Figure 2) to the calibrated TA spectrum (Figure 4a), we isolated the pure absorption spectrum of the long-lived excited state of **1** (Figure 4c). The excited state features five absorption bands (Table S6) that match very well with the TD-DFT calculated oscillator strengths of the optimized $^3\text{MLCT}$ state, supporting the previous assignment of the excited state character (Figures S52, S53, S71, and S72). The nature of the electronic transitions in the $^3\text{MLCT}$ state was further elucidated using a charge transfer number analysis⁷⁰ (Figure 4c and Table S6). Compared to the ^1GS , the $^3\text{MLCT}$ transitions ($\text{Mo}^{\text{I}} \rightarrow \text{py}_2$; py_2 = unreduced part of the tpe ligand) in the $^3\text{MLCT}$ state of **1** are blue-shifted with a band maximum at 375 nm. This is expected considering the lower electron density at the formally oxidized Mo^{I} center. Lower energy

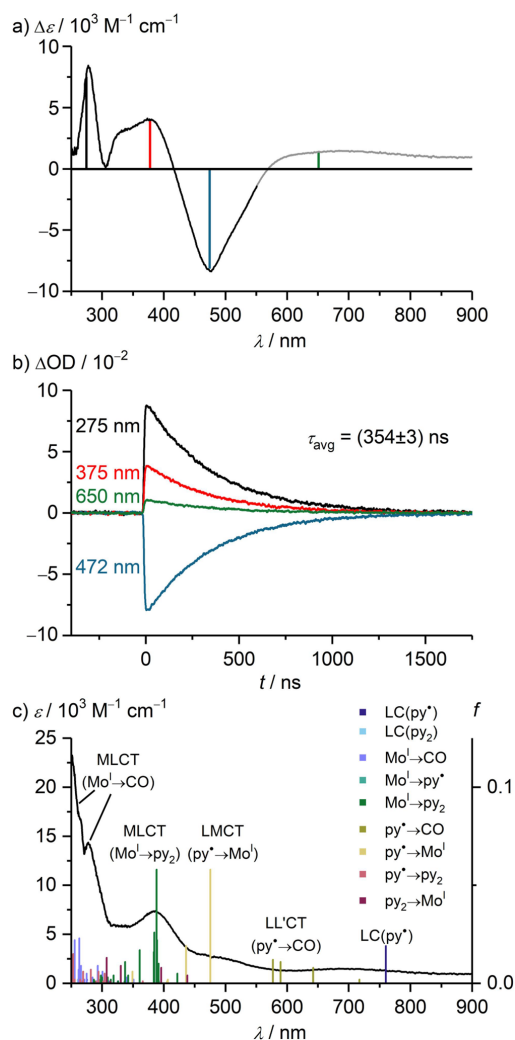


Figure 4. TA studies on **1** in deaerated THF at 20 °C. (a) UV/vis-ns-TA spectrum (black line, $\lambda_{\text{exc}} = 532 \text{ nm}$, delay: 10 ns, integration time: 110 ns) is calibrated using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in water as a reference (see the SI for details), and the vis/NIR-fs-TA spectrum (gray line, $\lambda_{\text{exc}} = 480 \text{ nm}$, integration time: 7.8 ns) is scaled to fit to the calibrated spectrum at 532 nm. (b) Kinetic traces of the ns-TA at selected wavelengths. (c) Absorption spectrum of the $^3\text{MLCT}$ state of **1** in THF (see the main text for details). The sticks represent oscillator strengths f of the DFT-optimized $^3\text{MLCT}$ state calculated using TD-DFT (B3LYP/D3BJ/ZORA/TZVP/CPCM(THF), see also Figures S52 and S72). The colors of the sticks indicate the dominant character of the transition derived from a charge transfer number⁷⁰ analysis ($\text{py}^{\bullet}$ = pyridine-centered radical anion, py_2 = unreduced part of the tpe ligand).

bands arise from transitions involving the ligand-centered radical anion $\text{py}^{\bullet}$ (i.e., LMCT, LL'CT, and LC($\text{py}^{\bullet}$) transitions) with additional MC transitions placed at $>2000 \text{ nm}$ by TD-DFT calculations (Figure S52).

In addition to UV–visible spectroscopy, the intense C=O stretching vibrations in carbonyl complexes present excellent probes for excited states. To confirm that the long-lived excited state in **1** is a ³MLCT state, we recorded ns-step-scan FTIR spectra in *d*₆-DMSO and in a KBr pellet (Figures S56–S62). In the ¹GS, **1** shows two intense IR absorption bands of the C–O stretching vibrations at 1777 and 1898 cm^{−1} (*E* and *A*₁ in C_{3v} symmetry) in DMSO. After pulsed excitation at 532 nm, a GS bleach as well as three new absorption bands (1829, 1870, and 1975 cm^{−1}) emerge. The splitting of the *E* band confirms the reduction in symmetry in the excited state. All IR features decay with a common time constant of 150 ns (Figure S61) that is consistent with the emission lifetime of 184 ns (Table 3). The excited state IR spectrum (Figure S62) can be reasonably described by DFT calculations of **1** in a relaxed ³MLCT geometry with CO bands at 1850, 1881, and 2012 cm^{−1}, confirming the experimental hypsochromic shifts and the splitting of the *E* band. This supports the ³MLCT assignment of the long-lived excited state. In an ultrafast fs-vis-pump-IR-probe experiment, the ³MLCT bands already appear 1 ps after photoexcitation, confirming the population of the long-lived ³MLCT state via rapid ISC (see the SI for details, Figures S63–S65). This also confirms the data from vis/NIR-fs-TA spectroscopy.

Stability. Transition metal carbonyl complexes are well known for their thermal and photochemical decarbonylation reactions, which is exploited in CO-releasing molecules for therapeutic treatments.⁸⁸ However, for other light-driven applications like photon upconversion or photocatalysis, a high photostability is desirable.

When stored in the dark, a solution of **1** in deaerated THF is stable at room temperature as demonstrated by the long half-life of 158 days determined by UV/vis absorption spectroscopy (Figure S66).

To probe the photostability of **1** and **2**, we irradiated isoabsorptive solutions (*A* = 0.16) of the complexes in THF and MeCN with a green cw-laser (514 nm, 827 mW, 20 °C). For comparison, we also measured the photodegradation of [Ru(bpy)₃][PF₆]₂ in MeCN. During irradiation, we monitored the luminescence intensity, which we assume to be proportional to the concentration of the complexes (Figures 5, S67, and S68, and Table S9). We obtained the absolute photodegradation quantum yields Φ_{degr} from the experimental parameters according to a procedure adapted from previous reports (see the SI for details).⁸⁹

The photodegradation quantum yields Φ_{degr} are summarized in Table 4. The values for **2** in THF and the ruthenium complex are in line with previous literature reports.^{53,89} Interestingly, **1** in MeCN appears to be one and two orders of magnitude more photostable than **2** and [Ru(bpy)₃]²⁺, respectively. In THF, **1** shows a lower stability than in MeCN, which is possibly due to its longer excited state lifetime and lower cage-escape yield in this solvent. We attribute the overall higher photodegradation quantum yields of **2** compared to **1** to the *trans*-Mo–CO bonds in **2** that labilize each other as they compete for the same d-orbitals, which weakens their π -backbonding (*trans* influence).⁵⁷ The difference in photostability becomes more apparent when comparing dissociation rate constants that can be estimated using $k_{\text{degr}} = \Phi_{\text{degr}}/\tau$ and take the excited state lifetime τ into account: While decomposition of **2** is very fast with $k_{\text{degr}} = 65,000$ – $93,000$ s^{−1}, **1** decomposes up to three orders of magnitude slower with rate constants of 12–79 s^{−1} (Table 4). Hence,

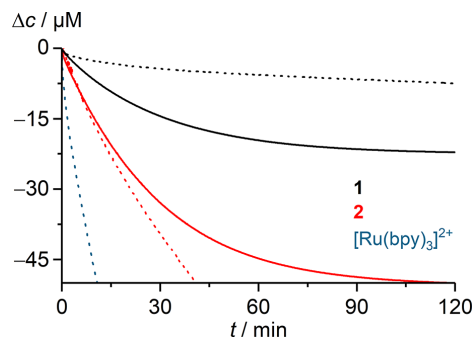


Figure 5. Photostability of **1** (black), **2** (red), and [Ru(bpy)₃][PF₆]₂ (blue) in deaerated THF (solid lines) and deaerated MeCN (dotted lines) under irradiation with a green cw-laser ($\lambda_{\text{exc}} = 514$ nm, $P = 827$ mW) at 20 °C. The concentration changes Δc were derived from photoluminescence measurements (see the SI for details, Figures S67 and S68 and Table S9).

Table 4. Quantum Yields Φ_{degr} and Rate Constants k_{degr} ^a of Photodegradation for **1**, **2**, and [Ru(bpy)₃]²⁺ in Deaerated MeCN and THF

complex	MeCN		THF	
	$\Phi_{\text{degr}}/\%$	$k_{\text{degr}}/\text{s}^{-1}$	$\Phi_{\text{degr}}/\%$	$k_{\text{degr}}/\text{s}^{-1}$
1	0.00015	12	0.0028	79
2	0.0054	93,000	0.0059	65,000
[Ru(bpy) ₃] ²⁺	0.022	270 ^b		

^a $k_{\text{degr}} = \Phi_{\text{degr}}/\tau$. ^bCalculated using $\tau = 806$ ns.⁷

avoiding *trans*-CO bonds is a useful strategy to significantly increase photostability.

In the following study, we discuss potential dissociation pathways to explain the difference in stability between **1** and **2**. To assess barriers for CO dissociation, we calculated potential energy wells for **1** and **2** in their respective ¹GS, ³MLCT, and ³MC states using DFT (Figures S76–S79 and Table S11).

In the ¹GS, the barriers for thermal dissociation of CO *trans* to a pyridyl unit are comparable in **1** (20,700 cm^{−1}) and **2** (19,500 cm^{−1}), while the two *trans*-CO ligands in **2** are labilized yielding a much lower energy barrier of 12,100 cm^{−1}, which suggests a lower thermal stability of **2** compared to **1** (Table S11).

Photoinduced ligand loss in transition metal carbonyl complexes usually occurs via their ³MC states,⁴ but direct ligand dissociation from ³MLCT states has been reported as well.^{90–92} While in **1** and **2**, photoexcitation initially leads to the population of ³MLCT states, their lowest-energy triplet states have ³MC character at long Mo–CO bond lengths (Figures S76–S79), which makes dissociation from ³MC states more likely. We estimate the energy barrier for CO dissociation on the triplet potential energy surface as the difference between the energy of the ³MC state at an infinite Mo–CO bond length and the energy at the minimum of the ³MLCT potential well (Figures S76–S79 and Table S11), so the ³MLCT→³MC conversion is included in this barrier. For the *trans*-pyridyl CO ligands, this again yields comparable values of 10,300, and 9900 cm^{−1} for **1** and **2**, respectively (Table S11). However, the *trans*-CO bonds in **2** are much more labile yielding a barrier for dissociation of 7400 cm^{−1}

(Table S11). Overall, this demonstrates that the reason for the high photostability in **1** in fact lies in its lack of *trans*-CO bonds.

Photon Upconversion. As a first application of the long-lived ³MLCT excited state of **1**, we explored sensitized triplet–triplet annihilation (sTTA) upconversion (UC). In sTTA-UC processes, the energy of a sensitizer's triplet state is transferred to a suitable (organic) acceptor via a Dexter energy transfer (k_{TTET}). Upon collision of two acceptors in their triplet states, the triplets can annihilate (TTA), which returns one acceptor to its GS and raises the other one to a high-energy singlet state. This singlet state can then show delayed anti-Stokes-shifted fluorescence and hence is called upconverted emission.^{1,93,94}

As an acceptor, we chose DPA, which dynamically quenches the ³MLCT state of **1** at a nearly diffusion-limited rate of $k_{\text{TTET}} = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in THF at 20 °C (Figures S80 and S81). This is almost one order of magnitude faster than the quenching of **B** with DPA,⁴³ which we attribute to the better orbital overlap between excited **1** and DPA due to the more compact ligand design and less steric shielding in **1**.

The formation of ³DPA from photoexcited **1** (**1**^{*}, ³MLCT state) was confirmed by TA spectroscopy following laser flash photolysis. The buildup of ³DPA mirrors the decay of the ³MLCT emission of **1** (Figure S82a). After full decay of the ³MLCT state (ca. 1 μs), ³DPA was detected via its characteristic TA band at 445 nm (Figure S82b).^{95,96} The decay of the ³DPA absorption signal was fitted using a previously reported model that considers the mixed first-order (k_{a}) and second-order (k_{TTA}) deactivation processes (Figure S83).⁹⁷

The upconverted ¹DPA emission at 435 nm was detected after excitation of a solution of **1** and DPA (10 mM) in THF at 514 nm (Figure 6a). The reduced lifetime of 55 ns revealed a quenching efficiency of 85%. A DPA concentration of 10 mM was chosen as it marked the sweet spot between efficient quenching and detrimental reabsorption of DPA fluorescence (Figure S84). In accordance with a two-photon process of the proposed TTA-UC mechanism, we found a quadratic increase of the emission intensity at low excitation power densities, which changed to a linear dependence above a threshold intensity of 0.09 W cm⁻² (Figure 6b). The UC quantum yield Φ_{UC} reaches a plateau value of 12% (max. 50%) at high laser power densities (Figure 6c, see the SI for details). This value is close to the theoretical maximum of 20% that is obtained when assuming that all steps in the sTTA-UC process (ISC, TTET, TTA, fluorescence) occur with unity quantum yields.²² No UC emission was found without the sensitizer **1** or without DPA (Figure S85). The photon-UC is also operative with excitation using a green LED (525 nm, Kessil lamp), highlighting the viability of the UC system even at very low-power densities (Figure S85).

Photoredox Catalysis. The promising redox and optical properties of **1** with its long-lived ³MLCT state outlined above motivated us to explore the photocatalytic capabilities of this complex as a proof of principle.

The energy of the ³MLCT state E_{00} is estimated to be 1.85 eV from low-temperature emission spectra and quenching experiments in MeCN (see the SI for details). The excited state reduction potential can be calculated using eq 1 (Coulomb term omitted) as −1.68 V vs SCE, suggesting a strong photoreducing power of **1**.

$$E(\text{I}^+/\text{I}^*) = E(\text{I}^+/\text{I}) - E_{00} \quad (1)$$

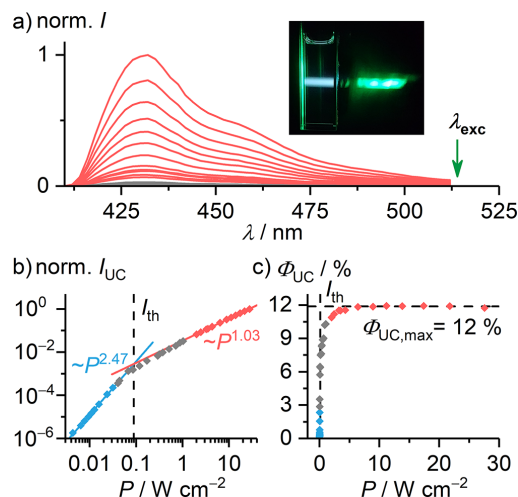
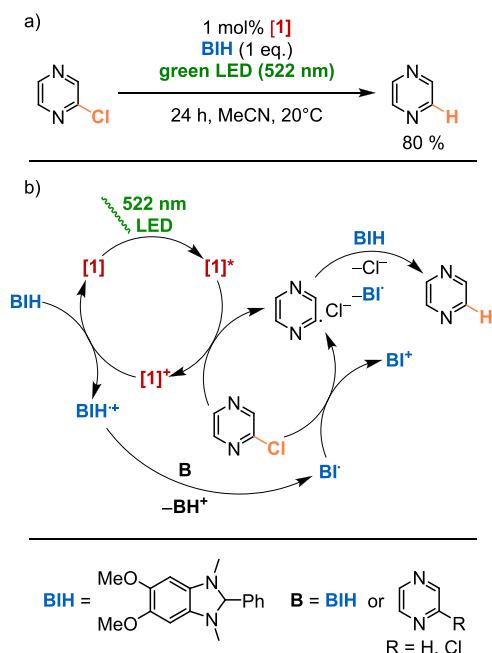


Figure 6. Photon upconversion experiments using **1** in THF in the presence of 10 mM DPA and excitation at 514 nm with a cw-laser ($A_{514} = 0.10$, laser spot size: 3 mm²). (a) Spectra of the upconverted DPA fluorescence at different laser power densities P . Inset: photograph of the green excitation light and blue upconverted emission. (b) Doubly logarithmic plot of the integrated upconverted fluorescence intensity I_{UC} vs laser power density P . I_{th} is the threshold intensity. (c) Relative upconversion quantum yield Φ_{UC} vs laser power density P .

As a test reaction, we selected the dehalogenation of chloropyrazine, which can also be performed by the one-electron-reduced form of $[\text{Ru}(\text{bpy})_3]^{2+}$ ($E([\text{Ru}(\text{bpy})_3]^{2+/+}) = -1.29 \text{ V vs SCE}$).⁹⁸ In fact, the luminescence of **1** in MeCN is quenched by the substrate with a rate constant k_q of $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Figure S86). The triplet energy of chloropyrazine is expected to be $\gg 2.5 \text{ eV}$ ⁹⁶ and thus way above the estimated ³MLCT energy of **1** (1.85 eV). Hence, triplet–triplet energy transfer can be excluded as a quenching mechanism, leaving photoinduced electron transfer as the most plausible alternative. The photoredox reaction with the substrate produces I^+ that needs to be reduced by a sacrificial donor to regenerate the catalyst **1**. The high potential for the I^+/I couple at +0.17 V vs SCE in MeCN requires a strong reductant for this step. We chose the previously reported benzimidazole derivative BIH (Scheme 3) for which a suitable reduction potential of +0.13 V vs SCE has been reported in THF.⁹⁹ The oxidized donor BIH^{*+} can undergo a second oxidation after deprotonation to BI^+ with a potential of −1.7 V vs SCE.^{99,100} On a side note, the final product BI^+ can be recycled to resynthesize the donor BIH.⁹⁹ We confirmed that BIH is able to regenerate **1** from I^+ in MeCN prepared by chemical oxidation (Figure S87) and does not quench the ³MLCT state of **1**.

After we have assessed the required elementary steps of a potential catalytic cycle, we attempted the dehalogenation of chloropyrazine employing 1 mol % **1** in MeCN, 1 equiv BIH, and a green LED as an excitation source at 20.0 °C (Scheme 3a and Table S12). Yields and conversions were determined using ¹H NMR spectroscopy with mesitylene as an internal standard. Under these conditions we obtained pyrazine in a yield of 80% after 24 h. Control experiments confirmed that

Scheme 3. Application of **1** in Photoredox Catalysis^a

^a(a) Overview of the reaction conditions. (b) Proposed mechanism for the dehalogenation of chloropyrazine with **1** in green-light-driven photoredox catalysis.

catalysts, sacrificial donors, and light were necessary for the reaction to occur (Table S12 entries 2–4).

Based on our results, we propose the mechanism in Scheme 3b. After photoexcitation of **1** and ultrafast ISC to the ³MLCT state (**1**^{*}), the complex reduces the substrate. The one-electron-reduced substrate dissociates into a pyrazyl σ -radical and a chloride ion. The product forms via H-atom transfer from BIH to the σ -radical. Meanwhile, BIH reduces the oxidized catalyst **1**⁺ forming **1** and BIH⁺. The latter radical cation can be deprotonated by a base such as BIH or the pyrazine to the radical BI[•], which can in turn reduce the substrate and **1**⁺. Since the photocatalytic conversion to the product is rather slow, we conclude that a conceivable photoinitiated radical chain mechanism only plays a minor role (Scheme S1).

CONCLUSIONS

By combining tripodal tpe with carbonyl ligands, we obtained the simple photoactive molybdenum(0) complex Mo(CO)₃(tpe) that emits deep-red phosphorescence at 720 nm with a lifetime of up to ca. 500 ns in solution at room temperature.

Time-resolved electronic and vibrational spectroscopy in combination with DFT/TD-DFT calculations showed that the emissive state is of ³MLCT character populated after ultrafast ISC. Thermal deactivation occurs via a distorted ³MC state with a barrier of 1600 cm⁻¹ as revealed by temperature-dependent luminescence and DFT calculations. This ³MC state possesses a bent CO ligand instead of a strongly

weakened linearly coordinated CO ligand, which would be prone to dissociation. The complex is very photostable under irradiation with a green laser with a photodecomposition quantum yield of merely 0.00015%. This is two orders of magnitude lower than that of [Ru(bpy)₃]²⁺. Compared to Mo(bpy)(CO)₄, the estimated rate constant for photodegradation of the tripodal complex is almost three orders of magnitude lower. We attribute this gain in stability to the lack of *trans*-CO bonds in the facial ligand configuration, which avoids additional Mo–C bond elongation in ground and excited states.

DFT calculations on Mo(CO)₃(tpe) match experimental data exceptionally well, including the energies of CO stretching vibrations and absorption spectra of the ground and ³MLCT states, the ³MLCT–³MC energy barrier, and emission energy.

The new complex served as a sensitizer in green-to-blue photon upconversion with DPA and achieved a high upconversion quantum efficiency of 12% close to the theoretical limit of ca. 19% (max. 50%). Even a cheap low-power LED sufficed to drive the upconversion process. Mo(CO)₃(tpe) successfully acts as a photoredox catalyst in the dehalogenation of chloropyrazine using a recyclable benzimidazole⁹⁹ derivative as a sacrificial donor.

Despite the rich literature on carbonyl complexes,^{41,42,53–56,71,101,102} their facial coordination with tripodal ligands remained underexplored for photochemical applications so far. Following this promising design strategy, our results delineate how to access photoactive complexes while avoiding precious metals and elaborate ligand syntheses alike. In addition, the exceptional agreement of measured and calculated properties allows for the *in silico* exploration of the chemical space to predict promising synthetic targets. Overall, we hope that this study can guide future research toward more sustainable photochemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c03832>.

General methods, synthetic procedures, spectroscopic data (NMR, FTIR, UV/vis absorption, luminescence, TA, step-scan FTIR, and fs-vis-pump-IR-probe spectroscopy), electrochemical data, details of the stability measurements, photon upconversion and photoredox catalysis, and DFT-optimized structures (PDF)

Accession Codes

CCDC 2251140 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Winald R. Kitzmann – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany; orcid.org/0000-0003-0339-2196; Email: kitzmann@uni-mainz.de

Katja Heinze – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany; orcid.org/0000-0003-1483-4156; Email: katja.heinze@uni-mainz.de

Authors

Maria-Sophie Bertrams – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany

Pit Boden – Department of Chemistry and State Research Center OPTIMAS, RPTU Kaiserslautern, 67663 Kaiserslautern-Landau, Germany

Alexander C. Fischer – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany

René Klauer – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany

Johannes Sutter – Max-Planck-Institute for Polymer Research, 55128 Mainz, Germany

Robert Naumann – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany; orcid.org/0000-0002-0912-7644

Christoph Förster – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany; orcid.org/0000-0003-4971-5368

Gereon Niedner-Schatteburg – Department of Chemistry and State Research Center OPTIMAS, RPTU Kaiserslautern, 67663 Kaiserslautern-Landau, Germany; orcid.org/0000-0001-7240-6673

Nicolas H. Bings – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany

Johannes Hunger – Max-Planck-Institute for Polymer Research, 55128 Mainz, Germany; orcid.org/0000-0002-4419-5220

Christoph Kerzig – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany; orcid.org/0000-0002-1026-1146

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacs.3c03832>

Author Contributions

All authors have given approval to the final version of the manuscript.

Funding

Max-Planck Graduate Center with the Johannes Gutenberg University (MPGC), Chemical Industry Funds (FCI), and Deutsche Forschungsgemeinschaft (DFG) through grants INST 247/1018-1 FUGG to K.H. and KE 2313/3-1 to C.K.

Notes

The authors declare no competing financial interest. CCDC 2251140 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

ACKNOWLEDGMENTS

The authors thank Dr. Charusheela Ramanan and Prof. Dr. Paul Blom (Max Planck Institute for Polymer Research) for providing access to the fs-TA spectrometer, Naz Uğur (Max Planck Institute for Polymer Research) for valuable experimental support during the fs-TA measurements, Jun.-Prof. Dr. Cui Wang (University of Osnabrück) for preliminary luminescence lifetime measurements, Dr. LucaM. Carrella for collecting the XRD data, Dr. Johannes Liermann for support with NMR spectroscopic experiments, Dimitri Zorn for support of the synthesis of the sacrificial donor, and Lukas Sorge for helpful discussions. W.R.K. is thankful for support by the German Academic Scholarship Foundation (Studienstiftung des Deutschen Volkes) and for financial support by the

Max-Planck Graduate Center with the Johannes Gutenberg University (MPGC). W.R.K., C.K., and M.-S.B. are grateful to the Chemical Industry Funds for financial support. Parts of this research were conducted using the supercomputer Elwetritsch and advisory services offered by the University of Kaiserslautern-Landau (<https://hpc.rz.rptu.de>), which is a member of the AHRP and the Gauss Alliance e.V.

REFERENCES

- (1) Schloemer, T.; Narayanan, P.; Zhou, Q.; Belliveau, E.; Seitz, M.; Congreve, D. N. Nanoengineering Triplet-Triplet Annihilation Upconversion: From Materials to Real-World Applications. *ACS Nano* **2023**, *17*, 3259–3288.
- (2) Larsen, C. B.; Wenger, O. S. Photoredox Catalysis with Metal Complexes Made from Earth-Abundant Elements. *Chem. – Eur. J.* **2018**, *24*, 2039–2058.
- (3) Förster, C.; Heinze, K. Photophysics and photochemistry with Earth-abundant metals - fundamentals and concepts. *Chem. Soc. Rev.* **2020**, *49*, 1057–1070.
- (4) Dorn, M.; East, N. R.; Förster, C.; Kitzmann, W. R.; Moll, J.; Reichenauer, F.; Reuter, T.; Stein, L.; Heinze, K. d-d and charge transfer photochemistry of 3d metal complexes. In *Comprehensive Inorganic Chemistry III*; Elsevier, 2023; pp. 707–788.
- (5) Wegeberg, C.; Wenger, O. S. Luminescent First-Row Transition Metal Complexes. *JACS Au* **2021**, *1*, 1860–1876.
- (6) Sinha, N.; Wenger, O. S. Photoactive Metal-to-Ligand Charge Transfer Excited States in 3d₆ Complexes with Cr⁰, Mn^I, Fe^{II}, and Co^{III}. *J. Am. Chem. Soc.* **2023**, *145*, 4903–4920.
- (7) Kitzmann, W. R.; Heinze, K. Charge-Transfer and Spin-Flip States: Thriving as Complements. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202213207.
- (8) Kitzmann, W. R.; Moll, J.; Heinze, K. Spin-flip luminescence. *Photochem. Photobiol. Sci.* **2022**, *21*, 1309–1331.
- (9) Förster, C.; Heinze, K. Bimolecular reactivity of 3d metal-centered excited states (Cr, Mn, Fe, Co). *Chem. Phys. Rev.* **2022**, *3*, 41302.
- (10) Zhang, Y.; Petersen, J. L.; Milsmann, C. A Luminescent Zirconium(IV) Complex as a Molecular Photosensitizer for Visible Light Photoredox Catalysis. *J. Am. Chem. Soc.* **2016**, *138*, 13115–13118.
- (11) Zhang, Y.; Lee, T. S.; Petersen, J. L.; Milsmann, C. A Zirconium Photosensitizer with a Long-Lived Excited State: Mechanistic Insight into Photoinduced Single-Electron Transfer. *J. Am. Chem. Soc.* **2018**, *140*, 5934–5947.
- (12) Zhang, Y.; Lee, T. S.; Favale, J. M.; Leary, D. C.; Petersen, J. L.; Scholes, G. D.; Castellano, F. N.; Milsmann, C. Delayed fluorescence from a zirconium(IV) photosensitizer with ligand-to-metal charge-transfer excited states. *Nat. Chem.* **2020**, *12*, 345–352.
- (13) Yang, M.; Sheykhi, S.; Zhang, Y.; Milsmann, C.; Castellano, F. N. Low power threshold photochemical upconversion using a zirconium(IV) LMCT photosensitizer. *Chem. Sci.* **2021**, *12*, 9069–9077.
- (14) Leary, D. C.; Martinez, J. C.; Akhmedov, N. G.; Petersen, J. L.; Milsmann, C. Long-lived photoluminescence from an eight-coordinate zirconium(IV) complex with four 2-(2'-pyridyl)pyrrolide ligands. *Chem. Commun.* **2022**, *58*, 11917–11920.
- (15) Dorn, M.; Kalmbach, J.; Boden, P.; Pöpcke, A.; Gómez, S.; Förster, C.; Kuczelinis, F.; Carrella, L. M.; Büldt, L. A.; Bings, N. H.; Rentschler, E.; Lochbrunner, S.; González, L.; Gerhards, M.; Seitz, M.; Heinze, K. A Vanadium(III) Complex with Blue and NIR-II Spin-Flip Luminescence in Solution. *J. Am. Chem. Soc.* **2020**, *142*, 7947–7955.
- (16) Fataftah, M. S.; Bayliss, S. L.; Laorenza, D. W.; Wang, X.; Phelan, B. T.; Wilson, C. B.; Mintun, P. J.; Kovos, B. D.; Wasielewski, M. R.; Han, S.; Sherwin, M. S.; Awschalom, D. D.; Freedman, D. E. Trigonal Bipyramidal V³⁺ Complex as an Optically Addressable Molecular Qubit Candidate. *J. Am. Chem. Soc.* **2020**, *142*, 20400–20408.

- (17) Dorn, M.; Kalmbach, J.; Boden, P.; Kruse, A.; Dab, C.; Reber, C.; Niedner-Schatteburg, G.; Lochbrunner, S.; Gerhards, M.; Seitz, M.; Heinze, K. Ultrafast and long-time excited state kinetics of an NIR-emissive vanadium(III) complex I: synthesis, spectroscopy and static quantum chemistry. *Chem. Sci.* **2021**, *12*, 10780–10790.
- (18) Zobel, J. P.; Knoll, T.; González, L. Ultrafast and long-time excited state kinetics of an NIR-emissive vanadium(III) complex II. Elucidating triplet-to-singlet excited-state dynamics. *Chem. Sci.* **2021**, *12*, 10791–10801.
- (19) Otto, S.; Grabolle, M.; Förster, C.; Kreitner, C.; Resch-Genger, U.; Heinze, K. [Cr(ddpd)₂]³⁺: A Molecular, Water-Soluble, Highly NIR-Emissive Ruby Analogue. *Angew. Chem., Int. Ed.* **2015**, *54*, 11572–11576.
- (20) Jiménez, J.-R.; Poncet, M.; Míguez-Lago, S.; Grass, S.; Lacour, J.; Besnard, C.; Cuerva, J. M.; Campaña, A. G.; Piguet, C. Bright Long-Lived Circularly Polarized Luminescence in Chiral Chromium(III) Complexes. *Angew. Chem., Int. Ed.* **2021**, *60*, 10095–10102.
- (21) Sinha, N.; Jiménez, J.-R.; Pfund, B.; Prescimone, A.; Piguet, C.; Wenger, O. S. A Near-Infrared-II Emissive Chromium(III) Complex. *Angew. Chem., Int. Ed.* **2021**, *60*, 23722–23728.
- (22) Wang, C.; Reichenauer, F.; Kitzmann, W. R.; Kerzig, C.; Heinze, K.; Resch-Genger, U. Efficient Triplet-Triplet Annihilation Upconversion Sensitized by a Chromium(III) Complex via an Underexplored Energy Transfer Mechanism. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202202238.
- (23) Wegeberg, C.; Häussinger, D.; Wenger, O. S. Pyrene-Decoration of a Chromium(0) Tris(diisocyanide) Enhances Excited State Delocalization: A Strategy to Improve the Photoluminescence of 3d6 Metal Complexes. *J. Am. Chem. Soc.* **2021**, *143*, 15800–15811.
- (24) Reichenauer, F.; Wang, C.; Förster, C.; Boden, P.; Ugur, N.; Báez-Cruz, R.; Kalmbach, J.; Carrella, L. M.; Rentschler, E.; Ramanan, C.; Niedner-Schatteburg, G.; Gerhards, M.; Seitz, M.; Resch-Genger, U.; Heinze, K. Strongly Red-Emissive Molecular Ruby [Cr(bmp)₂]³⁺ Surpasses [Ru(bpy)₃]²⁺. *J. Am. Chem. Soc.* **2021**, *143*, 11843–11855.
- (25) Kitzmann, W. R.; Ramanan, C.; Naumann, R.; Heinze, K. Molecular ruby: exploring the excited state landscape. *Dalton Trans.* **2022**, *51*, 6519–6525.
- (26) Sittel, S.; Naumann, R.; Heinze, K. Molecular Rubies in Photoredox Catalysis. *Front. Chem.* **2022**, *10*, No. 887439.
- (27) Kjær, K. S.; Kaul, N.; Prakash, O.; Chábera, P.; Rosemann, N. W.; Honarfar, A.; Gordivska, O.; Fredin, L. A.; Bergquist, K.-E.; Häggström, L.; Ericsson, T.; Lindh, L.; Yartsev, A.; Styring, S.; Huang, P.; Uhlig, J.; Bendix, J.; Strand, D.; Sundström, V.; Persson, P.; Lomoth, R.; Wärnmark, K. Luminescence and reactivity of a charge-transfer excited iron complex with nanosecond lifetime. *Science* **2019**, *363*, 249–253.
- (28) Dierks, P.; Vukadinovic, Y.; Bauer, M. Photoactive iron complexes: more sustainable, but still a challenge. *Inorg. Chem. Front.* **2022**, *9*, 206–220.
- (29) Leis, W.; Argüello Cordero, M. A.; Lochbrunner, S.; Schubert, H.; Berkefeld, A. A Photoreactive Iron(II) Complex Luminophore. *J. Am. Chem. Soc.* **2022**, *144*, 1169–1173.
- (30) Harris, J. P.; Reber, C.; Colmer, H. E.; Jackson, T. A.; Forshaw, A. P.; Smith, J. M.; Kinney, R. A.; Telser, J. Near-infrared ²E_g → ⁴A_{2g} and visible LMCT luminescence from a molecular bis(tris(carbene)-borate) manganese(IV) complex. *Can. J. Chem.* **2017**, *95*, 547–552.
- (31) Herr, P.; Kerzig, C.; Larsen, C. B.; Häussinger, D.; Wenger, O. S. Manganese(I) complexes with metal-to-ligand charge transfer luminescence and photoreactivity. *Nat. Chem.* **2021**, *13*, 956–962.
- (32) East, N.; Naumann, R.; Förster, C.; Ramanan, C.; Diezemann, G.; Heinze, K. Oxidative Two-State Photoreactivity of a Manganese(IV) Complex using NIR Light. *ChemRxiv*, DOI: 10.26434/chemrxiv-2023-bhl82.
- (33) Kaufhold, S.; Rosemann, N. W.; Chábera, P.; Lindh, L.; Bolaño Losada, I.; Uhlig, J.; Pascher, T.; Strand, D.; Wärnmark, K.; Yartsev, A.; Persson, P. Microsecond Photoluminescence and Photoreactivity of a Metal-Centered Excited State in a Hexacarbene-Co(III) Complex. *J. Am. Chem. Soc.* **2021**, *143*, 1307–1312.
- (34) Sinha, N.; Pfund, B.; Wegeberg, C.; Prescimone, A.; Wenger, O. S. Cobalt(III) Carbene Complex with an Electronic Excited-State Structure Similar to Cyclometalated Iridium(III) Compounds. *J. Am. Chem. Soc.* **2022**, *144*, 9859–9873.
- (35) Hossain, A.; Bhattacharyya, A.; Reiser, O. Copper's rapid ascent in visible-light photoredox catalysis. *Science* **2019**, *364*, No. eaav9713.
- (36) Hamze, R.; Peltier, J. L.; Sylvinson, D.; Jung, M.; Cardenas, J.; Haiges, R.; Soleilhavoup, M.; Jazzar, R.; Djurovich, P. I.; Bertrand, G.; Thompson, M. E. Eliminating nonradiative decay in Cu(I) emitters: 99% quantum efficiency and microsecond lifetime. *Science* **2019**, *363*, 601–606.
- (37) Beaudelot, J.; Oger, S.; Peruško, S.; Phan, T.-A.; Teunens, T.; Moucheron, C.; Evano, G. Photoactive Copper Complexes: Properties and Applications. *Chem. Rev.* **2022**, *122*, 16365–16609.
- (38) Gowda, A. S.; Petersen, J. L.; Milsman, C. Redox Chemistry of Bis(pyrrolyl)pyridine Chromium and Molybdenum Complexes: An Experimental and Density Functional Theoretical Study. *Inorg. Chem.* **2018**, *57*, 1919–1934.
- (39) Büldt, L. A.; Guo, X.; Prescimone, A.; Wenger, O. S. A Molybdenum(0) Isocyanide Analogue of Ru(2,2'-bipyridine)₃ (2+): A Strong Reductant for Photoredox Catalysis. *Angew. Chem., Int. Ed.* **2016**, *55*, 11247–11250.
- (40) Herr, P.; Schwab, A.; Kupfer, S.; Wenger, O. S. Deep-Red Luminescent Molybdenum(0) Complexes with Bi- and Tridentate Isocyanide Chelate Ligands. *ChemPhotoChem* **2022**, *6*, No. e202200052.
- (41) Boden, P.; Di Martino-Fumo, P.; Bens, T.; Steiger, S.; Albold, U.; Niedner-Schatteburg, G.; Gerhards, M.; Sarkar, B. NIR-Emissive Chromium(0), Molybdenum(0), and Tungsten(0) Complexes in the Solid State at Room Temperature. *Chem. – Eur. J.* **2021**, *27*, 12959–12964.
- (42) Boden, P.; Di Martino-Fumo, P.; Bens, T.; Steiger, S.; Albold, U.; Niedner-Schatteburg, G.; Gerhards, M.; Sarkar, B. Corrigendum: NIR-Emissive Chromium(0), Molybdenum(0), and Tungsten(0) Complexes in the Solid State at Room Temperature. *Chem. – Eur. J.* **2023**, *29*, No. e202301532.
- (43) Bilger, J. B.; Kerzig, C.; Larsen, C. B.; Wenger, O. S. A Photoreactive Mo(0) Complex Mimicking Os(2,2'-bipyridine)₃2+ and Its Application in Red-to-Blue Upconversion. *J. Am. Chem. Soc.* **2021**, *143*, 1651–1663.
- (44) Kübler, J. A.; Pfund, B.; Wenger, O. S. Zinc(II) Complexes with Triplet Charge-Transfer Excited States Enabling Energy-Transfer Catalysis, Photoinduced Electron Transfer, and Upconversion. *JACS Au* **2022**, *2*, 2367–2380.
- (45) Mrózek, O.; Mitra, M.; Hupp, B.; Belyaev, A.; Lüdtke, N.; Wagner, D.; Wang, C.; Wenger, O. S.; Marian, C. M.; Steffen, A. An Air- and Moisture-stable Zinc(II) Carbene Dithiolate Dimer Showing Fast Thermally Activated Delayed Fluorescence and Dexter Energy Transfer Catalysis. *Chem. – Eur. J.* **2023**, *29*, No. e202203980.
- (46) Bell, J. D.; Murphy, J. A. Recent advances in visible light-activated radical coupling reactions triggered by (i) ruthenium, (ii) iridium and (iii) organic photoredox agents. *Chem. Soc. Rev.* **2021**, *50*, 9540–9685.
- (47) Arias-Rotondo, D. M. The fruit fly of photophysics. *Nat. Chem.* **2022**, *14*, 716.
- (48) Arias-Rotondo, D. M.; McCusker, J. K. An Overview of the Physical and Photophysical Properties of [Ru(bpy)₃]²⁺. In *Visible Light Photocatalysis in Organic Chemistry*; Stephenson, C., Yoon, T., MacMillan, D. W. C., Eds.; Wiley-VCH, 2018; pp. 1–24.
- (49) Liu, Z.; Bian, Z.; Huang, C. Luminescent Iridium Complexes and Their Applications. In *Molecular Organometallic Materials for Optics*; Bozec, H., Guerschais, V., Eds.; Topics in Organometallic Chemistry; Springer: Berlin Heidelberg, 2010; pp. 113–142.
- (50) Chou, P.-T.; Chi, Y. Osmium- and Ruthenium-Based Phosphorescent Materials: Design, Photophysics, and Utilization in OLED Fabrication. *Eur. J. Inorg. Chem.* **2006**, *2006*, 3319–3332.
- (51) Herr, P.; Glaser, F.; Büldt, L. A.; Larsen, C. B.; Wenger, O. S. Long-Lived, Strongly Emissive, and Highly Reducing Excited States in

- Mo(0) Complexes with Chelating Isocyanides. *J. Am. Chem. Soc.* **2019**, *141*, 14394–14402.
- (52) Ardon, M.; Hogarth, G.; Ooscroft, D. T. Organometallic chemistry in a conventional microwave oven: the facile synthesis of group 6 carbonyl complexes. *J. Organomet. Chem.* **2004**, *689*, 2429–2435.
- (53) Manuta, D. M.; Lees, A. J. Emission and photochemistry of $M(\text{CO})_4(\text{diimine})$ ($M = \text{chromium, molybdenum, tungsten}$) complexes in room-temperature solution. *Inorg. Chem.* **1986**, *25*, 1354–1359.
- (54) Manuta, D. M.; Lees, A. J. Solvent and substituent effects on the lowest energy excited states of $M(\text{CO})_4(\text{diimine})$ ($M = \text{Cr, Mo, W}$) complexes. *Inorg. Chem.* **1983**, *22*, 3825–3828.
- (55) Boden, P. J.; Di Martino-Fumo, P.; Bens, T.; Steiger, S. T.; Marhöfer, D.; Niedner-Schatteburg, G.; Sarkar, B. Mechanistic and Kinetic Investigations of ON/OFF (Photo)Switchable Binding of Carbon Monoxide by Chromium(0), Molybdenum(0) and Tungsten(0) Carbonyl Complexes with a Pyridyl-Mesoionic Carbene Ligand. *Chem. – Eur. J.* **2022**, *28*, No. e202201038.
- (56) Tang, M.; Cameron, L.; Poland, E. M.; Yu, L.-J.; Moggach, S. A.; Fuller, R. O.; Huang, H.; Sun, J.; Thickett, S. C.; Massi, M.; Coote, M. L.; Ho, C. C.; Bissember, A. C. Photoactive Metal Carbonyl Complexes Bearing N-Heterocyclic Carbene Ligands: Synthesis, Characterization, and Viability as Photoredox Catalysts. *Inorg. Chem.* **2022**, *61*, 1888–1898.
- (57) Gade, L. H. *Koordinationschemie*, 1st ed.; Wiley, 1998.
- (58) Kunkely, H.; Vogler, A. Excited state properties of the (tropylium)molybdenum tricarbonyl cation. *Chem. Commun.* **1998**, *3*, 397–398.
- (59) Faller, J. W.; Ma, Y. Strong Lewis acids derived from molybdenum and tungsten nitrosyls containing the tri-2-pyridyl-methane ligand. Dynamic NMR studies of their adducts with aldehydes, ketones, and esters. *J. Am. Chem. Soc.* **1991**, *113*, 1579–1586.
- (60) García, F.; Hopkins, A. D.; Kowenicki, R. A.; McPartlin, M.; Rogers, M. C.; Silvia, J. S.; Wright, D. S. Syntheses and Structure of Heterometallic Complexes Containing Tripodal Group 13 Ligands $[\text{RE}(\text{2-py})_3]^-$ ($\text{E} = \text{Al, In}$). *Organometallics* **2006**, *25*, 2561–2568.
- (61) Kuo, C.-Y.; Fuh, Y.-S.; Shiue, J.-Y.; Joyce, Y. S.; Lee, G.-H.; Peng, S.-M. Syntheses and chemistry of $\text{Tris}(2\text{-pyridyl})\text{phosphine}$ complexes of Group VI transition metals. X-ray structural studies of the molybdenum complexes. *J. Organomet. Chem.* **1999**, *588*, 260–267.
- (62) Morales, D.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. Molybdenum and Tungsten Tricarbonyl Complexes with the Tripodal Ligands $[\text{BuSn}(2\text{-pyridyl})_3]$ and $[\text{RSn}(\text{methylthiomethyl})_3]$. *Organometallics* **2001**, *20*, 4517–4523.
- (63) Hanf, S.; Colebatch, A. L.; Stehr, P.; García-Rodríguez, R.; Hey-Hawkins, E.; Wright, D. S. An experimental and theoretical study of the coordination and donor properties of tris-2-pyridyl-phosphine ligands. *Dalton Trans.* **2020**, *49*, 5312–5322.
- (64) Santoro, A.; Sambaglio, C.; McGowan, P. C.; Halcrow, M. A. Synthesis and coordination chemistry of 1,1,1-tris-(pyrid-2-yl)ethane. *Dalton Trans.* **2015**, *44*, 1060–1069.
- (65) Elschenbroich, C. Organometallchemie. In *Lehrbuch Chemie*, 6th überarbeitete Auflage; Teubner: 2008.
- (66) Janiak, C. A critical account on π – π stacking in metal complexes with aromatic nitrogen-containing ligands. *J. Chem. Soc., Dalton Trans.* **2000**, *21*, 3885–3896.
- (67) Braga, S. S.; Coelho, A. C.; Gonçalves, I. S.; Almeida Paz, F. A. (2,2'-Bipyridine)tetracarbonylmolybdenum(0). *Acta Crystallogr. E* **2007**, *63*, m780–m782.
- (68) Ogata, K.; Yamaguchi, Y.; Kurihara, Y.; Ueda, K.; Nagao, H.; Ito, T. Twisted coordination mode of bis(N-heterocyclic carbene) ligands in octahedral geometry of group 6 transition metal complexes: Synthesis, structure, and reactivity. *Inorg. Chim. Acta* **2012**, *390*, 199–209.
- (69) Reichardt, C. Solvatochromic Dyes as Solvent Polarity Indicators. *Chem. Rev.* **1994**, *94*, 2319–2358.
- (70) Plasser, F. TheoDORE: A toolbox for a detailed and automated analysis of electronic excited state computations. *J. Chem. Phys.* **2020**, *152*, No. 084108.
- (71) Burgess, J. Solvent effects on the visible absorption spectra of $\text{Mo}(\text{CO})_4(\text{Bipy})$ and $\text{W}(\text{CO})_4(\text{Bipy})$. *J. Organomet. Chem.* **1969**, *19*, 218–220.
- (72) Nigam, S.; Rutan, S. Principles and Applications of Solvatochromism. *Appl. Spectrosc.* **2001**, *55*, 362A–370A.
- (73) Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishi, S.; Tobita, S. Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850–9860.
- (74) Lees, A. J. Luminescence properties of organometallic complexes. *Chem. Rev.* **1987**, *87*, 711–743.
- (75) Rawlins, K. A.; Lees, A. J. Photophysical properties of $\text{M}(\text{CO})_4(\alpha, \alpha'\text{-diimine})$ ($M = \text{molybdenum, tungsten}$) complexes. *Inorg. Chem.* **1989**, *28*, 2154–2160.
- (76) Wrighton, M.; Morse, D. L. Nature of the lowest excited state in tricarbonylchloro-1,10-phenanthroline-iridium(III) and related complexes. *J. Am. Chem. Soc.* **1974**, *96*, 998–1003.
- (77) Moll, J.; Wang, C.; Pöpcke, A.; Förster, C.; Resch-Genger, U.; Lochbrunner, S.; Heinze, K. Green-Light Activation of Push-Pull Ruthenium(II) Complexes. *Chem. – Eur. J.* **2020**, *26*, 6820–6832.
- (78) Wenger, O. S. Is Iron the New Ruthenium? *Chem. – Eur. J.* **2019**, *25*, 6043–6052.
- (79) Hager, G. D.; Crosby, G. A. Charge-transfer excited states of ruthenium(II) complexes. I. Quantum yield and decay measurements. *J. Am. Chem. Soc.* **1975**, *97*, 7031–7037.
- (80) van Houten, J.; Watts, R. J. Temperature dependence of the photophysical and photochemical properties of the tris(2,2'-bipyridyl)ruthenium(II) ion in aqueous solution. *J. Am. Chem. Soc.* **1976**, *98*, 4853–4858.
- (81) Soupart, A.; Alary, F.; Heully, J.-L.; Elliott, P. I. P.; Dixon, I. M. Exploration of Uncharted ^3PES Territory for $\text{Ru}(\text{bpy})_3^{2+}$: A New ^3MC Minimum Prone to Ligand Loss Photochemistry. *Inorg. Chem.* **2018**, *57*, 3192–3196.
- (82) Soupart, A.; Alary, F.; Heully, J.-L.; Elliott, P. I. P.; Dixon, I. M. Theoretical Study of the Full Photosolvolytic Mechanism of $\text{Ru}(\text{bpy})_3^{2+}$: Providing a General Mechanistic Roadmap for the Photochemistry of $\text{Ru}(\text{NAN})_3^{2+}$ -Type Complexes toward Both Cis and Trans Photoproducts. *Inorg. Chem.* **2020**, *59*, 14679–14695.
- (83) Goetz, M.; Kerzig, C.; Naumann, R. An “all-green” catalytic cycle of aqueous photoionization. *Angew. Chem., Int. Ed.* **2014**, *53*, 9914–9916.
- (84) Kerzig, C.; Goetz, M. Combining energy and electron transfer in a supramolecular environment for the “green” generation and utilization of hydrated electrons through photoredox catalysis. *Chem. Sci.* **2016**, *7*, 3862–3868.
- (85) Müller, P.; Brettel, K. $[\text{Ru}(\text{bpy})_3]^{2+}$ as a reference in transient absorption spectroscopy: differential absorption coefficients for formation of the long-lived (3)MLCT excited state. *Photochem. Photobiol. Sci.* **2012**, *11*, 632–636.
- (86) (a) Cannizzo, A.; van Mourik, F.; Gawelda, W.; Zgrablic, G.; Bressler, C.; Chergui, M. Broadband femtosecond fluorescence spectroscopy of $\text{Ru}(\text{bpy})_3^{2+}$. *Angew. Chem., Int. Ed.* **2006**, *45*, 3246–3248. (b) Cannizzo, A.; van Mourik, F.; Gawelda, W.; Zgrablic, G.; Bressler, C.; Chergui, M. Broadband femtosecond fluorescence spectroscopy of $\text{Ru}(\text{bpy})_3^{2+}$. *Angew. Chem., Int. Ed.* **2006**, *45*, 3174–3176.
- (87) Demas, J. N.; Taylor, D. G. On the “intersystem crossing” yields in ruthenium(II) and osmium(II) photosensitizers. *Inorg. Chem.* **1979**, *18*, 3177–3179.
- (88) Wright, M. A.; Wright, J. A. PhotoCORMs: CO release moves into the visible. *Dalton Trans.* **2016**, *45*, 6801–6811.
- (89) Schmid, L.; Kerzig, C.; Prescimone, A.; Wenger, O. S. Photostable Ruthenium(II) Isocyanoborato Luminophores and Their Use in Energy Transfer and Photoredox Catalysis. *JACS Au* **2021**, *1*, 819–832.

- (90) Loftus, L. M.; Rack, J. J.; Turro, C. Photoinduced ligand dissociation follows reverse energy gap law: nitrile photodissociation from low energy ³MLCT excited states. *Chem. Commun.* **2020**, *56*, 4070–4073.
- (91) Steinke, S. J.; Piechota, E. J.; Loftus, L. M.; Turro, C. Acetonitrile Ligand Photosubstitution in Ru(II) Complexes Directly from the ³MLCT State. *J. Am. Chem. Soc.* **2022**, *144*, 20177–20182.
- (92) Falahati, K.; Tamura, H.; Burghardt, I.; Huix-Rotllant, M. Ultrafast carbon monoxide photolysis and heme spin-crossover in myoglobin via nonadiabatic quantum dynamics. *Nat. Commun.* **2018**, *9*, 4502.
- (93) Uji, M.; Zähringer, T. J. B.; Kerzig, C.; Yanai, N. Visible-to-UV Photon Upconversion: Recent Progress in New Materials and Applications. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202301506.
- (94) Haeefe, A.; Blumhoff, J.; Khnayzer, R. S.; Castellano, F. N. Getting to the (Square) Root of the Problem: How to Make Noncoherent Pumped Upconversion Linear. *J. Phys. Chem. Lett.* **2012**, *3*, 299–303.
- (95) Chattopadhyay, S. K.; Kumar, C.; Das, P. K. Triplet-related photophysics of 9,10-diphenylanthracene. A kinetic study of reversible energy transfer from anthracene triplet by nanosecond laser flas. *Chem. Phys. Lett.* **1983**, *98*, 250–254.
- (96) Montalti, M.; Murov, S. L. *Handbook of photochemistry*, 3rd ed.; CRC/Taylor & Francis, 2006.
- (97) Kerzig, C.; Wenger, O. S. Sensitized triplet-triplet annihilation upconversion in water and its application to photochemical transformations. *Chem. Sci.* **2018**, *9*, 6670–6678.
- (98) Naumann, R.; Goez, M. How the sustainable solvent water unleashes the photoredox catalytic potential of ruthenium polypyridyl complexes for pinacol couplings. *Green Chem.* **2019**, *21*, 4470–4474.
- (99) Gimeno, L.; Queffelec, C.; Mall Haidaraly, K.; Blart, E.; Pellegrin, Y. Dehalogenation reaction photocatalyzed by homoleptic copper(i) complexes associated with strongly reductive sacrificial donors. *Catal. Sci. Technol.* **2021**, *11*, 6041–6047.
- (100) Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96*, 877–910.
- (101) Chun, S.; Getty, E. G.; Lees, A. J. Photophysics of metal carbonyl complexes. Excited states of a series of *cis*-M(CO)₄L₂ complexes (M = Cr, Mo, or W; L = pyridine or a pyridine derivative). *Inorg. Chem.* **1984**, *23*, 2155–2160.
- (102) Connor, J. A.; Overton, C.; El Murr, N. Electronic spectra and electrochemistry of disubstituted 2,2'-bipyridinetetracarbonylmolybdenum complexes. Solvent and substituent effects. *J. Organomet. Chem.* **1984**, *277*, 277–284.

3.2 Theoretical calculations supporting annihilator design and experimental findings

This section presents:

Blue-to-UVB Upconversion, Solvent Sensitization and Challenging Bond Activation Enabled by a Benzene-Based Annihilator

Till J. B. Zähringer, Julian A. Moghtader, Maria-Sophie Bertrams, Bibhisan Roy, Masanori Uji, Nobohiro Yanai, Christoph Kerzig,
Angew. Chem. Int. Ed., **2023**, 62, e202215340.

This section introduces an sTTA UC scheme, which produces singlet excited states significantly beyond 4.0 eV by combining the energy of two blue photons. Surpassing this barrier is challenging and highly dependent on carefully matched energies of the annihilator and the sensitizer to reduce energy losses and on the singlet and triplet energies of the annihilator ($2 \times E_T > E_S$, Section 1.3.5 for detailed explanation). The highly optimized system presented here consists of a TADF emitter as photosensitizer (4CzIPN) and an annihilator structure (bTIPS-Bz Figure 33) with triplet and singlet state energies that allow sTTA UC with visible light and avoid electron transfer. Additionally, high efficiency and selectivity for the annihilation - upconversion process are desirable, outcompeting undesired pathways such as excimer formation. In general, excimer formation can be avoided by substituting annihilator compounds with bulky aliphatic groups^[57,198,202,243,245] or with triisopropyl-ethynyl (TIPS-ethynyl) units.^[207,208]

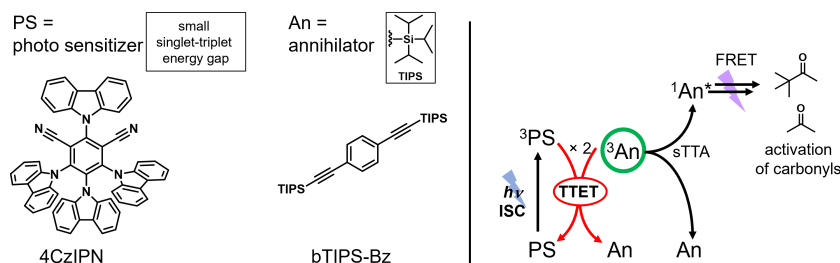


Figure 33: Compounds of the blue-to-UVB sTTA UC scheme including the photosensitizer, 4CzIPN and the annihilator bTIPS-Bz. The right part illustrates the blue photon-driven sTTA mechanism, which is capable of generating UVB photons for activation of inert carbonyls *via* FRET.

Furthermore, the TIPS-ethynyl groups likely induce a significant reduction of the triplet energy comparing the substituted to the unsubstituted annihilators, owing to the extension of the π -system.^[33,207,208,210] Consequently, to achieve the energetic prerequisites with upconverted emissions well beyond 4.0 eV, smaller conjugated systems than the known TIPS-ethynyl-substituted naphthalene and anthracene derivatives^[207,208] seem

promising. The selection of compounds fulfilling all requirements is very limited and TIPS decorated biphenyl and benzene structures are a promising choice. Both structures were successfully used as annihilators with different patterns for mono- or multi-TIPS substitution.^[33,210] For the benzene-based annihilators, the triplet energy of different TIPS-ethynyl-substitution patterns was estimated by DFT calculations. These results were used as guidance to preselect suitable structures (Figure 34 and Table 10), which were then synthesized for sTTA UC in solution.

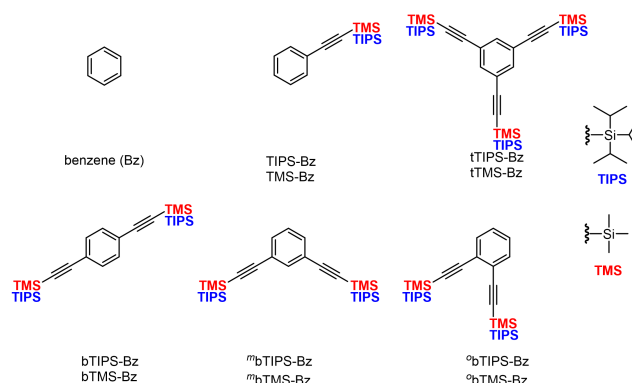


Figure 34: Benzene-based structures with different substitution patterns of TMS or TIPS groups. The calculated triplet energies of the different molecules are summarized in Table 10.

The general conditions for the calculations were chosen according to previous calculations tackling similar problems.^[37,63,102] Besides the differently substituted benzene derivatives the triplet energy of the unsubstituted version was calculated and compared to the experimentally determined triplet energy^[246] of benzene to obtain a general correction factor for the calculated data. For tTIPS-Bz, the *iso*-propyl substituents introduce several degrees of freedom resulting in increased computational effort compared to smaller substituents. Replacing *iso*-propyl with methyl resulted in almost identical triplet energies (difference between methyl and *iso*-propyl $\Delta E \sim 0.01$ eV). No optimized structure was obtained for tTIPS-Bz, and based on the previous findings its triplet energy was extrapolated from the tTMS-Bz derivative.

Two unpublished structures – the ortho- and meta- substituted benzene – were calculated, again resulting in nearly identical E_T ($\Delta E \sim 0.01$ eV) for the TMS or TIPS, too high for fast sensitization with the photosensitizer 4CzIPN (Figure 33). The small difference in triplet energy comparing the TMS to the TIPS substituents is in line with the conclusions and results from the publication.^[33] Spin density plots of the triplet states of TIPS-ethynyl substituted annihilators also mostly show no (or little) spin density located on the alkyl groups.^[33,210]

Three of the benzene derivatives (TIPS-Bz, bTIPS-BZ and tTIPS-Bz) were synthesized

for an investigation in a light-driven sTTA UC mechanism using the literature-known blue-light absorbing sensitizer 4CzIPN ($E_T = 2.72$ eV)^[33,210] (Figure 33 for structure and reaction scheme). The spectroscopic measurements confirmed the DFT predictions of the triplet energies^[33] and as suggested by the calculation (Table 10), the triplet energy of the sensitizer was only sufficient to sensitize bTIPS-Bz.

Table 10: DFT calculated and corrected triplet energies (E_T) of benzene and the TIPS- and TMS-ethynyl substituted derivatives. The corresponding structures are presented in Figure 34. This table is an extension with additional data to Table S1 in the supporting information (Section 6.11) of reference [33].

Compound	E_T / eV (DFT) ^a	E_T / eV (Lit.) ^b	E_T / eV (corr.) ^c
Benzene (Bz)	3.83	3.9 ^[246]	3.83
TIPS-Bz	3.01		3.06
TMS-Bz	3.02		3.07
bTIPS-Bz	2.53		2.57
bTMS-Bz	2.54		2.58
^o bTIPS-Bz	2.71		2.76
^o bTMS-Bz	2.72		2.77
^m bTIPS-Bz	2.90		2.96
^m bTMS-Bz	2.91		2.97
tTIPS-Bz	-		2.97 ^d
tTMS-Bz	2.92		2.98

^aDFT calculations at B3LYP/6-311+G(d,p) level of theory. ^bExperimental triplet energy. ^cAll values scaled by a factor of 1.02 based on the difference between calculated and measured triplet energy of benzene. ^dEstimated from the triplet energy of tTMS-Bz based on the comparison of the energies of the mono and bis substituted TIPS and TMS derivatives (energy difference = 0.01 eV).

This sensitizer - annihilator combination allowed the successful upconversion to UVB photons using blue light irradiation with a quantum yield close to $\phi_{UC} \sim 1\%$. The upconversion system was employed in a FRET-activated Norrish I reaction of UVB absorbing carbonyls, thereby replacing UV-lamps for direct excitation with blue light-emitting LEDs.^[33]

This is the peer reviewed version of the following article: T. J. B. Zähringer, J. A. Moghtader, M.-S. Bertrams, B. Roy, M. Uji, N. Yanai, C. Kerzig *Angew. Chem. Int. Ed.*, **2023**, 62, e2022153140. This is an open access journal licensed under CC BY-NC 4.0 (<https://creativecommons.org/licenses/by-nc/4.0/>) and was reproduced from reference[33].

Author contributions: M.-S.Bertrams performed the DFT calculations and the corresponding analysis for the benzene-based annihilators. T. J. B. Zähringer and J. Moghtader performed the synthesis and photochemical characterization and measurements. B. Roy and M. Uji performed the measurements for the upconversion quantum yield and analyzed the data supervised by N. Yanai. C. Kerzig conceptualized the study, supported the writing and revision of the manuscript.

Blue-to-UVB Upconversion, Solvent Sensitization and Challenging Bond Activation Enabled by a Benzene-Based Annihilator

Till J. B. Zähringer, Julian A. Moghtader, Maria-Sophie Bertrams, Bibhisan Roy, Masanori Uji, Nobuhiro Yanai,* and Christoph Kerzig*

Abstract: Several energy-demanding photoreactions require harsh UV light from inefficient light sources. The conversion of low-energy visible light to high-energy singlet states via triplet-triplet annihilation upconversion (TTA-UC) could offer a solution for driving such reactions under mild conditions. We present the first annihilator with an emission maximum in the UVB region that, combined with an organic sensitizer, is suitable for blue-to-UVB upconversion. The annihilator singlet was successfully employed as an energy donor in subsequent FRET activations of aliphatic carbonyls. This hitherto unreported UC-FRET reaction sequence was directly monitored using laser spectroscopy and applied to mechanistic irradiation experiments demonstrating the feasibility of Norrish chemistry. Our results provide clear evidence for a novel blue light-driven substrate or solvent activation strategy, which is important in the context of developing more sustainable light-to-chemical energy conversion systems.

Introduction

Highly energetic photons with wavelengths in the UVB region (280–315 nm) are unavoidably required to initiate numerous useful photochemical reactions^[1,2] and to detoxify many pollutants photochemically.^[3,4] However, two main drawbacks render the broad usage of UVB-driven reactions somewhat cumbersome. Firstly, UVB light is practically not contained in the solar spectrum and the generation of UVB

photons typically requires mercury lamps,^[5] excimer-based lamps,^[6] or the high-energy tail of xenon arc lamps^[4]—all of them suffer from rather short lifespans well below 2000 h and electricity-to-UVB conversion efficiencies close to zero. Secondly, conventional glassware used in chemical laboratories has a low UVB transparency, which is why more expensive quartz glass is required for conventional UVB photochemistry.

In principle, the energy of two visible photons efficiently generated by long-lived LEDs can be pooled to achieve similar reactivities as obtained by direct UVB excitation. Among all known photon pooling or two-photon mechanisms,^[7–11] upconversion via sensitized triplet-triplet annihilation (TTA-UC) provides the most attractive alternative to direct high-energy one-photon excitation, because TTA-UC can be employed to convert two low-energy photons at moderate photon fluxes into one highly energetic singlet-excited state.^[12–23] The latter can either emit one photon of higher energy or directly activate a compound being inert under one-photon conditions at the given excitation wavelength. This strategy has already been exploited for a variety of selective photoreactions upon excitation with inexpensive diode-based continuous wave (cw) light sources,^[24] including isomerizations,^[25–27] dehalogenations,^[28–30] cycloadditions,^[31,32] C–C coupling^[24,33,34] and cyclization^[30] reactions as well as polymerizations.^[30,35–37] While all these UC-driven reactions are elegant, in particular when red/NIR photons with high penetration depth are used,^[30,38–40] they can likely be initiated by LEDs in a direct manner. Efficient high-power LEDs are available with numerous visible and some UVA (315–400 nm) peak wavelengths, but efficient ready-to-use LEDs with UVB emission do not exist for technical reasons.^[41] Consequently, it is highly desirable to develop visible light-driven UC systems that are capable of producing UVB photons to potentially replace harmful and inefficient light sources.

The first visible light-driven TTA-UC system with pronounced UV emission was reported in 2009.^[42] The interest in this methodology recently received a boost by some applications under remarkably mild conditions and pioneering observations such as the blue-light driven photocatalytic activation of aryl bromides,^[43] water splitting,^[44,45] the quantitative decomposition of a typical water pollutant,^[28] and the development of systems with very high quantum yields for UVA generation.^[46–48] Nevertheless, only a few basic structures for UV annihilators have been identified until now (biphenyl,^[49–51] PPO and strongly related

[*] T. J. B. Zähringer, J. A. Moghtader, M.-S. Bertrams, Prof. Dr. C. Kerzig
Department of Chemistry, Johannes Gutenberg University Mainz
Duesbergweg 10–14, 55128 Mainz (Germany)
E-mail: ckerzig@uni-mainz.de

Dr. B. Roy, M. Uji, Prof. Dr. N. Yanai
Department of Applied Chemistry, Graduate School of Engineering,
Center for Molecular Systems (CMS), Kyushu University
744 Moto-oka, Nishi-ku, Fukuoka 819-0395 (Japan)
E-mail: yanai@mail.cstm.kyushu-u.ac.jp

© 2022 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

heterocycles,^[42,48,52–54] terphenyl,^[54,55] quarterphenyl,^[55] pyrene^[54,56–58] as well as naphthalene^[28,37,46,51,54,59–61] and all these annihilators mainly show UVA and violet emission with either a negligible fraction of emitted UVB^[62] photons or no UVB emission at all. The identification of an annihilator with dominant UVB emission and the concomitant high excited singlet state energy well beyond 4 eV could expand the toolbox of photochemists drastically, given that Vis-to-UV upconversion holds great promise for energy-demanding photochemical applications.^[63,64] Herein, we present the first compound that deserves the label UVB annihilator: Its emission peaks in the UVB region at 309 nm, about half of the photons emitted via fluorescence lie in the UVB range (Figure 1) and, in combination with a suitable blue light-absorbing sensitizer, blue-to-UV upconversion can be observed with diode-based light sources. The resulting upconversion system was characterized by in-depth mechanistic studies using several spectroscopic techniques and employed for an underexplored upconversion-Förster resonance energy transfer (UC-FRET)^[65,66] reaction sequence. As we will show by meaningful proof-of-concept experiments, this novel strategy can not only be exploited for solvent excitation—a typical approach in synthetic UVB photochemistry^[1,2,6,67]—but also for high-energy carbonyl photochemistry.^[68,69]

Results and Discussion

Chemical intuition suggests that reducing the conjugated π -system from biphenyl to benzene would increase the annihilator's singlet-excited state energy and shift its peak emission from the UVA into the high-energy UVB region. However, the triplet of unsubstituted benzene at 3.9 eV^[70] is inaccessible in blue light-driven upconversion schemes as the input photon energy is on the order of 2.7 eV in this case. Modifications on the annihilator scaffolds with the protection group TIPS-ethynyl (triisopropylsilyl ethynyl) have shown to lower the triplet energy substantially while

maintaining relatively high energies of the upconverted emission.^[46,50,71–74] Hence, we speculated that benzene would follow a similar trend although previous calculations predicted a very pronounced HOMO–LUMO gap decrease.^[75] Our DFT calculations of several benzene derivatives with different TIPS-ethynyl substitution patterns provided initial information about the triplet energies (Figure 2B, see Section S3 of the Supporting Information for details). While the calculated triplet energies of single-substituted **TIPS-Bz** (3.06 eV) and symmetrical threefold substituted **tTIPS-Bz** (2.97 eV) still exceed our input energy limit, the twofold substitution (**bTIPS-Bz**), however, yielded a rather low triplet energy of 2.57 eV. For that reason, we synthesized **bTIPS-Bz** (and reference compounds) via a Sonogashira coupling reaction (see Supporting Information for details, Section S2). The absorption and normalized emission spectra are shown in Figure 2C. As expected, the two TIPS-ethynyl substituents on benzene cause a red-shift of the absorption and emission peaks (compare Figure S5). Gratifyingly, the emission spectrum of **bTIPS-Bz** peaks in the UVB, about half of all emitted photons are in the UVB range, and its singlet-excited state energy is as high as 4.15 eV, corresponding to a photon energy of 299 nm. Owing to the superincense of the molar absorptivity (Figure S5), the fluorescence rate constant of **bTIPS-Bz** is increased drastically compared to that of benzene.^[76–78] In direct consequence, (i) the fluorescence lifetime in solution (Figure S14) is shortened from 30 ns (benzene) to 3.2 ns (**bTIPS-Bz**) and (ii) the fluorescence quantum yield reaches an attractive value of $\Phi_F = 0.48$ for **bTIPS-Bz**, compared to $\Phi_F = 0.07$ for benzene.^[79,80] From 77 K phosphorescence measurements, we obtained a triplet energy of 2.64 eV for **bTIPS-Bz** (Figure S17), which is in very good agreement

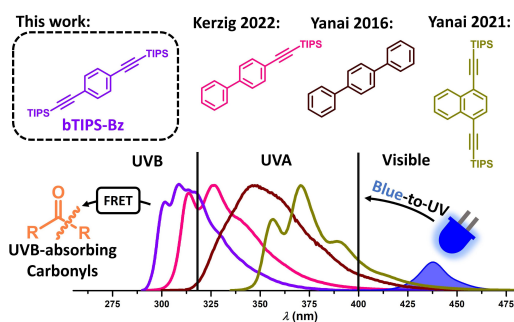


Figure 1. Structures and emission spectra of recently used annihilators for blue-to-UV upconversion. This work: Novel benzene-based annihilator (**bTIPS-Bz**) suitable for blue-to-UVB upconversion that has been successfully employed as an energy donor in a subsequent FRET activation of UVB-absorbing carbonyls.

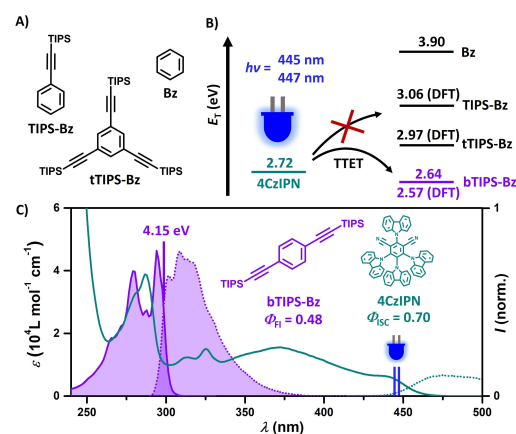


Figure 2. A) Structures of **TIPS-Bz**, **tTIPS-Bz** and **Bz**. B) Energy diagram visualizing the lowest triplet-excited state energies of **4CzIPN**, unsubstituted benzene, and TIPS-ethynyl substituted benzenes. C) Structures, absorption (solid line), and normalized emission (dotted line) spectra of **bTIPS-Bz** and **4CzIPN** in cyclohexane. The excitation wavelengths (445 nm and 447 nm) used for upconversion measurements are indicated by blue vertical lines.

with that estimated by DFT calculations. Given that isoenergetic and even slightly uphill sensitization is feasible,^[31,81–83] TTA-UC with **bTIPS-Bz** as annihilator is clearly within reach using blue photons.

For this study, we have chosen the well-known carbazoyl dicyanobenzene-based TADF emitter **4CzIPN** (Figure 2B and C) as the triplet sensitizer. In addition to OLED applications,^[84] **4CzIPN** has been successfully employed in energy transfer catalysis^[85,86] and TTA-UC schemes.^[50,55,87] Its high triplet energy (2.72 eV in cyclohexane), high triplet formation yield (about 70 %)^[88] and strong absorptivity in the blue make it ideal for our blue light-driven upconversion system.^[50] For solubility reasons, toluene was used as co-solvent (10 vol. %), which does not negatively affect the pertinent properties of our photoactive compounds (see ref. [50] and Figures S6/S14). The combined key properties of both **4CzIPN** and **bTIPS-Bz** are summarized in Figures 2B and C. Transient absorption (TA) and emission spectroscopy using laser flash photolysis (LFP) were performed with a 355 nm laser (≈ 5 ns pulse duration) to investigate the upconversion system in detail. The initial energy transfer from **34CzIPN** to **bTIPS-Bz** proceeds with a quenching rate constant of $k_{\text{TET}} = 6.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 3A), which is not only in line with the rather small triplet energy difference between **3bTIPS-Bz** and **34CzIPN**

but also sufficiently rapid for efficient quenching ($> 85\%$) of **34CzIPN** at moderate concentrations ($> 9 \text{ mM}$). In contrast, no quenching of the other TIPS-ethynyl substituted benzenes—**TIPS-Bz** and **tTIPS-Bz**—was observed, highlighting the unique photochemical properties of **bTIPS-Bz**. Further TA measurements were carried out to monitor the quenching product. The **34CzIPN** quenching by **bTIPS-Bz** gave rise to a TA spectrum with a pronounced absorption band peaking at 348 nm (purple spectrum in Figure 3B) that completely returns to baseline (Figure S18) with wavelength-independent kinetics and a much longer lifetime ($\approx 120 \mu\text{s}$) compared to **34CzIPN** alone ($7.9 \mu\text{s}$, see Figure S12 and corresponding discussion for further explanations). TD-DFT calculations on **3bTIPS-Bz** predict an intense absorption peak at 360 nm matching our experiments well (see calculated transitions in Figure 3B and Section S3 of the Supporting Information for details). We, therefore, assign the spectrum displayed in Figure 3B (purple) to **3bTIPS-Bz** generated through triplet-triplet energy transfer TTET.

Having established sensitized annihilator triplet formation, we next examined the TTA step. Three solutions containing either **bTIPS-Bz**, **4CzIPN**, or both in combination were prepared and investigated using time-gated emission spectroscopy. The detection window after 355 nm excitation was selected such that direct sensitizer and annihilator emission can be excluded. Out of the three solutions, only that with **4CzIPN** and **bTIPS-Bz** shows the expected singlet emission in the UV (Figure 3C) providing evidence for delayed annihilator emission, which has to be a result of TTA. The similar triplet energies imply the possibility of back-energy transfer in the triplet manifold. Kinetic emission traces monitoring delayed **3bTIPS-Bz*** emission at 350 nm with increasing sensitizer concentration confirm a back-TTET (Figure 3C, inset), as indicated by the delayed emission lifetime decrease.^[28,89,90] Moreover, we observed that the triplet lifetime of **3bTIPS-Bz** correlates with the weak elongated **4CzIPN** emission from back-TTET (Figure S13), and we attribute the remaining spectral emission of **4CzIPN** in Figure 3C to this energy transfer equilibrium.^[50,89]

More direct evidence for the UV emission originating from TTA-UC is given in Figure 3D. Kinetic traces simultaneously monitoring **3bTIPS-Bz** (absorption at 342 nm) and **3bTIPS-Bz*** (emission at 319 nm) show that both reach a maximum at $t = 6 \mu\text{s}$. Owing to the bimolecular nature of the annihilation process, the rise and fall of the singlet emission intensity are in a quadratic relation to the triplet concentration [**3bTIPS-Bz**], resulting in the characteristic behavior displayed in Figure 3D.^[91] We then characterized the efficiency of this novel blue-to-UVB TTA-UC scheme with two blue diode-based cw lasers at either 447 nm or 445 nm (see Supporting Information for detailed descriptions of both setups). We found that a sensitizer concentration of $44 \mu\text{M}$ gave a good compromise between the overall quantum yield and the threshold intensity I_{th} . Although higher sensitizer concentrations are regarded to be beneficial for lowering I_{th} ,^[92] i.e., for achieving high quantum yields at low light intensities, we found a higher I_{th} at $88 \mu\text{M}$ (see

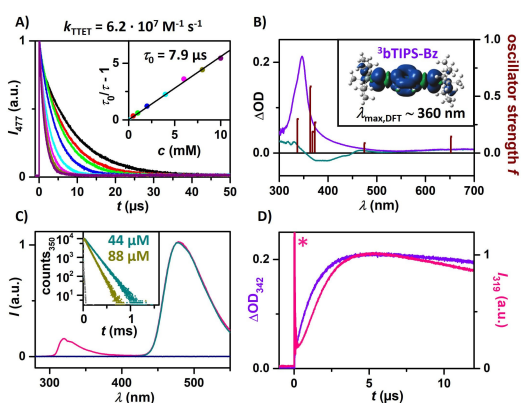


Figure 3. Mechanistic LFP experiments with 355 nm laser pulses of ≈ 5 ns duration. If not stated otherwise $20 \mu\text{M}$ **4CzIPN** and 10 mM **bTIPS-Bz** in Ar-saturated cyclohexane:toluene (9:1) were used. A) Luminescence quenching experiments of **4CzIPN** (detection wavelength, 477 nm) at different annihilator concentrations. Inset: corresponding Stern–Volmer plot. B) Transient absorption spectra of only **4CzIPN** (cyan) recorded $1 \mu\text{s}$ after the laser pulse and combined with **bTIPS-Bz** after $6 \mu\text{s}$ (purple) and oscillator strength of **3bTIPS-Bz** computed by TD-DFT. Inset: Computed spin density of the triplet state of **3bTIPS-Bz** with $\lambda_{\text{max,DFT}}$ of the predicted main absorption bands. C) Normalized time-gated (delay, $6 \mu\text{s}$; integration over $500 \mu\text{s}$) emission spectra of the complete upconversion system (pink), only **4CzIPN** (cyan), and only **bTIPS-Bz** (dark blue). Inset: Time-resolved upconversion emission plotted logarithmically at different sensitizer concentrations under pulsed excitation at 445 nm. D) Time-resolved emission (319 nm) and transient absorption (342 nm) traces upon excitation of the UC system. The asterisk marks laser stray light.

Figure S7). This observation is most likely a result of back-TTET with sensitizer ground state molecules as an additional deactivation pathway of the annihilator triplet.

The main plot in Figure 4A collates the upconverted emission with increasing laser intensity (10–800 mW) peaking at 318 nm with intense emission in the UVB region. The higher annihilator concentration causes filter effects of the annihilator emission in its absorption-emission overlap region (compare spectra in Figures 2C and 4A), thereby shifting the apparent emission maximum. However, the absorption of the ¹bTIPS-Bz*-emitted photons by additives in solution could occur below 310 nm—it would simply compete with annihilator self-absorption. Using the observed UC emission maximum in combination with the absorption maximum of 4CzIPN (435 nm), the anti-Stokes shift amounts to 1.04 eV.^[16] A frequently employed but less conservative anti-Stokes shift determination would yield a value as high as 1.24 eV, taking the excitation wavelength (447 nm) and the bTIPS-Bz emission peak in the absence of inner filter effects (309 nm). Regardless of the actual method, the anti-Stokes shift of our system is among the largest reported so far for visible light-driven UC schemes.^[72,82,93–100]

Figures 4B and C focus on power-dependent UC measurements. The achievable upconversion quantum yields Φ_{UC} at the highest laser intensities amount to values close to 1 % (with a theoretical maximum of 50 %) using both 447 nm and 445 nm excitation. A rather low I_{th} of 471 mW cm⁻² was determined (using the 445 nm setup with higher beam

quality), enabling decent UC efficiencies already with commercially available blue LEDs (Figure S15). Moreover, irradiating the UC system at the threshold intensity shows only minor degradation over one hour (Figure 4A, inset). Higher sensitizer concentrations (88 μ M) seem to be beneficial for the photostability of this system. A more systematic understanding of the factors governing efficient upconversion into the UV region seems to be required, considering the typically poor performance parameters of most known Vis-to-UV UC systems.^[49,101] The most straightforward future strategies for developing Vis-to-UVB UC systems with higher overall quantum yields are to increase the annihilator emission quantum yield (48%) by up to a factor of two and to avoid back-TTET with sensitizers possessing higher tripler energies that could also result in UC systems operating at lower annihilator concentrations (i.e., with less pronounced filter effects). Nevertheless, the promising efficiency and long-term stability led us to speculate that our unprecedented UC system with pronounced UVB emission could perhaps drive energy-demanding reactions that usually require high-energy UVB light sources, either with the singlet-excited annihilator as reacting key species or via an emission-reabsorption sequence.^[102]

We proposed that the high singlet-excited state energy of bTIPS-Bz could be exploited for a subsequent FRET activation of relatively inert substances (Figure 5A) with a rich UV photochemistry. UC-FRET reaction sequences have been suggested with less energetic excited states of the energy acceptor that would be accessible with efficient LEDs,^[65,66,103] but in our high-energy case, such an alternative does not exist. For our study, we chose pinacolone (PC) and acetone (AC)—both absorb only below 320 nm and thus usually require harmful UVB light sources for excitation. Figure 5B visualizes the spectral overlap between the bTIPS-Bz emission and the absorption of the carbonyl compounds. Although the molar absorption coefficients of such aliphatic carbonyls are rather low due to the symmetry-forbidden nature of the $n\pi^*$ transitions, the pronounced spectral overlap suggests that non-radiative energy transfer via the FRET mechanism is still feasible, whose efficiency linearly depends on the spectral overlap integrals.^[104] NMR-scale and mechanistic LFP experiments were conducted to monitor the UC-FRET sequence. Figure 5E shows kinetic traces of the bTIPS-Bz emission at 318 nm with increasing PC and AC concentrations. While the formation and decay rates of the singlet emission signals are essentially unaffected by the addition of the carbonyl compound, the overall emission intensity is reduced drastically. This contrasts strongly with time-resolved measurements of the bTIPS-Bz triplet state where no change with the addition of PC or AC (neither in concentration nor in lifetime) is observed (Figure S8). Thus, the initial amount of ¹bTIPS-Bz* produced via annihilation has to be unaffected by the addition of the carbonyls and we conclude that the attenuated UC emission signal must originate from direct excited-singlet state quenching^[43] (most likely via FRET) or reabsorption effects. An estimation of the latter, i.e., reabsorbed photons by the carbonyls through radiative energy transfer, revealed that non-radiative excited state quenching is the main pathway at

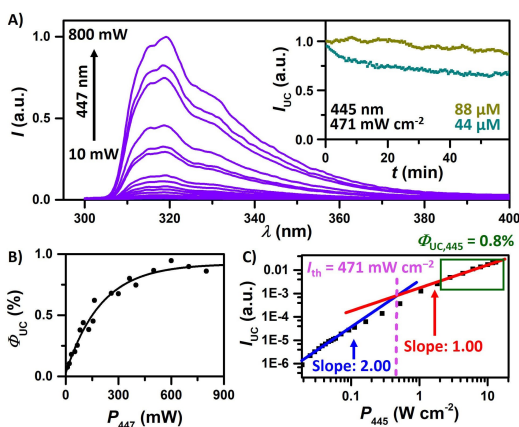


Figure 4. Photon upconversion studies with deoxygenated solutions containing 44 or 88 μ M 4CzIPN and 10 mM bTIPS-Bz in cyclohexane: toluene (9:1) using a cw laser for excitation at 447 nm or 445 nm. A) Power-dependent spectra of the normalized upconverted emission. Inset: Photostability measurement at different sensitizer concentrations at a cw laser power of 471 mW cm⁻². B) External upconversion quantum yield, Φ_{UC} , plotted against the laser power (with 44 μ M 4CzIPN). C) Normalized UC emission plotted against the laser power on a double-logarithmic scale (with 44 μ M 4CzIPN). The threshold intensity I_{th} was determined from the crossing point. See Supporting Information for details.

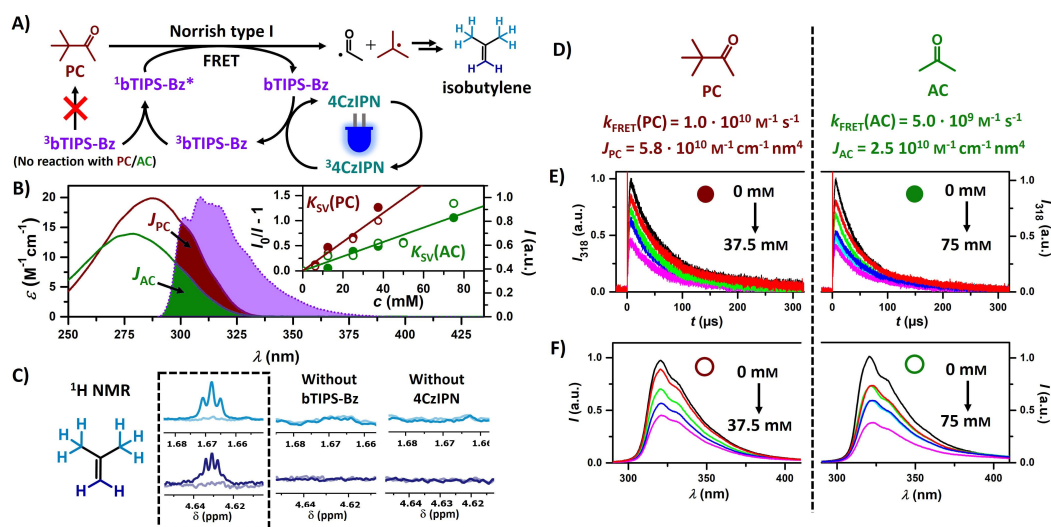


Figure 5. A) Upconversion mechanism and subsequent FRET sensitization of pinacolone resulting in a Norrish type I reaction and formation of isobutylene. B) Absorption spectra (solid line) of pinacolone (dark red), acetone (green), and normalized emission (dotted line) of $^3\text{bTIPS-Bz}$ in cyclohexane with the spectral overlap being highlighted. Inset: Stern–Volmer plot corresponding to quenching of upconverted $^3\text{bTIPS-Bz}$ emission by the carbonyl compounds. C) NMR scale experiment of 100 μM 4CzIPN, 10 mM $^3\text{bTIPS-Bz}$, and 100 mM pinacolone in Ar-saturated cyclohexane: toluene (9:1) with control experiments before and after 30 min irradiation at 447 nm with 1.1 W. Shown are the ^1H NMR signals of isobutylene as a stable product of the UC-FRET-driven Norrish reaction. D) Comparison of FRET efficiencies between pinacolone and acetone. E) and F) Mechanistic LFP experiments with 355 nm laser pulses of ≈ 10 ns duration of 20 μM 4CzIPN and 10 mM $^3\text{bTIPS-Bz}$ in Ar-saturated cyclohexane: toluene (9:1) with different concentrations of pinacolone and acetone used for the Stern–Volmer plots in the inset of panel B). E) Time-resolved emission at 318 nm. F) Normalized time-gated (delay, 6 μs ; integration over 500 μs) emission spectra.

our detection wavelength used in Figure 5E (see Supporting Information Section S6). Further time-gated spectra of the UV emission yielded a very similar decrease in intensity (Figure 5F). Moreover, the signal intensity in the region above 330 nm (where the carbonyls do not absorb) is almost equally reduced compared to the emission peak (318 nm) (Figure S9). All these findings are in perfect accordance with a FRET process between $^3\text{bTIPS-Bz}^*$ and the carbonyls being the main quenching mechanism of the upconverted emission. Similar quenching experiments were also performed with a cw laser (447 nm) to demonstrate the feasibility of this energy transfer sequence with a non-pulsed visible light source (Figure S10). Next, we investigated the energy transfer efficiency in detail. In principle FRET is still feasible at larger molecular distances (up to 100 nm), meaning that the energy transfer rate can exceed the classical diffusion limit for collision-induced quenching. As a result of the low molar absorption coefficients of the carbonyls, we pre-calculated rather small Förster distances of 0.7 nm and 0.8 nm for AC and PC (Section S1.8 of the Supporting Information), suggesting that the quenching constant will be close to or slightly higher than the diffusion-controlled rate constant in cyclohexane ($k_{\text{diff}} = 6.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^[105] The $^3\text{bTIPS-Bz}^*$ emission intensity from either kinetic measurements (filled circle, raw data from Figure 5E) or time-gated spectra (open circle, raw data from Figure 5F) are plotted against the carbonyl concentration in a Stern–Volmer graph

(Figure 5B, inset). Conventional Stern–Volmer analyses gave quenching constants k_{FRET} of $5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for AC and $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for PC, respectively (Figure 5D). Direct fluorescence lifetime quenching experiments upon UVB excitation of $^3\text{bTIPS-Bz}$ with different acetone concentrations gave a similar result ($k_{\text{FRET}} = 6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, see Figure S11 and corresponding discussion in the Supporting Information). The ratios of the energy transfer rate constants and the corresponding spectral overlap integrals J_{PC} and J_{AC} are practically identical, providing further evidence for the novel blue-to-UVB UC-FRET reaction sequence. Efficient photoredox reactions between the high-energy annihilator singlet and the carbonyl compounds or the sensitizer itself can be excluded as we could not detect any signatures of radical ions (Figures S8 and S18 in the Supporting Information).

The diverse photochemistry of carbonyl compounds is well described in the literature.^[1,2,67–69] Acetone almost quantitatively produces a highly energetic triplet state (triplet energy, $\approx 3.5 \text{ eV}$) upon direct excitation, which explains its dual use as solvent and sensitizer in conventional UVB photoreactions. Monitoring the acetone triplet produced via UC-FRET by spectroscopic methods is very challenging owing to its rather slow formation and the relatively high concentrations of potential triplet energy acceptors in our system. However, pinacolone undergoes efficient Norrish type I fragmentation generating a more

stabilized carbon-centered radical (Figure 5A)^[106] compared to that formed by acetone. This isobutyl radical is hard to track spectroscopically, but isobutylene as its stable disproportionation product^[107] (Figure 5A) is sufficiently soluble in our mixture and possesses a characteristic ¹H NMR spectrum.^[108] We, therefore, performed several NMR-scale irradiation experiments with **PC**. Irradiating the whole UC system together with 100 mM **PC** using our cw laser (447 nm) for 30 min resulted in the formation of new peaks in the NMR spectrum that unambiguously correspond to isobutylene (Figure 5C, see Section S8.2 for details). Control experiments with either annihilator or sensitizer missing did not show any evidence for product generation. To demonstrate that this high-energy Norrish chemistry is also viable with commercial blue LEDs, the same irradiation experiment was carried out with two blue LEDs (440 nm). Similar amounts of isobutylene were detected (Figure S29), confirming the promising performance parameters and the potential of our UC system for future lab-scale applications without UVB lamps.

Finally, we turned to the substrate dibenzyl ketone, which is known to undergo efficient Norrish fragmentation under UV photolysis ($\lambda < 325$ nm) and subsequent C–C bond formation of the resulting radicals.^[69] The coupling product dibenzyl has been observed clearly employing our UC-FRET strategy with blue LEDs (Figures S31–S33). This coupling reaction under mercury-free and very mild conditions highlights that more synthetically useful photoreactions are generally feasible employing our new approach.

Conclusion

In summary, we have demonstrated that UVB emitters can be incorporated in blue light-driven upconversion schemes. Reaching the UVB region with blue input photons for the first time is certainly beyond a pushing-the-limits study because this technology enables unreported substrate and solvent activation strategies that cannot be carried out with efficient and sustainable light sources in a direct manner. Our mechanistic investigations provide unambiguous evidence for a hitherto unreported blue-to-UVB UC-FRET sequence expanding the applicability of upconversion for driving challenging chemical reactions. These key findings pave the way for exploiting the full potential of this attractive two-photon mechanism in light-driven bond activation. The incorporation of such high-energy upconversion systems in solid or gel-like environments for large-scale applications might represent the next challenge and even LED-driven UVA-to-UVC upconversion systems, which have the potential to replace mercury lamps completely, seem to be within reach based on our results. The latter would require further efforts in developing both novel annihilators and energy-matched sensitizers that are highly photostable. For that, a deeper understanding of TTA^[73, 109–112] is required, and regarding sensitizer development, the upconversion community will strongly benefit from the recent progress in Dexter energy transfer catalysis.^[49, 113–116]

Acknowledgements

We acknowledge generous financial support from the JGU Mainz, SusInnoScience, the German Research Foundation (DFG, grant number KE 2313/3-1), the German Federal Environmental Foundation (DBU, PhD fellowship to T.J.B.Z., grant number 20022/028), the Murata Science Foundation, Research Foundation for Opto-Science and Technology and JSPS KAKENHI (JP20H02713, JP22K19051, JP22F21031). C.K. is grateful to the Chemical Industry Funds for a Liebig fellowship. B.R. acknowledges JSPS for a fellowship to conduct research in Japan (P21031). We thank Johannes Rocker for recording mass spectra and Prof. Till Opatz for allowing us to use his equipment. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article. The raw data sets presented in the main manuscript can be found under <http://doi.org/10.25358/openscience-8436>.

Keywords: Energy Transfer • Photochemistry • Sustainable Chemistry • Time-Resolved Spectroscopy • Upconversion

- [1] P. Klán, J. Wirz, *Photochemistry of Organic Compounds: From Concepts to Practice*, Wiley, Chichester, 2009.
- [2] N. Hoffmann, *Chem. Rev.* **2008**, *108*, 1052–1103.
- [3] G. S. Pozan, A. Kambur, *Appl. Catal. B* **2013**, *129*, 409–415.
- [4] N. Zhang, G. Liu, H. Liu, Y. Wang, Z. He, G. Wang, *J. Hazard. Mater.* **2011**, *192*, 411–418.
- [5] O. Shvydkiv, S. Gallagher, K. Nolan, M. Oelgemöller, *Org. Lett.* **2010**, *12*, 5170–5173.
- [6] A. G. Griesbeck, N. Maptue, S. Bondock, M. Oelgemöller, *Photochem. Photobiol. Sci.* **2003**, *2*, 450–451.
- [7] F. Glaser, C. Kerzig, O. S. Wenger, *Angew. Chem. Int. Ed.* **2020**, *59*, 10266–10284; *Angew. Chem.* **2020**, *132*, 10350–10370.
- [8] J. Castellanos-Soriano, J. C. Herrera-Luna, D. Díaz Díaz, M. C. Jiménez, R. Pérez-Ruiz, *Org. Chem. Front.* **2020**, *7*, 1709–1716.
- [9] Y. Kobayashi, J. Abe, *Chem. Soc. Rev.* **2022**, *51*, 2397–2415.
- [10] I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. König, *Acc. Chem. Res.* **2016**, *49*, 1566–1577.
- [11] M. Cybularczyk-Cecotka, J. Szczepanik, M. Giedyk, *Nat. Catal.* **2020**, *3*, 872–886.
- [12] V. Gray, D. Dzebo, M. Abrahamsson, B. Albinsson, K. Moth-Poulsen, *Phys. Chem. Chem. Phys.* **2014**, *16*, 10345–10352.
- [13] J. Zhao, S. Ji, H. Guo, *RSC Adv.* **2011**, *1*, 937–950.
- [14] T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.
- [15] T. F. Schulze, T. W. Schmidt, *Energy Environ. Sci.* **2015**, *8*, 103–125.
- [16] Y. Zhou, F. N. Castellano, T. W. Schmidt, K. Hanson, *ACS Energy Lett.* **2020**, *5*, 2322–2326.

- [17] Z. Xu, Z. Huang, T. Jin, T. Lian, M. L. Tang, *Acc. Chem. Res.* **2021**, *54*, 70–80.
- [18] J. Pedrini, A. Monguzzi, *J. Photonics Energy* **2017**, *8*, 022005.
- [19] L. Zeng, L. Huang, J. Han, G. Han, *Acc. Chem. Res.* **2022**, *55*, 2604–2615.
- [20] T. Lin, C. F. Perkinson, M. A. Baldo, *Adv. Mater.* **2020**, *32*, 1908175.
- [21] H. Liu, X. Yan, L. Shen, Z. Tang, S. Liu, X. Li, *Mater. Horiz.* **2019**, *6*, 990–995.
- [22] S. Balushev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda, G. Wegner, *Phys. Rev. Lett.* **2006**, *97*, 143903.
- [23] F. Edhborg, A. Olesund, B. Albinsson, *Photochem. Photobiol. Sci.* **2022**, *21*, 1143–1158.
- [24] R. Pérez-Ruiz, *Top. Curr. Chem.* **2022**, *380*, 23.
- [25] J. B. Bilger, C. Kerzig, C. B. Larsen, O. S. Wenger, *J. Am. Chem. Soc.* **2021**, *143*, 1651–1663.
- [26] Y. Wei, H. Xian, X. Lv, F. Ni, X. Cao, C. Yang, *Mater. Horiz.* **2021**, *8*, 606–611.
- [27] A. Tokunaga, L. M. Uriarte, K. Mutoh, E. Fron, J. Hofkens, M. Sliwa, J. Abe, *J. Am. Chem. Soc.* **2019**, *141*, 17744–17753.
- [28] B. Pfund, D. M. Steffen, M. R. Schreier, M.-S. Bertrams, C. Ye, K. Börjesson, O. S. Wenger, C. Kerzig, *J. Am. Chem. Soc.* **2020**, *142*, 10468–10476.
- [29] C. Kerzig, O. S. Wenger, *Chem. Sci.* **2018**, *9*, 6670–6678.
- [30] B. D. Ravetz, A. B. Pun, E. M. Churchill, D. N. Congreve, T. Rovis, L. M. Campos, *Nature* **2019**, *565*, 343–346.
- [31] C. Wang, F. Reichenauer, W. R. Kitzmann, C. Kerzig, K. Heinze, U. Resch-Genger, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202238; *Angew. Chem.* **2022**, *134*, e202202238.
- [32] R. R. Isangulov, F. N. Castellano, *Angew. Chem. Int. Ed.* **2006**, *45*, 5957–5959; *Angew. Chem.* **2006**, *118*, 6103–6105.
- [33] C. G. López-Calixto, M. Liras, V. A. de la Peña O'Shea, R. Pérez-Ruiz, *Appl. Catal. B* **2018**, *237*, 18–23.
- [34] F. Glaser, C. Kerzig, O. S. Wenger, *Chem. Sci.* **2021**, *12*, 9922–9933.
- [35] N. Awwad, A. T. Bui, E. O. Danilov, F. N. Castellano, *Chem* **2020**, *6*, 3071–3085.
- [36] A. Caron, G. Noirbent, D. Gigmes, F. Dumur, J. Lalevée, *Macromol. Rapid Commun.* **2021**, *42*, 2100047.
- [37] Y. Wei, K. Pan, X. Cao, Y. Li, X. Zhou, C. Yang, *CCS Chem.* **2022**, *4*, 3852–3863.
- [38] B. D. Ravetz, N. E. S. Tay, C. L. Joe, M. Sezen-Edmonds, M. A. Schmidt, Y. Tan, J. M. Janey, M. D. Eastgate, T. Rovis, *ACS Cent. Sci.* **2020**, *6*, 2053–2059.
- [39] L. Huang, W. Wu, Y. Li, K. Huang, L. Zeng, W. Lin, G. Han, *J. Am. Chem. Soc.* **2020**, *142*, 18460–18470.
- [40] P. Bharmoria, H. Bildirir, K. Moth-Poulsen, *Chem. Soc. Rev.* **2020**, *49*, 6529–6554.
- [41] H. Hirayama, S. Fujikawa, N. Kamata, *Electron. Commun. Jpn.* **2015**, *98*, 1–8.
- [42] T. N. Singh-Rachford, F. N. Castellano, *J. Phys. Chem. A* **2009**, *113*, 5912–5917.
- [43] M. Majek, U. Faltermeyer, B. Dick, R. Pérez-Ruiz, A. Jacobi von Wangelin, *Chem. Eur. J.* **2015**, *21*, 15496–15501.
- [44] A. Monguzzi, A. Oertel, D. Braga, A. Riedinger, D. K. Kim, P. N. Knüsel, A. Bianchi, M. Mauri, R. Simonutti, D. J. Norris, F. Meinardi, *ACS Appl. Mater. Interfaces* **2017**, *9*, 40180–40186.
- [45] M. Barawi, F. Fresno, R. Pérez-Ruiz, V. A. de la Peña O'Shea, *ACS Appl. Energy Mater.* **2019**, *2*, 207–211.
- [46] N. Harada, Y. Sasaki, M. Hosoyamada, N. Kimizuka, N. Yanai, *Angew. Chem. Int. Ed.* **2021**, *60*, 142–147; *Angew. Chem.* **2021**, *133*, 144–149.
- [47] M. Uji, N. Harada, N. Kimizuka, M. Saigo, K. Miyata, K. Onda, N. Yanai, *J. Mater. Chem. C* **2022**, *10*, 4558–4562.
- [48] A. Olesund, J. Johnsson, F. Edhborg, S. Ghasemi, K. Moth-Poulsen, B. Albinsson, *J. Am. Chem. Soc.* **2022**, *144*, 3706–3716.
- [49] L. Schmid, F. Glaser, R. Schaer, O. S. Wenger, *J. Am. Chem. Soc.* **2022**, *144*, 963–976.
- [50] T. J. B. Zähringer, M.-S. Bertrams, C. Kerzig, *J. Mater. Chem. C* **2022**, *10*, 4568–4573.
- [51] X. Lin, Z. Chen, Y. Han, C. Nie, P. Xia, S. He, J. Li, K. Wu, *ACS Energy Lett.* **2022**, *7*, 914–919.
- [52] S. He, X. Luo, X. Liu, Y. Li, K. Wu, *J. Phys. Chem. Lett.* **2019**, *10*, 5036–5040.
- [53] V. Gray, P. Xia, Z. Huang, E. Moses, A. Fast, D. A. Fishman, V. I. Vullev, M. Abrahamsson, K. Moth-Poulsen, M. Lee Tang, *Chem. Sci.* **2017**, *8*, 5488–5496.
- [54] L. Hou, A. Olesund, S. Thurakkal, X. Zhang, B. Albinsson, *Adv. Funct. Mater.* **2021**, *31*, 2106198.
- [55] N. Yanai, M. Kozue, S. Amemori, R. Kabe, C. Adachi, N. Kimizuka, *J. Mater. Chem. C* **2016**, *4*, 6447–6451.
- [56] W. Zhao, F. N. Castellano, *J. Phys. Chem. A* **2006**, *110*, 11440–11445.
- [57] Q. Chen, Y. Liu, X. Guo, J. Peng, S. Garakyaraghi, C. M. Papa, F. N. Castellano, D. Zhao, Y. Ma, *J. Phys. Chem. A* **2018**, *122*, 6673–6682.
- [58] P. Duan, N. Yanai, N. Kimizuka, *Chem. Commun.* **2014**, *50*, 13111–13113.
- [59] Y. Murakami, A. Motooka, R. Enomoto, K. Niimi, A. Kaiho, N. Kiyoyanagi, *Phys. Chem. Chem. Phys.* **2020**, *22*, 27134–27143.
- [60] Z. A. VanOrman, L. Nienhaus, *Matter* **2021**, *4*, 2625–2626.
- [61] J. A. Kübler, B. Pfund, O. S. Wenger, *JACS Au* **2022**, *2*, 2367–2380.
- [62] The only known Vis-to-UV upconversion system with pronounced UVB emission (ref. [49]) requires violet excitation light (405 nm) and operates with quantum yields and threshold intensities that are unattractive for lab-scale applications.
- [63] B. S. Richards, D. Hudry, D. Busko, A. Turshatov, I. A. Howard, *Chem. Rev.* **2021**, *121*, 9165–9195.
- [64] Y. Du, X. Ai, Z. Li, T. Sun, Y. Huang, X. Zeng, X. Chen, F. Rao, F. Wang, *Adv. Photonics Res.* **2021**, *2*, 2000213.
- [65] S. H. C. Askes, M. Klotz, G. Bruylants, J. T. M. Kennis, S. Bonnet, *Phys. Chem. Chem. Phys.* **2015**, *17*, 27380–27390.
- [66] W. Wang, Q. Liu, C. Zhan, A. Barhoumi, T. Yang, R. G. Wylie, P. A. Armstrong, D. S. Kohane, *Nano Lett.* **2015**, *15*, 6332–6338.
- [67] C. Michelin, N. Hoffmann, *ACS Catal.* **2018**, *8*, 12046–12055.
- [68] A. Albini, *Photochem. Photobiol. Sci.* **2021**, *20*, 161–181.
- [69] J. C. Scaiano, K. G. Stamplecoskie, G. L. Hallett-Tapley, *Chem. Commun.* **2012**, *48*, 4798–4808.
- [70] J. P. Doering, *J. Chem. Phys.* **1969**, *51*, 2866–2870.
- [71] P. Bharmoria, F. Edhborg, H. Bildirir, Y. Sasaki, S. Ghasemi, A. Mårtensson, N. Yanai, N. Kimizuka, B. Albinsson, K. Börjesson, K. Moth-Poulsen, *J. Mater. Chem. A* **2022**, *10*, 21279–21290.
- [72] N. Nishimura, V. Gray, J. R. Allardice, Z. Zhang, A. Pershin, D. Beljonne, A. Rao, *ACS Mater. Lett.* **2019**, *1*, 660–664.
- [73] K. J. Fallon, E. M. Churchill, S. N. Sanders, J. Shee, J. L. Weber, R. Meir, S. Jockusch, D. R. Reichman, M. Y. Sfeir, D. N. Congreve, L. M. Campos, *J. Am. Chem. Soc.* **2020**, *142*, 19917–19925.
- [74] A. Maliakal, K. Raghavachari, H. Katz, E. Chandross, T. Siegrist, *Chem. Mater.* **2004**, *16*, 4980–4986.
- [75] G. Mallocci, G. Cappellini, G. Mulas, A. Mattoni, *Thin Solid Films* **2013**, *543*, 32–34.
- [76] S. J. Strickler, R. A. Berg, *J. Chem. Phys.* **1962**, *37*, 814–822.
- [77] J. Mohanty, W. M. Nau, *Photochem. Photobiol. Sci.* **2004**, *3*, 1026.

- [78] M.-S. Bertrams, C. Kerzig, *Chem. Commun.* **2021**, 57, 6752–6755.
- [79] M. Luria, M. Ofra, G. Stein, *J. Phys. Chem.* **1974**, 78, 1904–1909.
- [80] W. R. Dawson, M. W. Windsor, *J. Phys. Chem.* **1968**, 72, 3251–3260.
- [81] S. He, Y. Han, J. Guo, K. Wu, *J. Phys. Chem. Lett.* **2022**, 13, 1713–1718.
- [82] J. Isokuortti, S. R. Allu, A. Efimov, E. Vuorimaa-Laukkanen, N. V. Tkachenko, S. A. Vinogradov, T. Laaksonen, N. A. Durandin, *J. Phys. Chem. Lett.* **2020**, 11, 318–324.
- [83] F. Strieth-Kalthoff, C. Henkel, M. Teders, A. Kahnt, W. Knolle, A. Gómez-Suárez, K. Dirian, W. Alex, K. Bergander, C. G. Daniliuc, B. Abel, D. M. Guldi, F. Glorius, *Chem* **2019**, 5, 2183–2194.
- [84] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, 492, 234–238.
- [85] M. A. Bryden, F. Millward, T. Matulaitis, D. Chen, M. Villa, A. Fermi, S. Cetin, P. Ceroni, E. Zysman-Colman, *J. Org. Chem.* **2022**, <https://doi.org/10.1021/acs.joc.2c01137>.
- [86] M. A. Bryden, E. Zysman-Colman, *Chem. Soc. Rev.* **2021**, 50, 7587–7680.
- [87] T. C. Wu, D. N. Congreve, M. A. Baldo, *Appl. Phys. Lett.* **2015**, 107, 031103.
- [88] R. Ishimatsu, S. Matsunami, K. Shizu, C. Adachi, K. Nakano, T. Imato, *J. Phys. Chem. A* **2013**, 117, 5607–5612.
- [89] D. Meroni, A. Monguzzi, F. Meinardi, *J. Chem. Phys.* **2020**, 153, 114302.
- [90] J. Perego, J. Pedrini, C. X. Bezuidenhout, P. E. Sozzani, F. Meinardi, S. Bracco, A. Comotti, A. Monguzzi, *Adv. Mater.* **2019**, 31, 1903309.
- [91] Y. Murakami, K. Kamada, *Phys. Chem. Chem. Phys.* **2021**, 23, 18268–18282.
- [92] A. Haefele, J. Blumhoff, R. S. Khayzer, F. N. Castellano, *J. Phys. Chem. Lett.* **2012**, 3, 299–303.
- [93] Z. A. VanOrman, C. R. Conti, G. F. Strouse, L. Nienhaus, *Chem. Mater.* **2021**, 33, 452–458.
- [94] C. J. Imperiale, P. B. Green, M. Hasham, M. W. B. Wilson, *Chem. Sci.* **2021**, 12, 14111–14120.
- [95] W. Yin, T. Yu, J. Chen, R. Hu, G. Yang, Y. Zeng, Y. Li, *ACS Appl. Mater. Interfaces* **2021**, 13, 57481–57488.
- [96] R. Haruki, Y. Sasaki, K. Masutani, N. Yanai, N. Kimizuka, *Chem. Commun.* **2020**, 56, 7017–7020.
- [97] C. Fan, L. Wei, T. Niu, M. Rao, G. Cheng, J. J. Chruma, W. Wu, C. Yang, *J. Am. Chem. Soc.* **2019**, 141, 15070–15077.
- [98] Y. Wei, Y. Li, M. Zheng, X. Zhou, Y. Zou, C. Yang, *Adv. Opt. Mater.* **2020**, 8, 1902157.
- [99] Y. Wei, M. Zheng, L. Chen, X. Zhou, S. Liu, *Dalton Trans.* **2019**, 48, 11763–11771.
- [100] L. Huang, Y. Zhao, H. Zhang, K. Huang, J. Yang, G. Han, *Angew. Chem. Int. Ed.* **2017**, 56, 14400–14404; *Angew. Chem.* **2017**, 129, 14592–14596.
- [101] V. Gray in *Photochemistry* (Eds.: A. Albini, S. Protti), Royal Society of Chemistry, Cambridge, **2019**, pp. 404–420.
- [102] S. H. C. Askes, A. Bahreman, S. Bonnet, *Angew. Chem. Int. Ed.* **2014**, 53, 1029–1033; *Angew. Chem.* **2014**, 126, 1047–1051.
- [103] M. S. Meijer, V. S. Talens, M. F. Hilbers, R. E. Kieltyka, A. M. Brouwer, M. M. Natile, S. Bonnet, *Langmuir* **2019**, 35, 12079–12090.
- [104] Th. Förster, *Ann. Phys.* **1948**, 437, 55–75.
- [105] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Handbook of Photochemistry*, CRC/Taylor & Francis, Boca Raton, **2006**.
- [106] M. C. Jiménez, P. Leal, M. A. Miranda, R. Tormos, *J. Chem. Soc. Chem. Commun.* **1995**, 2009–2010.
- [107] D. H. Slater, S. S. Collier, J. G. Calvert, *J. Am. Chem. Soc.* **1968**, 90, 268–273.
- [108] S. J. Peters, T. M. Blood, M. E. Kassabaum, *Eur. J. Org. Chem.* **2009**, 6104–6108.
- [109] V. Gray, A. Dreos, P. Erhart, B. Albinsson, K. Moth-Poulsen, M. Abrahamsson, *Phys. Chem. Chem. Phys.* **2017**, 19, 10931–10939.
- [110] C. Ye, V. Gray, J. Mårtensson, K. Börjesson, *J. Am. Chem. Soc.* **2019**, 141, 9578–9584.
- [111] D. G. Bossanyi, Y. Sasaki, S. Wang, D. Chekulaev, N. Kimizuka, N. Yanai, J. Clark, *JACS Au* **2021**, 1, 2188–2201.
- [112] L. Vaghi, F. Rizzo, J. Pedrini, A. Mauri, F. Meinardi, U. Cosentino, C. Greco, A. Monguzzi, A. Papagni, *Photochem. Photobiol. Sci.* **2022**, 21, 913–921.
- [113] Y. Zhang, Y. Niu, Y. Guo, J. Wang, Y. Zhang, S. Liu, X. Shen, *Angew. Chem. Int. Ed.* **2022**, 61, e202212201; *Angew. Chem.* **2022**, 134, e202212201.
- [114] M. R. Schreier, X. Guo, B. Pfund, Y. Okamoto, T. R. Ward, C. Kerzig, O. S. Wenger, *Acc. Chem. Res.* **2022**, 55, 1290–1300.
- [115] E. A. Martynova, V. A. Voloshkin, S. G. Guillet, F. Bru, M. Beliš, K. Van Heck, C. S. J. Cazin, S. P. Nolan, *Chem. Sci.* **2022**, 13, 6852–6857.
- [116] T. O. Paulisch, L. A. Mai, F. Strieth-Kalthoff, M. J. James, C. Henkel, D. M. Guldi, F. Glorius, *Angew. Chem. Int. Ed.* **2022**, 61, e202112695; *Angew. Chem.* **2022**, 134, e202112695.

Manuscript received: October 18, 2022
Accepted manuscript online: November 18, 2022
Version of record online: January 16, 2023

3.3 Insights into properties of triplet excited ligand-centered states in heteroleptic platinum(II) complexes

This section presents:

Cyclometalated Spirobifluorene Imidazolydiene Platinum(II) Complexes with Predominant ^3LC Emissive Character and High Photoluminescence Quantum Yields

Tim Riesebeck, Maria-Sophie Bertrams, Sergej Stipurin, Kai Konowski, Christoph Kerzig, Thomas Strassner, *Inorg. Chem.*, **2022**, 61, 15499-15509.

In this last section, the excited triplet states of two heteroleptic platinum(II) complexes are characterized in different solvents and in a PMMA matrix with a special focus on the lifetimes, reactivities and excited state energies. One of the ligands was designed to achieve a high ΔE between the ground and the excited state to generate blue photons (~ 2.8 eV).^[7,172] This ligand consists of an imidazole unit covalently linked to a spirobifluorene, thereby providing two cyclometallating carbenes ($\text{C}^\wedge\text{C}^*_{\text{spiro}}\text{-NHC}$ ligand, structure in Figure 35, left part). Spirobifluorene motifs are known for their large HOMO-LUMO gap providing the prerequisites for a high E_T in the complex. The two heteroleptic complexes differ in the choice of the second bidentate ligand, which is either an acetylacetonate ligand or a mesitylene substituted derivative.

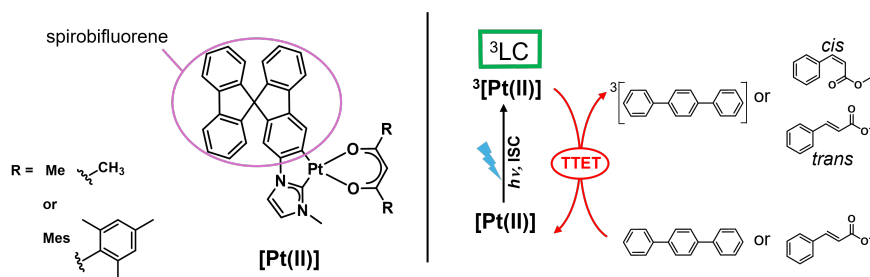


Figure 35: Structures of the Pt(II) complexes, featuring the $\text{C}^\wedge\text{C}^*_{\text{spiro}}\text{-NHC}$ ligand and the second acetylacetonate derived ligand on the left part of the figure. The right part is a schematic illustration of the investigated energy transfer reactivity of the ^3LC excited state, which was explored by sensitizing *p*-terphenyl or a *cis/trans* isomerization.

Transient absorption and emission spectroscopy combined with DFT calculations revealed a triplet nature of the purely ligand-centered excited state (^3LC), located on the $\text{C}^\wedge\text{C}^*_{\text{spiro}}\text{-NHC}$ ligand. Time-resolved measurements resulted in lifetimes around 30 μs for both complexes. Spectroscopic data and DFT results reveal a minor influence of the acetylacetonate (-derived) ligand on the excited state. Opposite to that, in previous studies on platinum(II) complexes lacking the spirobifluorene motive on the NHC ligand, the excited state was partially located on the acetylacetonate ligand and its substitution (methyl, mesityl or duryl) allowed to modify the excited state properties.^[247,248]

The long-lived triplet of both complexes was employed as sensitizer for TTET to *p*-terphenyl, which has a known triplet energy (2.5 eV at 77 K)^[48,249] spectrum of the triplet excited state^[145,250]. The nearly identical k_{TTET} ($\sim 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) for the quenching of both $^3\text{Pt(II)}$ complexes with *p*-terphenyl, a *cis/trans*-isomerization reaction, together with 77 K emission measurements resulted in almost identical triplet energy ($E_{\text{T}} \sim 2.5 \text{ eV}$) for both complexes (Figure 35, right part).

These findings confirm the minor influence of the acetylacetonato (derived) ligand on the excited state, which is in line with the DFT calculations. Their blue-turquoise-colored emission makes both complexes suitable candidates for blue-turquoise OLED applications.

Reprinted with permission from T. Riesebeck, M.-S. Bertrams, S. Stipurin, K. Konowski, C. Kerzig, T. Strassner, *Inorg. Chem.* **2022**, *61*, 39, 15499-15509. Copyright 2022 American Chemical Society.

The reference is attached in the following pages and can be cited corresponding to reference[172] and the supporting information can be found in Section 6.12.

Author contributions: M.-S. Bertrams performed the optical spectroscopy measurements, which include the ϕ_{F} , excited state kinetic measurements, TA and emission spectroscopy (see publication Figure 6), energy transfer to *p*-terphenyl, and wrote the corresponding section of the publication. The SI provides the corresponding experiments for the second Pt-complex as well as the *cis/trans*-isomerization experiments performed and written by M.-S. Bertrams. This contribution was supervised and reviewed by C. Kerzig. Synthesis, UV Vis spectroscopy and DFT calculations were performed by T. Riesebeck, who also wrote the corresponding parts in the main publication and SI and for the X-ray data. T. Riesebeck was supervised by T. Strassner. S. Stipurin and K. Konowski performed and analyzed X-ray diffractometry measurements.

Cyclometalated Spirobifluorene Imidazolylidene Platinum(II) Complexes with Predominant ^3LC Emissive Character and High Photoluminescence Quantum Yields

Tim Riesebeck, Maria-Sophie Bertrams, Sergej Stipurin, Kai Konowski, Christoph Kerzig,* and Thomas Strassner*

Cite This: *Inorg. Chem.* 2022, 61, 15499–15509

Read Online

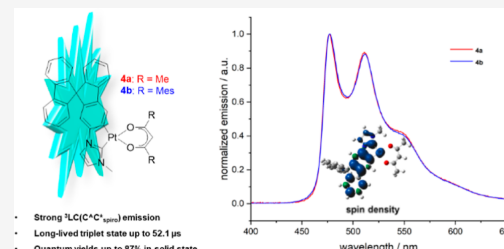
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Two novel bidentate C^*C^* spiro cyclometalated platinum(II) complexes comprising a spiro-conjugated bifluorene ligand and different β -diketonate auxiliary ligands are synthesized and characterized. Their preparation employs a robust and elaborate synthetic protocol commencing with an *N*-heterocyclic carbene precursor. Structural characterization by means of NMR techniques and solid-state structures validate the proposed and herein presented molecular scaffolds. Photophysical studies, including laser flash photolysis methods, reveal an almost exclusively ligand-centered triplet state, governed by the C^*C^* spiro-NHC ligand. The high triplet energies and the long triplet lifetimes in the order of 30 μs in solution make the complexes good candidates for light-emitting diode-driven photocatalysis, as initial energy transfer experiments reveal. In-depth time-dependent density functional theory investigations are in excellent accordance with our spectroscopic findings. The title compounds are highly emissive in the bluish-green color region with quantum yields of up to 87% in solid-state measurements.



- Strong $^3\text{LC}(\text{C}^*\text{C}^*)_{\text{spiro}}$ emission
- Long-lived triplet state up to 52.1 μs
- Quantum yields up to 87% in solid state

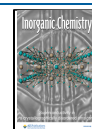
INTRODUCTION

Currently, luminescent metal complexes are the subject of intensified research efforts as materials for optoelectronic devices. Such metal complexes typically possess high emission quantum yields and sufficiently long-lived excited states due to heavy metal atom-induced intersystem crossing processes. Chemists can modify the structural design and thus rigorously tweak their photophysical properties. This qualifies these materials for application in organic light-emitting diodes (OLEDs)^{1–15} and other technologies, for example, chemo- and oxygen sensors.^{16–23} Novel technologies of this kind represent an imperative contribution of the scientific community to make climate change a success story since energy consumption can be drastically lowered utilizing (opto-)electronic devices based on (metal-)organic compounds. Recently, purely organic emitters based on spiro-conjugated donor–acceptor systems demonstrated excellent emissive properties, especially in the urgently sought-after blue-color spectrum. Organic spiro-conjugated emitters exploit small singlet–triplet energy gaps which permit reverse intersystem crossing (RISC) leading to a luminescence mechanism called thermally activated delayed fluorescence (TADF).^{24–30} State-of-the-art TADF OLED emitters have proven to be at least as compatible as established phosphorescent OLED (PhOLED) emitters. However, long delayed fluorescence lifetimes due to slow RISC events render efficiency and long-term stability at

higher brightness problematic.^{31,32} To address this issue, scientists rationalized the use of metal-based TADF emitters which eventually show decreased lifetimes of excited states because of increased spin–orbit coupling (SOC).^{33–41} Next to widely explored Ir(III) complexes,^{1,5,42} square-planar Pt(II) complexes have drawn significant attention onto their capability to act as promising phosphorescent emitters in OLEDs due to large SOC and fast radiative transitions which affords quantum efficiencies of up to 100% for electroluminescence.⁴³ A smaller ligand sphere of square-planar Pt(II) complexes compared to that of Ir(III) complexes renders Pt(II) complexes more suitable for vacuum deposition techniques with respect to device fabrication.⁴⁴ Bidentate square-planar Pt(II) complexes were successfully synthesized by multiple research groups and showcased impressive luminescent properties.^{45–51} Tackling the issue of establishing stable blue phosphorescent emitters, molecular design strategies have comprised strong-field bidentate cyclometalated

Received: June 20, 2022

Published: September 20, 2022



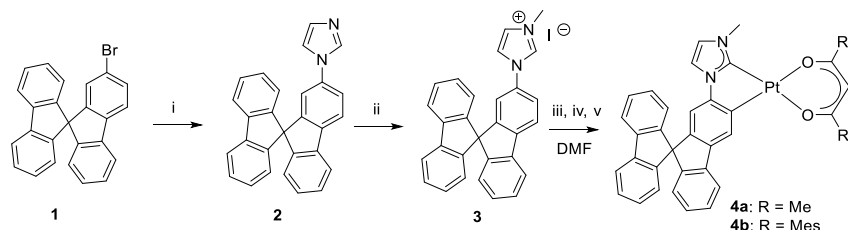


Figure 1. Reaction conditions for the synthesis of ligand precursors and Pt(II) complexes. (i) Imidazole, K_2CO_3 , cat. CuI, DMF, 160 °C. (ii) MeI, THF, 90 °C. (iii) Ag_2O , rt. (iv) $Pt(COD)Cl_2$, rt to 115 °C. (v) Sodium acetylacetonate, 50 °C or 1,3-bis(2,4,6-trimethylphenyl)propane-1,3-dione, potassium *tert*-butoxide, 50 °C.

N-heterocyclic carbene ligands (NHC),^{45,46} thereby avoiding population of thermal deactivation through energetically low-lying metal-centered (MC) d–d states which form a significant non-radiative decay channel.⁵ Typically, the population of d–d states is concomitant with severe geometrical distortions. Since most of the literature-known phosphorescent Pt(II) complexes demonstrate mixed-ligand-centered (LC) π – π^* and metal-to-ligand charge transfer character (MLCT), the population of d–d states poses a problem for the design of blue phosphorescent bidentate cyclometalated C^{*}C^{*} imidazolylidene Pt(II) complexes.⁵² As a consequence, research efforts focused on tridentate^{53–59} and tetradentate^{44,52,60–62} phosphorescent metal complexes with the aim to increase the rigidity of the ligand sphere of such complexes and prevent deformations in the excited state. Alternatively, employing ligands possessing large LC π – π^* energy gaps and strong σ -donating NHC ligands could effectively avoid the population of undesired MC d–d states as well.⁵² On the other hand, fabrication of OLEDs consists of multiple layers which ideally provide efficient electron and hole transport, while the main emitting molecule remains embedded in a host matrix.⁵ The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level of these materials generally has to match certain requirements depending on the properties of the emitter. Energy transfer from the phosphor to the triplet state of the host leads to efficiency loss. Therefore, the host material should have a higher triplet energy E_T than the phosphor which it accommodates.⁵ In particular, reports of efficient host materials for blue phosphors remain scarce. However, some researchers reported potential host materials with suitable E_T (~ 3.0 eV) for blue emitters. Their reported molecular design has repeatedly been reported to consist of spirobifluorene and spiroxanthene units displaying large HOMO–LUMO gaps.^{63–68} Due to their large band gaps, such spiro-conjugated molecules could also act as excellent ligands for the design of blue phosphorescent emitters. Phosphorescent metal complexes which bear such inherent electron-donating (or hole-transporting) functional groups have been referred to as bipolar phosphors.^{69,70} Steric bulkiness defined by the orthogonal spiro center can effectively suppress undesired intermolecular stacking (π – π or Pt–Pt interactions) which diminishes photophysical efficiency. In this context, van Pee and Catinat patented a tris homoleptic C^{*}N Ir(III) complex based on a spirobifluorene pyrazolyl motif.⁷¹ Related work⁷² from Yun et al. reported Ir(III) based on 9,9-dimethylfluorene as blue dopants for PhOLEDs. In this work, we convey the synthesis and photophysical properties of two novel bidentate cyclometalated C^{*}C^{*}_{spiro} imidazolylidene Pt(II) complexes **4a** and **4b** based on spirobifluorene in an

effort to combine the well-established photophysics of spirobifluorene with strong-field cyclometalated C^{*}C^{*} NHC ligands at a platinum center. Transient spectroscopic experiments and time-dependent density functional theory [(TD-)DFT] calculations were conducted in order to rationalize their absorbing and emissive photophysical behavior.

RESULTS AND DISCUSSION

Synthesis. The synthesis of the herein described emitter commenced from commercially available 2-bromo-9,9'-spirobifluorene (**1**) (compare Figure 1). Ligand-free Ullmann coupling conditions with imidazole provided the desired coupling product **2** with 48% yield after removal of the solvent and subsequent column chromatography with a mixture of dichloromethane (DCM) and 5% of methanol. Subsequent methylation of the imine nitrogen atom of the imidazole moiety with excess iodomethane yielded the respective imidazolium salt **3** in high yield (95%). With this precursor in hand, the syntheses of platinum complexes **4a** and **4b** were carried out in accordance with previous protocols, developed in our laboratories.⁴ Imidazolium salt **3** reacted with silver(I) oxide, resulting in its silver(I)carbene complex. Transmetalation with $Pt(COD)Cl_2$ and subsequent cyclometalation at elevated temperature furnished the C^{*}C^{*} platinum intermediate which was either treated with sodium acetylacetonate without prior deprotonation to afford **4a** or with 1,3-bis(2,4,6-trimethylphenyl)propane-1,3-dione and a base to afford **4b**.

Structural Characterization. All compounds were analyzed by 1H NMR, ^{13}C NMR, electrospray ionization-high-resolution mass spectrometry, and elemental analysis. Furthermore, the obtained Pt complexes were analyzed using ^{195}Pt -NMR and 2D-NMR techniques to facilitate the assignment of relevant signals (Figures S1–S20). The proton spectrum of **2** indicated that the NCHN signal appears as a singlet which is covered by further aromatic signals in the area between 8.5 and 8.3 ppm. The C_{spiro} is clearly observable at 65 ppm in the ^{13}C spectrum of **2** and for the precursor **3**. The NCHN signal, however, is clearly shifted down-field to 9.5 ppm, which is comparable to that of structurally related motifs.⁴⁵ Successful formation of the carbene–metal bond of **3** with respect to the Pt complexes **4a** and **4b** is confirmed by disappearance of the previously observed NCHN signal in the proton NMR of **3**. Singlets at –3324 and –3336 ppm in the ^{195}Pt NMR of **4a** and **4b** and the typical 1H – ^{195}Pt hetero-coupling in the proton spectra indicate the formation of the desired complexes.

Solid-state structures could be measured for **4a** and **4b**. Single crystals were grown by slow diffusion of *n*-heptane into a concentrated solution of the Pt complexes in DCM. The acetylacetonate containing Pt complex **4a** crystallizes in the triclinic crystal system with an assigned P1 space group, whereas **4b** prefers to crystallize in a monoclinic P2₁/n system. A Pt(1)–C(1) bond length of 1.946 Å is measured in Pt complex **4a** and 1.944 Å in complex **4b** (see Figures 2 and 3).

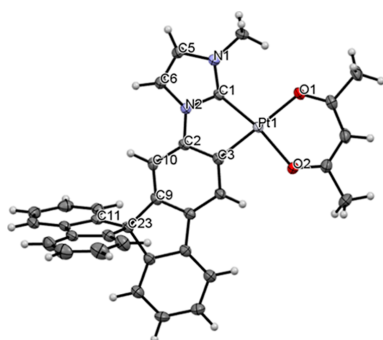


Figure 2. Depiction of the solid-state structure of compound **4a**. Thermal ellipsoids at 50% probability. Selected bond lengths [Å] and angles [°] for **4a**: Pt(1)–C(1) 1.946(3), Pt(1)–C(3) 1.983 (5), Pt(1)–O(1) 2.090(3), Pt(1)–O(2) 2.046(2), C(5)–C(6) 1.352(8), C(1)–Pt(1)–C(3) 79.7(1), O(1)–Pt(1)–O(2) 90.0(1), O(1)–Pt(1)–C(1)–N(1) 7.8(4), C(1)–N(2)–C(2)–C(3) –0.7(4), and C(10)–C(9)–C(23)–C(11) 56.1(1).

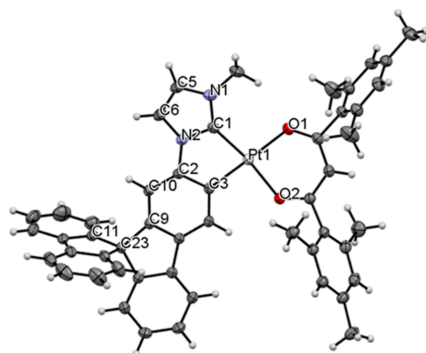


Figure 3. Depiction of the solid-state structure of compound **4b**. Thermal ellipsoids at 50% probability. Selected bond lengths [Å] and angles [°] for **4b**: Pt(1)–C(1) 1.944(2), Pt(1)–C(3) 1.987 (2), Pt(1)–O(1) 2.094(1), Pt(1)–O(2) 2.050(1), C(5)–C(6) 1.341(3), C(1)–Pt(1)–C(3) 80.07(8), O(1)–Pt(1)–O(2) 89.45(5), O(1)–Pt(1)–C(1)–N(1) 6.9(2), C(1)–N(2)–C(2)–C(3) –1.2(2), and C(10)–C(9)–C(23)–C(11) 49.3(3).

The Pt(1)–C(3) bond in **4a** is 1.983 Å long, while the same bond measures 1.987 Å in **4b**. These values and the Pt–O bonds are within the same range as those of related structural motifs.⁷³ The C(5)–C(6) bond measures 1.353 Å (1.341 Å) and indicates double bond character in both complexes. Additionally, selected bond angles and dihedral angles in both complexes are indicative of a slightly distorted square-planar coordination geometry around the platinum central atom. For

example, in complex **4a**, the C(1)–Pt(1)–O(1) bond angle measures 79.7° and the O(1)–Pt(1)–O(2) 90.0° and, respectively, for **4b**, 80.07 and 89.45°. The planarity of the complexes is further confirmed by the dihedral angle between the two ligands attached to the platinum metal center, O(1)–Pt(1)–C(1)–N(1) 7.8° for **4a** and O(1)–Pt(1)–C(1)–N(1) 6.9° for **4b**. The closest Pt–Pt distance observed in the packing diagram measures 3.458 Å for complex **4a**. The Pt–Pt distance in **4b** measures 9.150 Å (see Figures S21 and S22). In the solid state, the quasi-orthogonal spirobifluorene forces the C^{Ac}* ligand to overlap with the auxiliary acetylacetonate ligand which results in a short Pt–Pt distance of only 3.458 Å, which could be indicative of weak Pt–Pt interactions since the value is slightly below the sum of the van der Waals radii. In contrast, the bulky mesityl groups of the auxiliary ligand in **4b** and the orthogonally positioned spirobifluorene unit of the C^{Ac}* ligand result in a more distorted solid-state structure and a large Pt–Pt distance of 9.150 Å. Thermogravimetric analysis was carried out with a heat rate of 5 K/min and suggested that **4b** with the bulky mesityl-substituted β-diketonate ligand leads to increased thermal stability. Mass loss in **4b** can be observed at temperatures above 300 °C, whereas a mass loss of 5% can be already observed starting at 150 °C for complex **4a** (Figures S23 and S24).

Basic Photophysics and Characterization of Poly(methylmethacrylate) Films. Furthermore, quantum yield, color coordinates, and emission lifetimes were determined for the complexes in poly(methylmethacrylate) (PMMA) films. The absorption measurements were performed in DCM solutions with an analyte concentration of 5×10^{-5} mol·L^{−1} (Figure 4). Both spectra are nearly identical with stronger

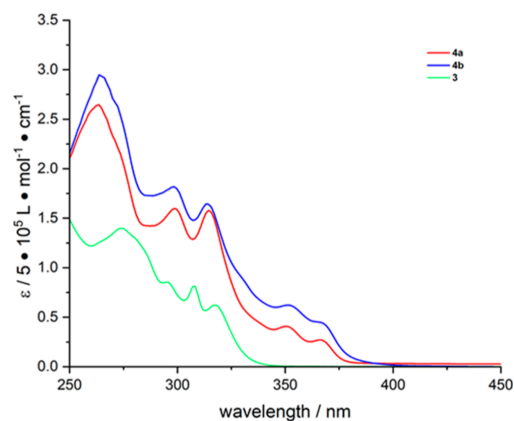


Figure 4. UV/vis absorption spectra of the precursor **3** and its respective platinum complexes **4a** and **4b** recorded in DCM solutions ($c = 5 \times 10^{-5}$ M) in a quartz glass cuvette ($d = 1$ cm) at room temperature.

absorption observed for complex **4b** due to its mesityl-substituted acetylacetonate auxiliary ligand. The first two weak absorption bands appear close to the UV/vis border at 345–375 nm. Two additional stronger transitions are observed between 300 and 325 nm. The absorption band at 325 nm is more pronounced compared to the transition at 300 nm for

both complexes. The strongest absorption band is observed at 265 nm.

Additionally, the absorption spectrum of ligand **3** was measured. The transitions at lower wavelengths are in good accordance with those of the Pt complexes **4a** and **4b**; however, the two transitions ranging from 345 to 375 nm cannot be observed for ligand **3**.

The solid-state emission spectra were recorded in PMMA (for results in solution, see the next section and Supporting Information) matrices which were prepared prior to the measurements with 2 wt % emitter load, effectively mimicking the amorphous environment of PhOLEDs.⁷⁴ The obtained emission spectra are depicted in Figure 5. Contrary to our

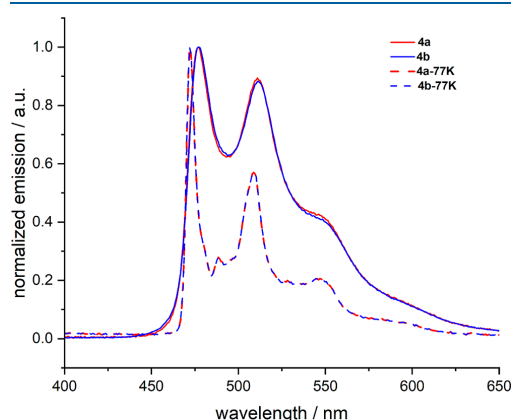


Figure 5. Emission spectra of complexes **4a** and **4b** in a PMMA matrix (2 wt % emitter load) at room temperature. Dashed lines: emission spectra of **4a** and **4b** measured at 77 K in a glassy matrix (2-MeTHF) with a concentration of 5×10^{-4} M in an argon atmosphere.

expectations, both spectra are virtually identical, almost solvent-/matrix-independent and they show equal emission maxima at 478 nm. Two further weaker emission bands are observed at 515 and 550 nm displaying a profound vibrational fine structure which suggests a ligand-centered (³LC) π - π^* transition in the emissive state.

Additionally, emission spectra were recorded at 77 K in proper glassy matrices of 2-methyltetrahydrofuran (2-MeTHF) in an argon atmosphere. The spectra of both complexes display identical emissive behavior at low temperature. In comparison to the room temperature measurements, emission spectra at 77 K only slightly differ. The emission bands are more resolved, and a small hypsochromic shift of 6 nm can be observed.

Both complexes demonstrate high photoluminescence quantum yields of 81 and 87%, respectively. Their Commission internationale de l'éclairage (CIE) coordinates of (0.218; 0.482) and (0.216; 0.480) render both complexes bluish-green emitters. The excited-state lifetimes of both complexes are too long for a conventional time-correlated single photon counting (TCSPC) setup with laser diodes pulsed at very high frequencies, which is why these quantities have been measured using laser flash photolysis (LFP, see below and the Experimental Section for details). Emission lifetime measurements in the solid state revealed that the photo-excited complexes have biexponential decay traces (see Supporting Information, Figures S26 and S27), which is most

likely due to self-quenching in the PMMA films. At the lowest laser power employed, **4a** has an amplitude-weighted average excited-state lifetime of 52.1 μ s and **4b** 38.8 μ s. These comparatively long decay times also indicate that the effect of SOC between the metal center and ligand is small which causes a small zero-field splitting which is a typical feature of ³LC emissive states in metal complexes.⁵ The low non-radiative decay rates k_{nr} further suggest that the population of undesired d-d-states and thus molecular distortions are effectively suppressed. This permits radiative decay which is reflected in the high quantum yields of both complexes. In comparison to previous imidazole-based cyclometalated platinum(II) complexes, the spirobifluorene-substituted complexes presented herein show identical emission independently of the auxiliary ligand. Previously, the introduction of mesityl-substituted acetylacetonate ligands leads to a bathochromic shift of the emission maximum wavelength concomitant with significant increase in quantum yield.⁷⁵ This known effect of the auxiliary ligand is completely shut off for the spirobifluorene-derived Pt(II) complexes **4a** and **4b**. This observation is indicative of a photophysical profile which is predominantly governed by the novel C[∧]C^{*}_{spiro}-NHC ligand (Table 1).

Table 1. Photoluminescence Data of **4a** and **4b**^a

	Φ^b (%)	λ_{em}^c (nm)	CIE ^d $x; y$	τ_0^e (μ s)	k_r^f ($10^3 \cdot s^{-1}$)	k_{nr}^g ($10^3 \cdot s^{-1}$)
4a	81	478	0.218; 0.482	52.1	15.5	3.65
4b	87	478	0.216; 0.480	38.8	22.4	3.35

^aPL in a PMMA matrix (2 wt % emitter load, $\lambda_{exc} = 305$ nm). ^bPLQY at room temperature and $\lambda_{exc} = 305$ nm. ^cEmission wavelength with maximum intensity at room temperature. ^dCIE color coordinates. ^eAmplitude-averaged experimental τ_0 measured upon 355 nm excitation using 10 ns pulses (7.5 mJ pulse energy). ^f $k_r = \Phi/\tau_0$. ^g $k_{nr} = (1 - \Phi)/\tau_0$.

Time-Resolved Optical Spectroscopy and Applications in Solution. The excited states of complexes **4a** and **4b** were investigated by the LFP monitoring of both transient absorption (TA) and emission signals upon 355 nm excitation with laser pulses of ~ 10 ns duration⁷⁶ in different environments (DCM, THF, and PMMA). Additional quenching experiments with a literature-known triplet energy acceptor (*p*-terphenyl⁷⁷) allowed us to obtain clear evidence for the triplet nature of both excited Pt(II) complexes and their high triplet energies.

Similar to the emission spectra (previous section Figures 5 and S25), the TA spectra of both Pt(II) complexes in THF are nearly identical considering the shifts and relative intensities of the absorption (emission) bands. These excited species are also very long-lived in solution (averaged from three independent kinetic measurements as displayed in Figure 6: $36.4 \pm 1.7 \mu$ s for **4a** and $31.9 \pm 0.9 \mu$ s for **4b**), compared to most of their structural congeners.⁴ In contrast to the experiments in PMMA films, the kinetic emission traces obtained for the complexes in solution possess clear first-order decays. The TA and emission lifetime measurements of Figure 6 allow us to draw two main conclusions: First, both emission and absorption lifetimes for one complex are essentially identical, which is a strong indicator for only one excited species. Second, the similar lifetimes of both complexes further confirm the minor influence originating from the substituents

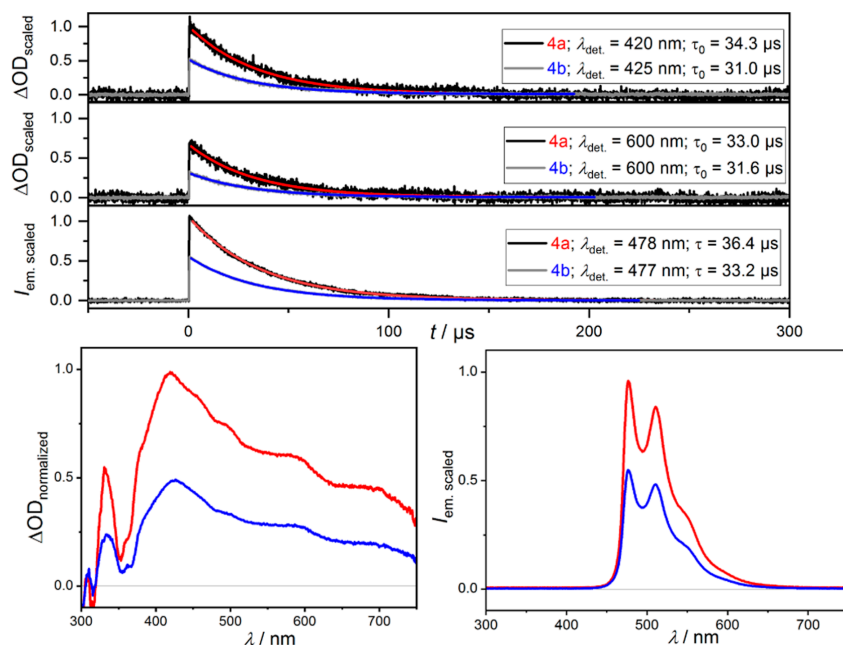


Figure 6. Spectra (top) and excited-state decay (bottom) of **4a** (red) and **4b** (blue), normalized to 1 (**4a**) or 0.5 (**4b**) for a clear distinction between the two complexes. The relative intensities were maintained within the spectra and kinetic traces (for original TA spectra, compare Figures S32 and S33). Upper panel: TA (left) and emission spectra (right) of **4a** (red) and **4b** (blue) in deoxygenated THF after 355 nm pulsed laser excitation. Lower panel: decay traces at selected wavelengths (upper and middle panel for TA, lower panel for emission), with color-coded monoexponential fitting functions and resulting lifetimes.

of the β -diketonate ligands on the excited state of **4a** or **4b** (see also the previous section and spin densities in Figure 10 for **4a** and Figure S37 for **4b**). Spectral and kinetic data in PMMA (Supporting Information Figures S25–S27, S32, and S33 and Table S1) lead to similar results, that is, nearly identical TA and emission spectra, which can be assigned to one long-lived excited species in each of the complexes. Consistent with expectation, the excited-state lifetimes for **4a** and **4b** are longer in the solid matrix compared to those in liquid THF (by about 40 and 20%, respectively). However, we regard the kinetic results obtained in THF as more reliable owing to their clear first-order decays under our laser excitation conditions. Both complexes showed pronounced photodecomposition during the laser measurements in DCM, but these undesired effects are completely absent in THF, which was confirmed by control UV/vis measurements before and after the LFP experiments.

The solvent has essentially no effect on the excited-state properties since emission spectra in DCM, THF, and PMMA (Figure S25, recorded on the same fluorimeter under identical conditions, no decomposition throughout the measurement) do not show any solvatochromic shifts for **4a** and **4b**. This is also in line with the lowest excited states being ligand-centered rather than charge-transfer states.

From the maximum of the emission spectra, the lower limit for the excited-state energy of **4a** and **4b** can be estimated with ~ 2.5 eV, thereby making a triplet–triplet energy transfer (TTET) to *p*-terphenyl (triplet energy: $E_T = 2.5$ eV)⁷⁷ thermodynamically feasible.^{77,78} This TTET from $^3[4a]$ to *p*-terphenyl was observed spectroscopically (Figure 7 for **4a** and

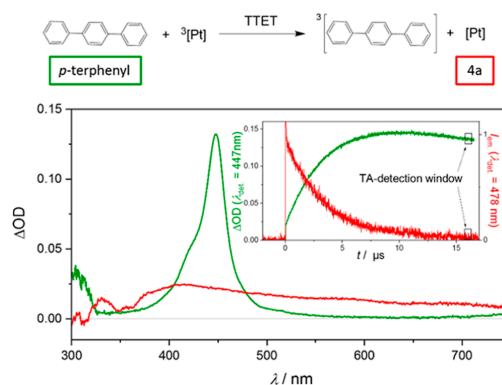


Figure 7. Reaction scheme of TTET from $^3[4a]$ to *p*-terphenyl. TA spectra of $^3[4a]$ (red trace, time delay 20 ns) and 3p -terphenyl after TTET (green trace, time delay 16 μ s). Inset: emission decay of $^3[4a]$ with 1 mM *p*-terphenyl (red trace) and corresponding 3p -terphenyl formation (green trace). The boxes indicate the delay time for the detection of the 3p -terphenyl spectrum.

Figure S30 for **4b**): The emission lifetime decreases (compared to the lifetime without the quencher present, Figure 6), and a new absorption signal arises within the same timeframe (inset Figure 7). The TA spectrum of the newly formed species can be unambiguously assigned to 3p -

terphenyl.^{77,79,80} The TTET rate constants with *p*-terphenyl as the energy acceptor were estimated from Stern–Volmer analyses, and they are essentially identical for both complexes ($\sim 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Hence, steric effects of the different β -diketonate auxiliary ligands do not significantly affect the donor–acceptor orbital overlap, further confirming the very similar excited-state character of both compounds with mainly C^{*}C^{*}–spiro–NHC-localized triplets (see also DFT calculations below).

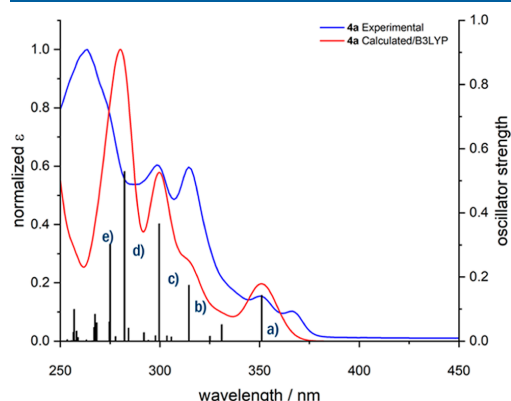


Figure 8. Comparison of the experimental (blue) and calculated (red, 0.333 eV half-width) absorbance spectrum of **4a**. Transitions are represented by oscillator strengths (black) as obtained from the calculations.

The high triplet energy of both complexes was further confirmed in an LED (370 nm)-driven irradiation reaction using **4a** or **4b** as the photocatalyst for the *cis*–*trans* isomerization of methyl cinnamate (Figure S31 and Table S2), which is known to proceed via TTET.^{78,81,82}

In the photostationary state, the *cis*–*trans* ratio is close to 1:1; therefore, the E_T of **4a** and **4b** seems to surpass that of both cinnamate isomers (i.e., amounts to $>2.4 \text{ eV}^{77}$), resulting in similar rates for the *cis*-to-*trans* and the *trans*-to-*cis* conversion via energy transfer.^{78,82,83} These initial NMR-scale irradiation experiments in DCM gave turnover numbers for both photosensitizers in the order of 40. These results are quite promising considering the much lower photostability of the complexes in this solvent compared to THF (see above). The LFP and NMR-scale energy transfer experiments of this section indicate that the novel Pt complexes might as well be employed as photosensitizers for energy transfer photocatalysis.^{84–87}

Quantum Chemical Calculations. DFT and TD-DFT calculations were carried out in order to provide a more profound understanding of the photophysical behavior of both Pt complexes presented herein.

For this purpose, the Gaussian16 program package^{88,89} was utilized. The calculations were carried out using the hybrid functionals B3LYP^{90–94} and PBE0^{95,96} together with the triple-zeta 6-311G*^{97–99} basis set and dispersion correction (D3BJ).^{100,101} Additionally, Pt was described by a LANL2DZ^{102–105} effective core potential. The combination of PBE0/6-311G* yielded slightly but not significantly better results for the bond lengths and angles when compared with

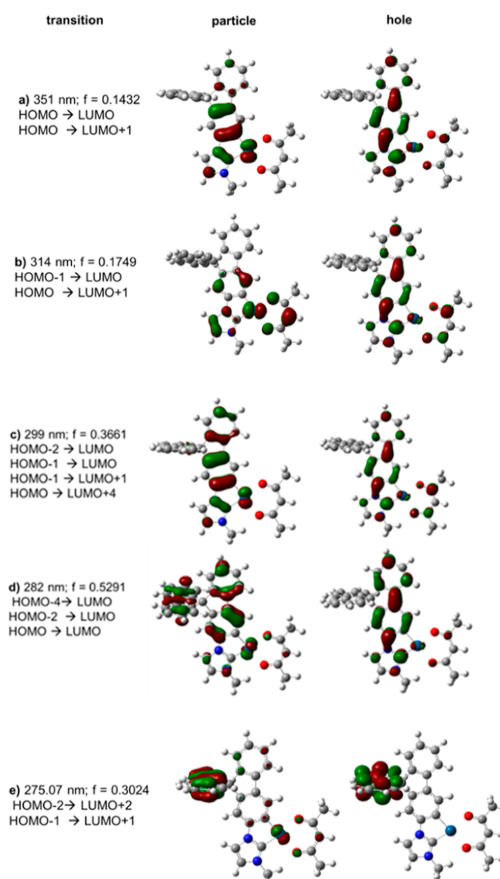


Figure 9. NTO analysis (isoval: MO = 0.04) of complex **4a** for the transitions (a–e) labeled in Figure 8.

the experimentally measured solid-state structure. However, based on comparison with the experimental absorbance spectra, the combination of B3LYP/6-311G* afforded slightly better results than PBE0. The frontier molecular orbitals of **4a** and **4b** are given in Figures S34 and S35 and the excited-state spin densities in Figures S36 and S37.

To gain deeper insights into the absorption processes of both Pt complexes, (TD-)DFT calculations of the ground-state structure of **4a** were carried out in DCM to simulate the absorbance spectrum and attribute orbital transitions to the experimentally observed absorption bands. Figure 8 compares the experimentally obtained spectrum with the simulated spectrum (see Figure S38 for **4b**). Of the first two low-energy bands at 350 and 360 nm, only the one at 350 nm is resolved in good correspondence. The remaining higher-energy bands are represented well by transitions b and c. The broadest and most intense absorbance band at 260 nm can be described by strongest transitions d and e which are red-shifted by approximately 20 nm in the simulated spectrum.

For better visualization, the corresponding natural transition orbitals (NTOs) were calculated (Figures 9 and S39 for **4b**).

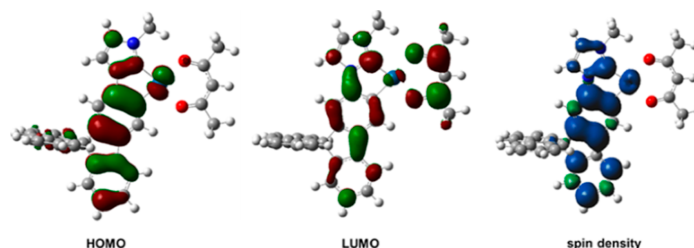


Figure 10. Calculated frontier molecular orbitals for the ground state (left and center, isoval: MO = 0.03) and spin density for the thermodynamically favored excited state (right, isoval: density = 0.002) for complex **4a**.

Transition a is assigned to the low-energy band at 350 nm which is mainly a result of a charge transfer which takes places from orbitals located on the cyclometalated ligand with metal contribution to orbitals which are also located on the C[∧]C* ligand. Therefore, this transition can be defined as an intraligand charge transfer (ILCT) mixed with a metal to ligand charge transfer (MLCT).

Transitions b and c are mainly characterized by charge transfers from orbitals which are located all over the in-plane conjugated parts of the complex, while the perpendicular fluorene unit connected with the spiro-C atom does not participate in these charge transfer processes. The opposite is observed for transitions d and e. Here, charge transfer occurs from the perpendicularly arranged fluorene unit to the cyclometalated part of the ligand (ILCT) alongside the contribution of the metal center (MLCT). Almost exclusive ILCT is observed for transition e. All transitions seem to be little influenced by the auxiliary acetylacetonate ligand. The emissive process was modeled by plotting the frontier molecular orbitals of the ground state and the spin density of the excited triplet state (Figure 10 for **4a** and Figures S35 and S37 for **4b**). The HOMO is distributed over the C[∧]C* ligand and the metal with little electron density remaining on the perpendicular fluorene motif. The LUMO is spread over the entire molecule except for the perpendicularly connected fluorene unit. The spin density in the emissive state is solely located on the cyclometalated ligand and the metal. Exactly the same spin density distribution is observed for complex **4b**. Consequently, the emissive state can be ascribed as an ³LC_{C[∧]C*} (ligand-centered) state with little contribution of the metal center. The auxiliary ligand plays no role in the emissive process which explains why equal photophysical data is obtained for both complexes (vide supra).

CONCLUSIONS

Two novel phosphorescent C[∧]C* cyclometalated Pt(II) complexes with an adjacent spirofluorene motif were synthesized, characterized, and reported in this paper. Both complexes feature high quantum yields of up to 87% and show identical photophysical properties which is a result of a pronounced ³LC_{C[∧]C*} state, effectively avoiding the population of undesired d–d states and thereto related molecular distortions. TA measurements of both complexes further indicate that the dominant emissive process in both complexes originates from a long-lived ligand-centered triplet state with a high triplet energy of about 2.5 eV. Additional energy transfer experiments with *p*-terphenyl and a cinnamate as the olefinic substrate provide further experimental evidence

of the triplet character of the emissive species. DFT and TD-DFT calculations are in good agreement with experimental results and emphasize the strongly dominating influence of the cyclometalated spiro-conjugated NHC ligand.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02141>.

1D/2D NMR spectra, additional photoluminescence and TA data, frontier molecular orbitals and spin densities, TGA plots of compounds **4a/4b**, details of the solid-state structure determination and the synthesis and characterization, computational details, and electrochemistry data (PDF). xyz-Coordinates of the optimized geometries (XYZ) (PDF)

Accession Codes

CCDC 2179090–2179091 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Thomas Strassner – *Physikalische Organische Chemie, Technische Universität Dresden, 01069 Dresden, Germany*; orcid.org/0000-0002-7648-457X; Phone: (+49)351-463-38571; Email: thomas.strassner@tu-dresden.de; Fax: (+49)351-463-39679

Christoph Kerzig – *Department of Chemistry, Johannes Gutenberg University, 55128 Mainz, Germany*; orcid.org/0000-0002-1026-1146; Phone: (+49)6131-39-22479; Email: ckkerzig@uni-mainz.de

Authors

Tim Riesebeck – *Physikalische Organische Chemie, Technische Universität Dresden, 01069 Dresden, Germany*
Maria-Sophie Bertrams – *Department of Chemistry, Johannes Gutenberg University, 55128 Mainz, Germany*
Sergej Stipurin – *Physikalische Organische Chemie, Technische Universität Dresden, 01069 Dresden, Germany*
Kai Konowski – *Physikalische Organische Chemie, Technische Universität Dresden, 01069 Dresden, Germany*

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.inorgchem.2c02141>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. S.S. and K.K. carried out X-ray diffractometry measurements.

Funding

Financial support provided by the Chemical Industry Fonds (Liebig Fellowship to C.K.) is gratefully acknowledged.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We want to thank the ZIH Dresden for allocating computational time on their high-performance computing system.

■ REFERENCES

- (1) Lee, S.; Han, W.-S. Cyclometalated Ir(III) complexes towards blue-emissive dopant for organic light-emitting diodes: fundamentals of photophysics and designing strategies. *Inorg. Chem. Front.* **2020**, *7*, 2396–2422.
- (2) Pal, A. K.; Hanan, G. S. Design, synthesis and excited-state properties of mononuclear Ru(II) complexes of tridentate heterocyclic ligands. *Chem. Soc. Rev.* **2014**, *43*, 6184–6197.
- (3) Chi, Y.; Tong, B.; Chou, P.-T. Metal complexes with pyridyl azolates: Design, preparation and applications. *Coord. Chem. Rev.* **2014**, *281*, 1–25.
- (4) Strassner, T. Phosphorescent Platinum(II) Complexes with CAC* Cyclometalated NHC Ligands. *Acc. Chem. Res.* **2016**, *49*, 2680–2689.
- (5) Yersin, H. *Highly Efficient OLEDs with Phosphorescent Materials*; Wiley-VCH: Weinheim, 2007.
- (6) Yam, V. W.-W.; Chan, A. K.-W.; Hong, E. Y.-H. Charge-transfer processes in metal complexes enable luminescence and memory functions. *Nat. Rev. Chem.* **2020**, *4*, 528–541.
- (7) Ravaro, L. P.; Zannoni, K. P.; de Camargo, A. S. de. Luminescent Copper(I) complexes as promising materials for the next generation of energy-saving OLED devices. *Energy Rep.* **2020**, *6*, 37–45.
- (8) Au, V. K.-M. Organic Light-Emitting Diodes Based on Luminescent Self-Assembled Materials of Copper(I). *Energy Fuels* **2021**, *35*, 18982–18999.
- (9) De Cola, L.; Belser, P.; von Zelewsky, A.; Vögtle, F. Design, synthesis and photophysics of ruthenium and osmium complexes through 20 years of collaboration. *Inorg. Chim. Acta* **2007**, *360*, 775–784.
- (10) Chang, S.-H.; Chang, C.-F.; Liao, J.-L.; Chi, Y.; Zhou, D.-Y.; Liao, L.-S.; Jiang, T.-Y.; Chou, T.-P.; Li, E. Y.; Lee, G.-H.; Kuo, T.-Y.; Chou, P.-T. Emissive osmium(II) complexes with tetradentate bis(pyridylpyrazolate) chelates. *Inorg. Chem.* **2013**, *52*, S867–S875.
- (11) Chou, P.-T.; Chi, Y. Osmium- and Ruthenium-Based Phosphorescent Materials: Design, Photophysics, and Utilization in OLED Fabrication. *Eur. J. Inorg. Chem.* **2006**, *2006*, 3319–3332.
- (12) Tang, C. W.; VanSlyke, S. A. Organic electroluminescent diodes. *Appl. Phys. Lett.* **1987**, *51*, 913–915.
- (13) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. High-efficiency organic electrophosphorescent devices with tris(2-phenylpyridine)iridium doped into electron-transporting materials. *Appl. Phys. Lett.* **2000**, *77*, 904–906.
- (14) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. Very high-efficiency green organic light-emitting devices based on electrophosphorescence. *Appl. Phys. Lett.* **1999**, *75*, 4–6.
- (15) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. Nearly 100% internal phosphorescence efficiency in an organic light-emitting device. *Int. J. Appl. Phys.* **2001**, *90*, S048–S051.
- (16) Zhao, Q.; Li, F.; Huang, C. Phosphorescent chemosensors based on heavy-metal complexes. *Chem. Soc. Rev.* **2010**, *39*, 3007–3030.
- (17) Wenger, O. S. Vapochromism in organometallic and coordination complexes: chemical sensors for volatile organic compounds. *Chem. Rev.* **2013**, *113*, 3686–3733.
- (18) Ladouceur, S.; Zysman-Colman, E. A Comprehensive Survey of Cationic Iridium(III) Complexes Bearing Nontraditional Ligand Chelation Motifs. *Eur. J. Inorg. Chem.* **2013**, *2013*, 2985–3007.
- (19) You, Y.; Cho, S.; Nam, W. Cyclometalated iridium(III) complexes for phosphorescence sensing of biological metal ions. *Inorg. Chem.* **2014**, *53*, 1804–1815.
- (20) Zhou, J.; Li, J.; Zhang, K. Y.; Liu, S.; Zhao, Q. Phosphorescent iridium(III) complexes as lifetime-based biological sensors for photoluminescence lifetime imaging microscopy. *Coord. Chem. Rev.* **2022**, *453*, 214334.
- (21) Chang, K.-C.; Sun, S.-S.; Odago, M. O.; Lees, A. J. Anion recognition and sensing by transition-metal complexes with polarized N H recognition motifs. *Coord. Chem. Rev.* **2015**, *284*, 111–123.
- (22) Huynh, L.; Wang, Z.; Yang, J.; Stoeva, V.; Lough, A.; Manners, I.; Winnik, M. A. Evaluation of Phosphorescent Rhenium and Iridium Complexes in Polythiophenylphosphazene Films for Oxygen Sensor Applications. *Chem. Mater.* **2005**, *17*, 4765–4773.
- (23) Pang, Z.; Gu, X.; Yekta, A.; Masoumi, Z.; Coll, J. B.; Winnik, M. A.; Manners, I. Phosphorescent oxygen sensors utilizing sulfur-nitrogen-phosphorus polymer matrices. *Adv. Mater.* **1996**, *8*, 768–771.
- (24) Zhang, Q.; Li, J.; Shizu, K.; Huang, S.; Hirata, S.; Miyazaki, H.; Adachi, C. Design of efficient thermally activated delayed fluorescence materials for pure blue organic light emitting diodes. *J. Am. Chem. Soc.* **2012**, *134*, 14706–14709.
- (25) Youn Lee, S.; Yasuda, T.; Nomura, H.; Adachi, C. High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazine-based donor–acceptor hybrid molecules. *Appl. Phys. Lett.* **2012**, *101*, 093306.
- (26) Serevičius, T.; Nakagawa, T.; Kuo, M.-C.; Cheng, S.-H.; Wong, K.-T.; Chang, C.-H.; Kwong, R. C.; Xia, S.; Adachi, C. Enhanced electroluminescence based on thermally activated delayed fluorescence from a carbazole-triazine derivative. *Phys. Chem. Chem. Phys.* **2013**, *15*, 15850–15855.
- (27) Méhes, G.; Nomura, H.; Zhang, Q.; Nakagawa, T.; Adachi, C. Enhanced electroluminescence efficiency in a spiro-acridine derivative through thermally activated delayed fluorescence. *Angew. Chem., Int. Ed.* **2012**, *51*, 11311–11315.
- (28) Nakagawa, T.; Ku, S.-Y.; Wong, K.-T.; Adachi, C. Electroluminescence based on thermally activated delayed fluorescence generated by a spirobifluorene donor-acceptor structure. *Chem. Commun.* **2012**, *48*, 9580–9582.
- (29) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly efficient organic light-emitting diodes from delayed fluorescence. *Nature* **2012**, *492*, 234–238.
- (30) Xia, G.; Qu, C.; Zhu, Y.; Ye, J.; Ye, K.; Zhang, Z.; Wang, Y. A TADF Emitter Featuring Linearly Arranged Spiro-Donor and Spiro-Acceptor Groups: Efficient Nondoped and Doped Deep-Blue OLEDs with CIEy < 0.1. *Angew. Chem., Int. Ed.* **2021**, *60*, 9598–9603.
- (31) Karthik, D.; Jung, Y. H.; Lee, H.; Hwang, S.; Seo, B.-M.; Kim, J.-Y.; Han, C. W.; Kwon, J. H. Acceptor-Donor-Acceptor-Type Orange-Red Thermally Activated Delayed Fluorescence Materials Realizing External Quantum Efficiency Over 30% with Low Efficiency Roll-Off. *Adv. Mater.* **2021**, *33*, No. e2007724.
- (32) Jeon, S. K.; Lee, H. L.; Yook, K. S.; Lee, J. Y. Recent Progress of the Lifetime of Organic Light-Emitting Diodes Based on Thermally Activated Delayed Fluorescent Material. *Adv. Mater.* **2019**, *31*, No. e1803524.
- (33) Yang, J.-G.; Song, X.-F.; Wang, J.; Li, K.; Chang, X.; Tan, L.-Y.; Liu, C.-X.; Yu, F.-H.; Cui, G.; Cheng, G.; To, W.-P.; Yang, C.; Che, C.-M.; Chen, Y. Highly Efficient Thermally Activated Delayed Fluorescence from Pyrazine-Fused Carbene Au(I) Emitters. *Chem.—Eur. J.* **2021**, *27*, 17834–17842.
- (34) Zhou, D.; To, W.-P.; Tong, G. S. M.; Cheng, G.; Du, L.; Phillips, D. L.; Che, C.-M. Tetradentate Gold(III) Complexes as Thermally Activated Delayed Fluorescence (TADF) Emitters:

Microwave-Assisted Synthesis and High-Performance OLEDs with Long Operational Lifetime. *Angew. Chem., Int. Ed.* **2020**, *59*, 6375–6382.

(35) Shi, S.; Jung, M. C.; Coburn, C.; Tadler, A.; Sylvinson, M. R.; Djurovich, P. I.; Forrest, S. R.; Thompson, M. E. Highly Efficient Photo- and Electroluminescence from Two-Coordinate Cu(I) Complexes Featuring Nonconventional N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2019**, *141*, 3576–3588.

(36) Di, D.; Romanov, A. S.; Yang, L.; Richter, J. M.; Rivett, J. P. H.; Jones, S.; Thomas, T. H.; Abdi Jalebi, M.; Friend, R. H.; Linnolahti, M.; Bochmann, M.; Credgington, D. High-performance light-emitting diodes based on carbene-metal-amides. *Science* **2017**, *356*, 159–163.

(37) Feng, J.; Yang, L.; Romanov, A. S.; Ratanapreechachai, J.; Reponen, A.-P. M.; Jones, S. T. E.; Linnolahti, M.; Hele, T. J. H.; Köhler, A.; Bässler, H.; Bochmann, M.; Credgington, D. Environmental Control of Triplet Emission in Donor–Bridge–Acceptor Organometallics. *Adv. Funct. Mater.* **2020**, *30*, 1908715.

(38) To, W.-P.; Cheng, G.; Tong, G. S. M.; Zhou, D.; Che, C.-M. Recent Advances in Metal-TADF Emitters and Their Application in Organic Light-Emitting Diodes. *Front. Chem.* **2020**, *8*, 653.

(39) Ravinson, D. S. M.; Thompson, M. E. Thermally assisted delayed fluorescence (TADF): fluorescence delayed is fluorescence denied. *Mater. Horiz.* **2020**, *7*, 1210–1217.

(40) Gernert, M.; Balles-Wolf, L.; Kerner, F.; Müller, U.; Schmiedel, A.; Holzapfel, M.; Marian, C. M.; Pflaum, J.; Lambert, C.; Steffen, A. Cyclic (Amino)aryl carbenes Enter the Field of Chromophore Ligands: Expanded π System Leads to Unusually Deep Red Emitting CuI Compounds. *J. Am. Chem. Soc.* **2020**, *142*, 8897–8909.

(41) Zhang, Y.; Lee, T. S.; Favale, J. M.; Leary, D. C.; Petersen, J. L.; Scholes, G. D.; Castellano, F. N.; Milsman, C. Delayed fluorescence from a zirconium(IV) photosensitizer with ligand-to-metal charge-transfer excited states. *Nat. Chem.* **2020**, *12*, 345–352.

(42) Yam, V. W.-W.; Au, V. K.-M.; Leung, S. Y.-L. Light-Emitting Self-Assembled Materials Based on d(8) and d(10) Transition Metal Complexes. *Chem. Rev.* **2015**, *115*, 7589–7728.

(43) Fleetham, T.; Li, G.; Li, J. Phosphorescent Pt(II) and Pd(II) Complexes for Efficient, High-Color-Quality, and Stable OLEDs. *Adv. Mater.* **2017**, *29*, 1601861.

(44) Moon, Y. K.; Huh, J.-S.; Kim, S.; Kim, S.; Yi, S. Y.; Kim, J.-J.; You, Y. Synthetic Strategy for Preserving Sky-Blue Electrophosphorescence in Square-Planar Pt(II) Complexes. *ACS Appl. Electron. Mater.* **2020**, *2*, 604–617.

(45) Unger, Y.; Meyer, D.; Molt, O.; Schildknecht, C.; Münster, I.; Wagenblast, G.; Strassner, T. Green-blue emitters: NHC-based cyclometalated Pt(C[∧]C*)(acac) complexes. *Angew. Chem., Int. Ed.* **2010**, *49*, 10214–10216.

(46) Hudson, Z. M.; Sun, C.; Helander, M. G.; Chang, Y.-L.; Lu, Z.-H.; Wang, S. Highly efficient blue phosphorescence from triarylboron-functionalized platinum(II) complexes of N-heterocyclic carbenes. *J. Am. Chem. Soc.* **2012**, *134*, 13930–13933.

(47) Huang, L.-M.; Tu, G.-M.; Chi, Y.; Hung, W.-Y.; Song, Y.-C.; Tseng, M.-R.; Chou, P.-T.; Lee, G.-H.; Wong, K.-T.; Cheng, S.-H.; Tsai, W.-S. Mechanoluminescent and efficient white OLEDs for Pt(II) phosphors bearing spatially encumbered pyridinyl pyrazolate chelates. *J. Mater. Chem. C* **2013**, *1*, 7582–7592.

(48) Soellner, J.; Pinter, P.; Stipurin, S.; Strassner, T. Platinum(II) Complexes with Bis(pyrazolyl)borate Ligands: Increased Molecular Rigidity for Bidentate Ligand Systems. *Angew. Chem., Int. Ed.* **2021**, *60*, 3556–3560.

(49) Stipurin, S.; Strassner, T. C[∧]C* Platinum(II) Complexes with Electron-Withdrawing Groups and Beneficial Auxiliary Ligands: Efficient Blue Phosphorescent Emission. *Inorg. Chem.* **2021**, *60*, 11200–11205.

(50) Arnal, L.; Fuentes, S.; Martín, A.; Sicilia, V. The Use of Cyclometalated NHCs and Pyrazoles for the Development of Fully Efficient Blue Pt^{II} Emitters and Pt/Ag Clusters. *Chem.—Eur. J.* **2018**, *24*, 9377–9384.

(51) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. Synthesis and characterization of

phosphorescent cyclometalated platinum complexes. *Inorg. Chem.* **2002**, *41*, 3055–3066.

(52) Li, K.; Cheng, G.; Ma, C.; Guan, X.; Kwok, W.-M.; Chen, Y.; Lu, W.; Che, C.-M. Light-emitting platinum(II) complexes supported by tetradentate dianionic bis(N-heterocyclic carbene) ligands: towards robust blue electrophosphors. *Chem. Sci.* **2013**, *4*, 2630.

(53) Strassert, C. A.; Chien, C.-H.; Galvez Lopez, M. D.; Kourkoulos, D.; Hertel, D.; Meerholz, K.; De Cola, L. Switching on luminescence by the self-assembly of a platinum(II) complex into gelating nanofibers and electroluminescent films. *Angew. Chem., Int. Ed.* **2011**, *50*, 946–950.

(54) Cebrián, C.; Mauro, M.; Kourkoulos, D.; Mercandelli, P.; Hertel, D.; Meerholz, K.; Strassert, C. A.; De Cola, L. Luminescent neutral platinum complexes bearing an asymmetric $\text{NN}^{\wedge}\text{N}$ ligand for high-performance solution-processed OLEDs. *Adv. Mater.* **2013**, *25*, 437–442.

(55) Galstyan, A.; Naziruddin, A. R.; Cebrián, C.; Iordache, A.; Daniliuc, C. G.; De Cola, L.; Strassert, C. A. Correlating the Structural and Photophysical Features of Pincer Luminescent and Monodentate Ancillary Ligands in Pt(II) Phosphors. *Eur. J. Inorg. Chem.* **2015**, *2015*, 5822–5831.

(56) Harris, C. F.; Vezzu, D. A. K.; Bartolotti, L.; Boyle, P. D.; Huo, S. Synthesis, structure, photophysics, and a DFT study of phosphorescent C[∧]NAN- and C[∧]NAN-coordinated platinum complexes. *Inorg. Chem.* **2013**, *52*, 11711–11722.

(57) Fleetham, T.; Wang, Z.; Li, J. Efficient deep blue electrophosphorescent devices based on platinum(II) bis(n-methylimidazolyl)benzene chloride. *Org. Electron.* **2012**, *13*, 1430–1435.

(58) Yang, X.; Wang, Z.; Madakuni, S.; Li, J.; Jabbour, G. E. Efficient Blue- and White-Emitting Electrophosphorescent Devices Based on Platinum(II) [1,3-Difluoro-4,6-di(2-pyridinyl)benzene] Chloride. *Adv. Mater.* **2008**, *20*, 2405–2409.

(59) Zhang, X.; Wright, A. M.; DeYonker, N. J.; Hollis, T. K.; Hammer, N. I.; Webster, C. E.; Valente, E. J. Synthesis, Air Stability, Photobleaching, and DFT Modeling of Blue Light Emitting Platinum CCC-N-Heterocyclic Carbene Pincer Complexes. *Organometallics* **2012**, *31*, 1664–1672.

(60) Vezzu, D. A. K.; Deaton, J. C.; Jones, J. S.; Bartolotti, L.; Harris, C. F.; Marchetti, A. P.; Kondakova, M.; Pike, R. D.; Huo, S. Highly luminescent tetradentate bis-cyclometalated platinum complexes: design, synthesis, structure, photophysics, and electroluminescence application. *Inorg. Chem.* **2010**, *49*, S107–S119.

(61) Lo, K.-W.; Tong, G. S. M.; Cheng, G.; Low, K.-H.; Che, C.-M. Dinuclear Pt(II) Complexes with Strong Blue Phosphorescence for Operationally Stable Organic Light-Emitting Diodes with EQE up to 23 % at 1000 cd m⁻². *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202115515.

(62) Sun, J.; Ahn, H.; Kang, S.; Ko, S.-B.; Song, D.; Um, H. A.; Kim, S.; Lee, Y.; Jeon, P.; Hwang, S.-H.; You, Y.; Chu, C.; Kim, S. Exceptionally stable blue phosphorescent organic light-emitting diodes. *Nat. Photonics* **2022**, *16*, 212–218.

(63) Romain, M.; Thierry, S.; Shirinskaya, A.; Declairieux, C.; Tondelier, D.; Geffroy, B.; Jeannin, O.; Rault-Berthelot, J.; Métivier, R.; Poriel, C. ortho-, meta-, and para-dihydroindeno[fluorene] derivatives as host materials for phosphorescent OLEDs. *Angew. Chem., Int. Ed.* **2015**, *54*, 1176–1180.

(64) Ma, J.; Idris, M.; Li, T. Y.; Ravinson, D. S. M.; Fleetham, T.; Kim, J.; Djurovich, P. I.; Forrest, S. R.; Thompson, M. E. Symmetric “Double Spiro” Wide Energy Gap Hosts for Blue Phosphorescent OLED Devices. *Adv. Opt. Mater.* **2022**, *10*, 2101530.

(65) Wang, Y.-K.; Sun, Q.; Wu, S.-F.; Yuan, Y.; Li, Q.; Jiang, Z.-Q.; Fung, M.-K.; Liao, L.-S. Thermally Activated Delayed Fluorescence Material as Host with Novel Spiro-Based Skeleton for High Power Efficiency and Low Roll-Off Blue and White Phosphorescent Devices. *Adv. Funct. Mater.* **2016**, *26*, 7929–7936.

(66) Liu, T.; Sun, H.; Fan, C.; Ma, D.; Zhong, C.; Yang, C. High efficiency blue PhOLEDs using spiro-annulated triphenylamine/fluorene hybrids as host materials with high triplet energy, high HOMO level and high T_g. *Org. Electron.* **2014**, *15*, 3568–3576.

- (67) Li, Z.; Jiao, B.; Wu, Z.; Liu, P.; Ma, L.; Lei, X.; Wang, D.; Zhou, G.; Hu, H.; Hou, X. Fluorinated 9,9'-spirofluorene derivatives as host materials for highly efficient blue organic light-emitting devices. *J. Mater. Chem. C* **2013**, *1*, 2183.
- (68) Poriol, C.; Sicard, L.; Rault-Berthelot, J. New generations of spirofluorene regioisomers for organic electronics: tuning electronic properties with the substitution pattern. *Chem. Commun.* **2019**, *55*, 14238–14254.
- (69) Liao, K.-Y.; Hsu, C.-W.; Chi, Y.; Hsu, M.-K.; Wu, S.-W.; Chang, C.-H.; Liu, S.-H.; Lee, G.-H.; Chou, P.-T.; Hu, Y.; Robertson, N. Pt(II) metal complexes tailored with a newly designed spiro-arranged tetradentate ligand: harnessing of charge-transfer phosphorescence and fabrication of sky blue and white OLEDs. *Inorg. Chem.* **2015**, *54*, 4029–4038.
- (70) Wong, W.-Y.; Ho, C.-L. Heavy metal organometallic electrophosphors derived from multi-component chromophores. *Coord. Chem. Rev.* **2009**, *253*, 1709–1758.
- (71) van Pee, V.; Catinat, J.-P. Preparation of a fac-Isomer for a tris homoleptic metal complex. WO 2012/084219 A1, June 24, 2012.
- (72) Yun, B.-S.; Kim, S.-Y.; Kim, J.-H.; Lee, S.; Son, H.-J.; Kang, S. O. Excited-state modulation via alteration of the heterocyclic moiety in 9,9-dimethylfluorene-based Ir(III) phosphorescent dopants for blue PhOLEDs. *J. Mater. Chem. C* **2022**, *10*, 4196–4207.
- (73) Stipurin, I.; Strassner, T. Phosphorescent Cyclometalated Platinum(II) Imidazolynilidene Complexes. *Eur. J. Inorg. Chem.* **2021**, *2021*, 804–813.
- (74) Yersin, H.; Rausch, A. F.; Czerwieniec, R.; Hofbeck, T.; Fischer, T. The triplet state of organo-transition metal compounds. Triplet harvesting and singlet harvesting for efficient OLEDs. *Coord. Chem. Rev.* **2011**, *255*, 2622–2652.
- (75) Tronnier, A.; Nischan, N.; Metz, S.; Wagenblast, G.; Münster, I.; Strassner, T. Phosphorescent C[∧]C* Cyclometalated Pt(II) Dibenzofuran-NHC Complexes - An Auxiliary Ligand Study. *Eur. J. Inorg. Chem.* **2014**, *2014*, 256–264.
- (76) Zähringer, T. J. B.; Bertrams, M.-S.; Kerzig, C. Purely organic Vis-to-UV upconversion with an excited annihilator singlet beyond 4 eV. *J. Mater. Chem. C* **2022**, *10*, 4568–4573.
- (77) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*; CRC Press, 2006.
- (78) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. Energy transfer catalysis mediated by visible light: principles, applications, directions. *Chem. Soc. Rev.* **2018**, *47*, 7190–7202.
- (79) Carmichael, I.; Hug, G. L. Triplet–Triplet Absorption Spectra of Organic Molecules in Condensed Phases. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1–250.
- (80) Kocia, R. Pulse radiolysis studies of intermediates derived from p-terphenyl in the oxygenated methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide ionic liquid. *Int. J. Chem. Kinet.* **2019**, *51*, 958–964.
- (81) Nevesely, T.; Wienhold, M.; Molloy, J. J.; Gilmour, R. Advances in the E → Z Isomerization of Alkenes Using Small Molecule Photocatalysts. *Chem. Rev.* **2022**, *122*, 2650–2694.
- (82) Schreier, M. R.; Guo, X.; Pfund, B.; Okamoto, Y.; Ward, T. R.; Kerzig, C.; Wenger, O. S. Water-Soluble Tris(cyclometalated) Iridium(III) Complexes for Aqueous Electron and Energy Transfer Photochemistry. *Acc. Chem. Res.* **2022**, *55*, 1290–1300.
- (83) Hammond, G. S.; Leermakers, P. A.; Turro, N. J. Photosensitized Cis-Trans Isomerization Of The Piperlyenes. *J. Am. Chem. Soc.* **1961**, *83*, 2396–2397.
- (84) Bertrams, M.-S.; Kerzig, C. Converting p-terphenyl into a novel organo-catalyst for LED-driven energy and electron transfer photo-reactions in water. *Chem. Commun.* **2021**, *57*, 6752–6755.
- (85) Li, K.; Wan, Q.; Yang, C.; Chang, X.-Y.; Low, K.-H.; Che, C.-M. Air-Stable Blue Phosphorescent Tetradentate Platinum(II) Complexes as Strong Photo-Reductant. *Angew. Chem., Int. Ed.* **2018**, *57*, 14129–14133.
- (86) Luo, Z.; Liu, Y.; Tong, K.-C.; Chang, X.-Y.; To, W.-P.; Che, C.-M. Luminescent Platinum(II) Complexes with Bidentate Diacetylde Ligands: Structures, Photophysical Properties and Application Studies. *Chem.—Asian J.* **2021**, *16*, 2978–2992.
- (87) Zhou, Q.-Q.; Zou, Y.-Q.; Lu, L.-Q.; Xiao, W.-J. Visible-Light-Induced Organic Photochemical Reactions through Energy-Transfer Pathways. *Angew. Chem., Int. Ed.* **2019**, *58*, 1586–1604.
- (88) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*; Wallingford, CT, 2016.
- (89) Dennington, R. *GaussView*, version 6.0, 2016.
- (90) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (91) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, *157*, 200–206.
- (92) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (93) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.
- (94) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.
- (95) Ernzerhof, M.; Scuseria, G. E. Assessment of the Perdew–Burke–Ernzerhof exchange-correlation functional. *J. Chem. Phys.* **1999**, *110*, 5029–5036.
- (96) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- (97) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980**, *72*, 650–654.
- (98) McLean, A. D.; Chandler, G. S. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z = 11–18. *J. Chem. Phys.* **1980**, *72*, 5639–5648.
- (99) Francel, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **1982**, *77*, 3654–3665.
- (100) Grimme, S. Density functional theory with London dispersion corrections. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2011**, *1*, 211–228.
- (101) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- (102) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.
- (103) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270–283.
- (104) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 284–298.

(105) Roy, L. E.; Hay, P. J.; Martin, R. L. Revised Basis Sets for the LANL Effective Core Potentials. *J. Chem. Theory Comput.* **2008**, *4*, 1029–1031.

Recommended by ACS

Dicationic Diimine Pt(II) Bis(*N*-heterocyclic allenylidene) Complexes: Extended Pt...Pt Chains, NIR Phosphorescence, and Chromonics

Jinqiang Lin, Wei Lu, *et al.*

MAY 05, 2023
INORGANIC CHEMISTRY

READ 

Luminescent Complexes of Platinum, Iridium, and Coinage Metals Containing *N*-Heterocyclic Carbene Ligands: Design, Structural Diversity, and Photophysical Properties

Hani Amouri.

OCTOBER 31, 2022
CHEMICAL REVIEWS

READ 

Platinum(II) Complexes of Nonsymmetrical NCN-Coordinating Ligands: Unimolecular and Excimeric Luminescence Properties and Comparison with Symmetric...

Rebecca J. Salthouse, J. A. Gareth Williams, *et al.*

JULY 27, 2023
INORGANIC CHEMISTRY

READ 

Cyclometalated Platinum(II) Complexes with 10-(Aryl)phenoxarsine Ligands: Synthesis, Structure, and Photophysical Properties

Milyausha F. Galimova, Andrey A. Karasik, *et al.*

MAY 31, 2023
ORGANOMETALLICS

READ 

Get More Suggestions >

4 Conclusion and future perspectives

This chapter summarizes the most important results and major aspects from the thesis. Possible future developments that can be pursued based on this thesis are presented.

4.1 Photochemistry of triplet excited states in aqueous solution

Four completely different photochemical mechanisms have been investigated in aqueous solutions, with emphasis on utilizing and combining the properties of involved chromophores and their triplet excited states efficiently. The triplet species were accessed *via* different inter- and intramolecular pathways, which could be analyzed using several spectroscopic techniques. Mechanistic evidence and versatile test reactions in the "green" but demanding solvent water demonstrate the general relevance. Based on these results, possible future developments and applications of the investigated systems are suggested (Figure 36).

4.1.1 Sensitization-initiated electron transfer

Systems reported in the literature^[5,57,122,150] have established that the general concept of combined energy and electron transfer mechanisms bears great potential. So far, mostly the energy of two photons was converted into chemical energy to drive photoreactions using this strategy.^[5,57,122,150,151] Section 2.1 shows the "proof-of-concept" for a one-photon-driven version of the mechanism (for general catalytic mechanism see Figure 36, A) with iridium-based metal complexes. A second system using a ruthenium-based metal complex as a photosensitizer relies on this mechanism and clearly establishes the benefits of combining a metal complex with an organic chromophore in a catalytic scheme.

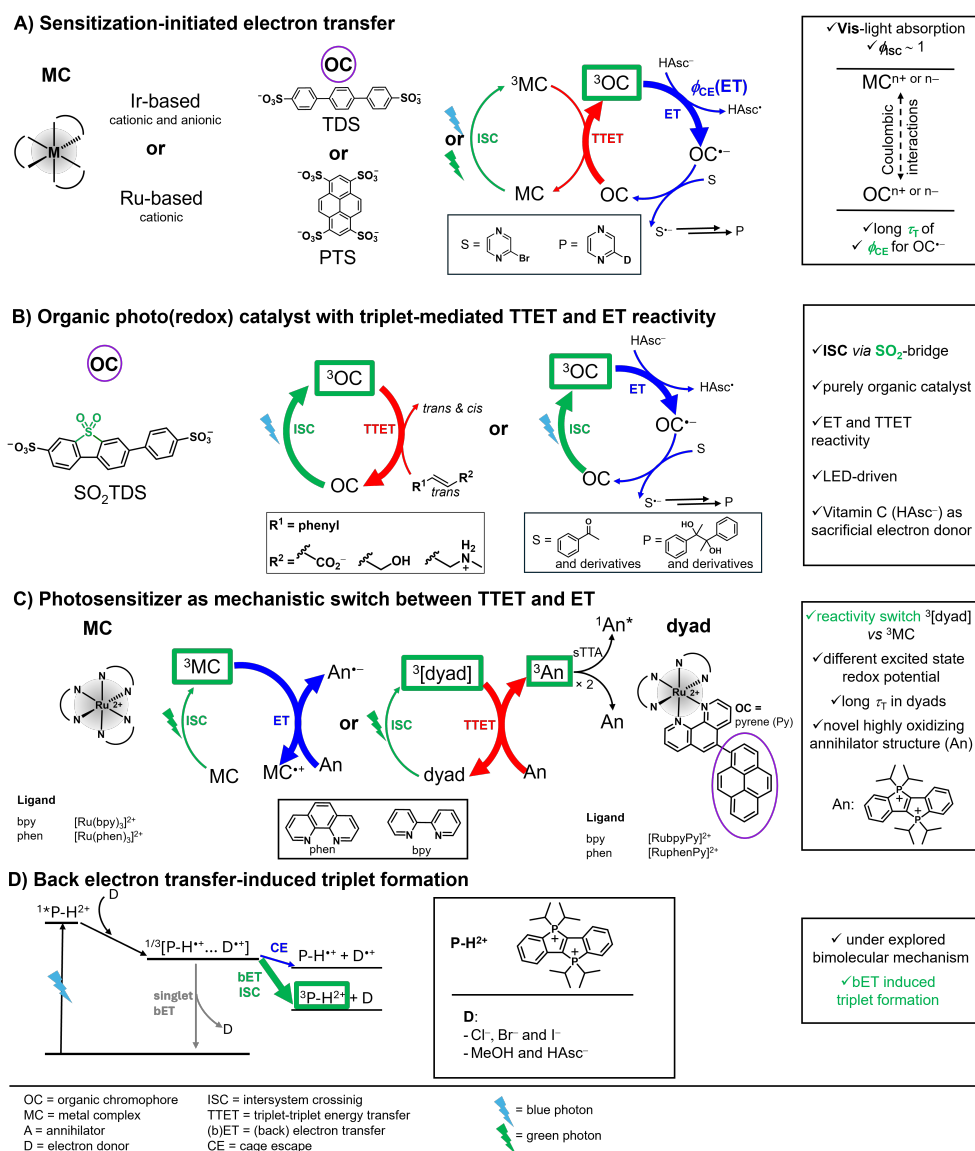


Figure 36: Schematic summary of the four projects realized in aqueous solution discussed in this thesis. Highlighted in color are the relevant triplet excited species (green boxes) and/or are the key pathways and mechanisms discussed in this thesis.

Sensitization-initiated electron transfer with blue light:

In the blue light-driven catalysis, water-soluble Ir-based metal complexes were combined with ionic naphthalene or *p*-terphenyl derivatives as OC. Some system-inherent challenges were encountered throughout investigating the individual MC - OC combinations.

[Ir(sppy)₃]³⁻ as MC with TDS as OC was the most promising out of all blue light-driven

systems. The general principle for this mechanism was established by the triplet-triplet energy transfer from $^3[\text{Ir}(\text{sppy})_3]^{3-}$ to TDS and the sensitized ^3TDS was subsequently reduced to the catalytically active intermediate $\text{TDS}^{\bullet-}$. Besides demonstrating the general feasibility of the one-photon driven mechanism, this MC - OC combination provides a high conversion of the energy of the input-photon into redox potential available for substrate activation. However, the $^3[\text{Ir}(\text{sppy})_3]^{3-}$ was also quenched by the substrate, thereby competing unproductively with the desired energy transfer to TDS.

To realize the concept in a more convincing manner, the Coulombic interaction between MC and OC was sought to be beneficial, and anionic Ir-complexes were combined with cationic naphthalene derivatives. A higher TTET rate constant for energy transfer from ^3MC to the OC was found. However, the reactive intermediates of the cationic naphthalenes were not stable in protic environments. Further attempts involving surfactants resulted in precipitation of the surfactant molecules with different OCs. Future perspectives on this blue light-driven mechanism therefore can include different supra-molecular environments (*e.g.* cyclodextrines^[36]) or new combinations of Ir-based MC and naphthalene-based OC (Ir-complex as cation and naphthalene as anion). The identification of a system driven by blue photons is desirable as higher potentials can be achieved compared to the ruthenium-based system (see below).

Sensitization-initiated electron transfer with green light:

The second version of this mechanism involved a Ru-based cationic MC combined with a tetraanionic OC (PTS), which is highly soluble in water.^[36] Beneficial static quenching effects paved the way for highly efficient sensitization to obtain the ^3OC . The following reductive electron transfer was nearly quantitative and the reactive intermediate $\text{PTS}^{\bullet-}$ was obtained with a cage escape quantum yield close to unity, rendering competing reactions irrelevant. In a sample dehalogenation reaction, a substantially higher product formation was observed for the combined $[\text{Ru}(\text{phen})_3]^{2+}$ - PTS system compared to $[\text{Ru}(\text{phen})_3]^{2+}$ alone. The one-photon-driven catalytic mechanism presented here can be further established in organic solvents in the future, and high redox potentials of the catalytic species can be obtained for different pyrene derivatives (such as the monoanionic pyrene, PMS).

4.1.2 Organic photo(redox) catalysis with triplet-mediated energy and electron transfer reactivity

In this section (Section 2.2) a water-soluble organic photo(redox) catalyst with a versatile triplet reactivity was presented (Figure 36, B). The introduction of an SO_2 -bridge in the *p*-terphenyl-backbone enabled ISC and the triplet excited state was studied spectroscopically. The energy and electron transfer reactivity was observed in spectroscopic quenching studies and in NMR scale reactions. The photocatalytic sample reactions

were successfully carried out in aqueous solution with a purely organic catalyst driven by LEDs. Energy transfer reactivity was demonstrated in *cis/trans* isomerizations of differently charged cinnamic acid derivatives and the electron transfer reactivity was shown in pinacol coupling reactions. Both reaction types tolerated micellar environments, which can be used for activating water-insoluble substrates.

This organic, water-soluble photo(redox)catalyst contributes towards realizing sustainable principles in (photo)chemistry by replacing metal-based photocatalysts.

4.1.3 Dyads as mechanistic switch between energy and electron transfer

This section (Section 2.3) presented a two-photon sTTA system in aqueous solution. The pure singlet chromophore $P-H^{2+}$ was sensitized into its triplet excited state by suitable molecular dyads as photosensitizers. $^3P-H^{2+}$ was additionally identified as an annihilator in aqueous solution. Unlike the energy transfer quenching with the triplet excited dyads, the parent metal complexes, from which the dyads were derived, were oxidized by the annihilator. Two properties of the dyads, that are not found in the metal complexes cause the different reactivities: i) The elongated triplet excited state lifetime allowed the usage of small annihilator concentrations for efficient energy transfer. ii) The pyrene-based triplet excited state of the dyads is less redox reactive than the parent metal complex.

The annihilator is highly oxidizing in its singlet excited state, which, besides its water solubility, is a remarkable property. Other sTTA UC systems in aqueous solution, which were exploited for photochemical reactions, produced highly reducing singlet excited states.^[102,155] Furthermore, the low triplet energy of the annihilator should allow sensitization with a red light-absorbing photosensitizer, which makes the system interesting for applications with excitation wavelengths in the biological window.

The general concept of switching the reactivity by introducing an organic chromophore into a metal complex is also promising for further investigations. Initial experiments with Ir-based metal complexes and derived dyads show strongly divergent ET vs TTET reactivities, which could be used for switching between TTET and sensitizer reduction.

4.1.4 Back electron transfer-induced triplet formation

The last system in aqueous solution (Section 2.4) introduced a rarely observed pathway towards triplet formation.^[90,185] After an initial electron transfer between the singlet-excited chromophore ($^1P-H^{2+}$) and a suitable heavy atom-containing electron donor, the radical species of chromophore and quencher are still in close proximity within the solvent cage. Favorable thermodynamic prerequisites allow recombination to populate the triplet excited state of the chromophore. Such recombination processes yielding the triplet of the chromophore have been observed mainly in organic solvents^[90,185] and for mono-molecular structures^[143]. The high polarity of water usually supports the

electron transfer pathway resulting in the diffusion of the two radicals into solution.^[48] However, with the chosen quencher (chloride and bromide), initial experiments point towards $^3\text{P}-\text{H}^{2+}$ formation based on a recombination process of the spin-correlated radical pair $^3[\text{P}-\text{H}^{\bullet+} \dots \text{D}^{\bullet+}]$.

Further experiments to support this pathway are still required, as well as possibly extending this underexplored triplet-producing pathway to other chromophores and solvents. The investigation of such mechanisms is of great interest to avoid unproductive recombination pathways in photochemical devices.^[90,185] Changing the multiplicity of a chromophore in its excited state is an interesting strategy in photochemistry and expanding the established mechanisms is highly desirable.

4.2 Photochemistry of triplet excited states in organic solvents

The contributions to all projects realized in organic solvents (discussed in Section 3) provided insights into the key triplet excited species. Different analysis methods (transient absorption spectroscopy, DFT calculations and lab-scale test reactions) contributed to a better understanding of the respective triplet excited states and the application of the individual triplet species in photo(redox) catalysis or photon-induced mechanisms.

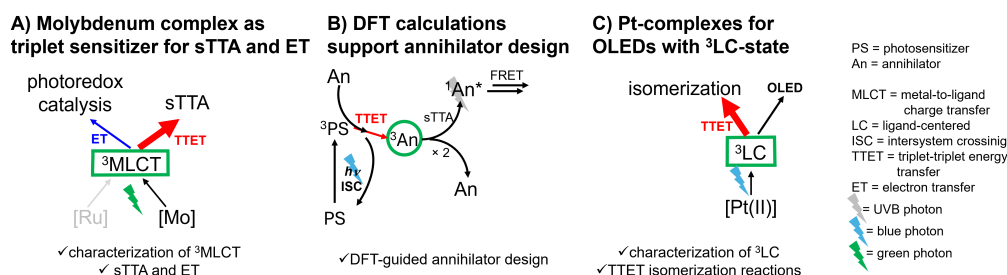


Figure 37: Schematic summary of the three projects realized in organic solvents. Highlighted in color are the relevant triplet excited species (green boxes) and/or the key pathways and mechanisms discussed in this thesis.

4.2.1 Molybdenum complex as triplet sensitizer for upconversion and as photoredox catalyst

The long-lived $^3\text{MLCT}$ excited state of a molybdenum(0)-complex (Section 3.1, and Figure 37, A) was analyzed in detail using quantitative transient absorption techniques. In an approach towards replacing precious ruthenium(II) metal sensitizers, this isoelectronic Mo(0)-complex was employed in an sTTA UC scheme with a benchmark annihilator compound and in an electron transfer test reaction. This study contributes to the general understanding of excited-states and related properties in earth-abundant metal complexes in a pioneering study.

4.2.2 Theoretical calculations supporting annihilator design and experimental findings

The first UVB-light emitting sTTA UC scheme with an unprecedented excited-singlet state energy significantly beyond 4.0 eV was identified (Section 3.2, Figure 37, B) and the annihilator design was guided by DFT calculations, which allowed a preselection of the most promising annihilator structures. The predicted energies of the most promising annihilator candidates were reproduced experimentally. With the full upconversion system, an sTTA UC-FRET mechanism was implemented, activating highly inert substrates. This complex mechanism paves the way for replacing the highly energetic and harmful light of mercury lamps for substrate activation by combining the energy of two blue photons from efficient LEDs.

4.2.3 Insights into properties of ligand-centered triplet excited states in heteroleptic platinum(II) complexes

Aiming at high triplet energies for blue light-emitting excited states, two spirobifluorene imidazolydene platinum(II)-complexes ($E_T \sim 2.5$ eV) with different acetylacetonate ligands were designed and synthesized with OLED applications in mind (Section 3.3, Figure 37, C).^[172] Transient absorption spectroscopy allowed the characterization of the long-lived ligand-centered triplet excited state of both platinum(II) complexes and the minor influence of the acetylacetonate ligand on the lowest excited species. Quenching experiments and energy transfer isomerization reactions further confirmed the highly similar reactivity and nearly identical triplet energies for both complexes. The design of the spirobifluorene-imidazolydene ligand and combined with the acetylacetonate ligand provide the unique properties of the long-lived ^3LC state. This design concept could stimulate further development of such ligand-systems as evidenced by the subsequent study, published by the group of Prof. Strassner in 2023.^[251]

This thesis presents triplet excited states in various forms. Different possibilities of inter- (sensitization, recombination) and intramolecular (ISC, intramolecular energy transfer) pathways for accessing the triplet species and their reactivities (ET, TTET, sTTA) are investigated and discussed in detail. The combination of steady-state and time-resolved optical spectroscopy with laboratory-scale test reactions allows a general understanding of the individual photosensitizer, photocatalyst (catalytic system) or chromophore in general. In summary, this thesis contributes to a better understanding as well as an improved performance of photochemical reactions, reaction sequences, processes and devices relying on triplet states and the (inter)conversion of spin states with implications for various research fields.

5 References

- (1) Ciamician, G. *Science* **1912**, *36*, 385–394.
- (2) Lee, Y.-M.; Nam, W.; Fukuzumi, S. *Chem. Sci.* **2023**, *14*, 4205–4218.
- (3) Bochet, C. G. *Chimia* **2019**, *73*, 720–723.
- (4) Kawashima, Y.; Kouno, H.; Orihashi, K.; Nishimura, K.; Yanai, N.; Kimizuka, N. *Mol. Syst. Des. Eng.* **2010**, *5*, 792–796.
- (5) Kerzig, C.; Goetz, M. *Chem. Sci.* **2016**, *7*, 3862–3868.
- (6) Louno, H.; Sasaki, Y.; Yanai, N.; Kimizuka, N. *Chem. Eur. J.* **2019**, *25*, 6124–6130.
- (7) Hong, G.; Gan, X.; Leonhardt, C.; Zhang, Z.; Seibert, J.; Busch, J. M.; Bräse, S. *Adv. Mater.* **2021**, *33*, 2005630.
- (8) Schulze, T. F.; Schmidt, T. W. *Energy Environ. Sci.* **2015**, *8*, 103–125.
- (9) Bousecroft, C. E.; Constable, E. C. *Chem. Sci.* **2022**, *13*, 1225–1262.
- (10) Arias-Alpizar, G.; Kong, L.; Vlieg, R. C.; Rabe, A.; Papabopoulou, P.; Meijer, M. S.; Bonnet, S.; Vogel, S.; Noort, J.; Kros, A.; Campbell, F. *Nat. Comm.* **2020**, *11*, 3638.
- (11) Vepris, O.; Eich, C.; Feng, Y.; Fuentes, G.; Zhang, H.; Cruz, L. J. *Biomedicines* **2022**, *10*, 1070.
- (12) Van Rixel, V. H. S.; Siewert, B.; Hopkins, S. L.; Askes, S. H. C.; Busemann, A.; Siegler, M. A.; Bonnet, S. *Chem. Sci.* **2016**, *7*, 4922–4929.
- (13) Cao, R.; Jia, J.; Ma, X.; M. Zhou; Fei, H. *J. Med. Chem.* **2013**, *56*, 3636–3644.
- (14) Shamara, A.; Verwilt, P.; Li, M.; Ma, D.; Singh, N.; Yoo, J.; Kim, Y.; Yang, Y.; Zhu, J.-H.; Huang, H.; Hu, X.-L.; He, X.-P.; Zeng, L.; James, T. D.; Peng, X.; Sessler, J. L.; Kim, J. S. *Chem. Rev.* **2024**, *124*, 2699–2804.
- (15) Kim, D.; Dang, V. Q.; Teets, T. S. *Chem. Sci.* **2024**, *15*, 77–94.
- (16) Noel, T.; Zysman-Colman, E. *Chem. Catalysis* **2022**, *2*, 468–476.
- (17) Sakakibara, Y.; Murakami, K. *ACS Catal.* **2022**, *12*, 1857–1878.
- (18) Hojo, R.; Polgar, A. M.; Hudson, Z. M. *ACS Sustainable Chem. Eng.* **2022**, *10*, 9665–9678.
- (19) Kopetzki, D.; Lévesque, F.; Seeberger, P. H. *Chem. Eur. J.* **2013**, *19*, 5450–5456.
- (20) Anastas, P. T.; Warner, J. C., *Green Chemistry: Theory and Practice*; Oxford University Press, New York: 1998.
- (21) Anastas, P.; Eghbali, N. *Chem. Soc. Rev.* **2010**, *39*, 301–312.

-
- (22) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. *Chem. Soc. Rev.* **2018**, *47*, 7190–7202.
- (23) Hessel, V.; Tran, N. N.; Asrami, M. R.; Tran, Q. C.; Long, N. V. D.; Escribà-Gelonch, M.; Tejada, J. O.; Linke, S.; Sundmacher, K. *Green Chem.* **2022**, *24*, 410–437.
- (24) Winterton, N. *Clean Technol. Environment. Pol.* **2021**, *23*, 2499–2522.
- (25) Russo, C.; F. Brunelli; Tron, G. C.; Giustiniano, M. J. *Org. Chem.* **2023**, *88*, 6282–6293.
- (26) Barata-Vallejo, S.; Yerien, D. E.; Postigo, A. *ACS Sust. Chem. Eng.* **2021**, *9*, 10016–10047.
- (27) Wenger, O. S. *Chem. Eur. J.* **2019**, *24*, 6043–6052.
- (28) Gualandi, A.; Anselmi, M.; Calogero, F.; Potenti, S.; Bassan, E.; Ceroni, P.; Cozzi, P. G. *Org. Biomol. Chem.* **2021**, *19*, 3527–3550.
- (29) Sinha, N.; Wegeberg, C.; Häussinger, D.; Prescimone, A.; Wenger, O. S. *Nat. Chem.* **2023**, *15*, 1730–1736.
- (30) Ito, H.; Sudo, A. *Results in Chemistry* **2021**, *3*, 100123.
- (31) Glaser, F.; Schmitz, M.; Kerzig, C. *Nanoscale* **2024**, *16*, 123–137.
- (32) Glaser, F.; Wenger, O. S. *JACS Au* **2022**, *2*, 1488–1503.
- (33) Zähringer, T. J. B.; Moghtader, J. A.; Bertrams, M.-S.; Roy, B.; Uji, M.; Yanai, N.; Kerzig, C. *Angew. Chem. Int. Ed.* **2023**, *62*, e202215340.
- (34) Uji, M.; Zähringer, T. J. B.; Kerzig, C.; Yanai, N. *Angew. Chem. Int. Ed.* **2023**, *62*, e202301506.
- (35) Barawi, M.; F. Fresno; Pérez-Ruiz, R.; de la Pena O’Shea, V. A. *ACS Appl. Energy Mater.* **2019**, *2*, 207–211.
- (36) Schmitz, M.; Bertrams, M.-S.; Sell, A. C.; Glaser, F.; Kerzig, C. *manuscript submitted* **2024**.
- (37) Fischer, C.; Kerzig, C.; Zilate, B.; Wenger, O. S.; Sparr, C. *ACS Catal.* **2020**, *10*, 210–215.
- (38) Glaser, F.; Wenger, O. S. *Chem. Sci.* **2022**, *14*, 149–161.
- (39) Xu, J.; Cao, J.; Wu, X.; Wang, H.; Yang, X.; Tang, X.; Toh, R. W.; Zhou, R.; Yeow, E. K.; Wu, J. *J. Am. Chem. Soc.* **2021**, *143*, 13266–13273.
- (40) Kwon, Y.; Lee, J.; Noh, Y.; Kim, D.; Lee, Y.; Yu, C.; Roldao, J. C.; Feng, S.; Gierschner, J.; Wannemacher, R.; Kwon, M. S. *Nat. Commun.* **2023**, *14*, 92.

-
- (41) Connell, C. U.; Fraser, C. L.; Czyz, M. L.; Smith, Z. M. .; Hayne, D. J.; Doeven, E. H.; Agugiaro, J.; Wilson, D. J. D.; Adcock, J. L.; Scully, A. D.; Gómez, D. E.; Barnett, N. W.; Polyzos, A.; Francis, P. S. *J. Am. Chem. Soc.* **2019**, *141*, 17646–17658.
- (42) Zähringer, T. J. B.; Wienhold, M.; Gilmour, R.; Kerzig, C. *J. Am. Chem. Soc.* **2023**, *145*, 21576–21586.
- (43) Wang, C.; Reichenauer, F.; Kitzmann, W. R.; Kerzig, C.; Heinze, K.; Resch-Genger, U. *Angew. Chem. Int. Ed.* **2022**, *27*, e202202238.
- (44) Kitzmann, W. R.; Bertrams, M.-S.; Boden, P.; Fischer, A. C.; Klauer, R.; Sutter, J.; Naumann, R.; Förster, C.; Niedner-Schatteburg, G.; Bings, N. H.; Hunger, J.; Kerzig, C.; Heinze, K. *J. Am. Chem. Soc.* **2023**, *145*, 16597–16609.
- (45) Wegeberg, C.; Wenger, O. S. *J. Am. Chem. Soc.* **2021**, *11*, 1860–1876.
- (46) Förster, C.; Heinze, K. *Chem. Soc. Rev.* **2020**, *49*, 1057–1070.
- (47) DeRosa, M. C.; Crutchley, R. J. *Coord. Chem. Rev.* **2002**, *223-234*, 351–371.
- (48) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T., *Handbook of Photochemistry*, 3rd ed.; Taylor & Francis Group: 2006.
- (49) Atkins, P.; Friedman, R., *Molecular Quantum Mechanics*, 4th ed.; Oxford University Press: 2005.
- (50) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Nature* **2000**, *403*, 750–753.
- (51) Speckmeier, E.; Fisher, T. G.; Zeitler, K. *J. Am. Chem. Soc.* **2018**, *140*, 1535–15365.
- (52) Bryden, M. A.; Zysman-Colman, E. *Chem. Soc. Rev.* **2021**, *50*, 7587–7680.
- (53) Olesund, A.; Johnsson, J.; Edhborg, F.; Ghasemi, S.; Moth-Poulsen, K.; Albinsson, B. *J. Am. Chem. Soc.* **2022**, *144*, 3706–3716.
- (54) Xu, Z.; Climent, C.; Brown, C. M.; Hean, D.; Bardeen, C. J.; Casanova, D.; Wolf, M. O. *Chem. Sci.* **2021**, *12*, 188–195.
- (55) Gibbons, D. J.; Farawar, A.; Mazzella, P.; Leroy-Lhez, S.; Williams, R. M. *Photochem. Photobiol. Sci.* **2020**, *19*, 136–158.
- (56) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.
- (57) Glaser, F.; Kerzig, C.; Wenger, O. S. *Chem. Sci.* **2021**, *12*, 9922–9933.
- (58) Becker, H. G. O.; Böttcher, H.; Dietz, F.; Rehorek, D.; Roewer, G.; Schiller, K.; Timpe, H.-J., *Einführung in die Photochemie*, 3rd ed.; Dutscher Verlag der Wissenschaften: 1991.
- (59) Klán, P.; Wirz, J., *Photochemistry of Organic Compounds*, 1st ed.; Wiley: 2009.

-
- (60) Marian, C. M. *Annu. Rev. Phys. Chem.* **2021**, 72, 617–640.
- (61) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, 37, 814–822.
- (62) Mohanty, J.; Nau, W. M. *Photochem. Photobiol. Sci.* **2004**, 3, 1026–1031.
- (63) Bertrams, M.-S.; Kerzig, C. *Chem. Commun.* **2021**, 57, 6752–6755.
- (64) Bell, J. D.; Murphy, J. A. *Chem. Soc. Rev.* **2021**, 50, 9540–9685.
- (65) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, 116, 10075–10166.
- (66) Thielert, P.; ElBitarNehme, M.; Mayländer, M.; Franz, M.; Zimmermann, S. L.; Fisch, F.; Gilch, P.; Jentzsch, A. V.; Rickhaus, M.; Richert, S. *Chem. Sci.* **2024**, 15, 7515–7523.
- (67) Tero-Kubota, S.; Katsuki, A.; Kobori, Y. *J. Photoch. Photobio. C* **2001**, 2, 17–33.
- (68) Lakowicz, J. R., *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer: 2006.
- (69) Goodwin, M. J.; Dickenson, J. C.; Ripak, A.; Deetz, A. M.; McCarthy, J. S.; Meyer, G. J.; Troian-Gautier, L. *Chem. Rev.* **2024**, 124, 7379–7464.
- (70) Stern, O.; Volmer, M. *Physik. Z.* **1919**, 20, 183–188.
- (71) Housecroft, C. E.; Sharpe, A. G., *Inorganic Chemistry*, 4th ed.; PEARSON: 2012.
- (72) Dexter, D. L. *J. Chem. Phys.* **1953**, 21, 836–850.
- (73) Förster, T. *Ann. Phys.* **1948**, 1-2, 1–112.
- (74) Braslavsky, S. E.; Fron, W.; Rodriguez, H. B.; SanRomán, E.; Scholes, G. D.; Schweitzer, G.; Valeur, B.; Wirz, J. *Photochem. Photobiol. Sci.* **2008**, 7, 1444–1448.
- (75) Sandros, K.; Haglid, F.; Ryhage, R.; Stevens, R. *Acta Chem. Scand.* **1964**, 18, 2355–2374.
- (76) Edhborg, F.; Olesund, A.; Albinsson, B. *Photochem. Photobiol. Sci.* **2022**, 21, 1143–1158.
- (77) Farid, S.; Dinnocenzo, J. P.; Merkel, P. B.; Young, R. H.; Shukla, D.; Guirado, G. *J. Am. Chem. Soc.* **2011**, 133, 11580–11587.
- (78) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, 8, 259–271.
- (79) Rehm, D.; Weller, A. *Berich. Bunsen. Gesell.* **1969**, 73, 834–839.
- (80) Bürgin, T.; Glaser, F.; Wenger, O. S. *J. Am. Chem. Soc.* **2022**, 144, 14181–14194.
- (81) Naumann, R.; Goez, M. *Green Chem.* **2019**, 21, 4470–4474.

-
- (82) Sau, S. C.; Schmitz, M.; Baumert, C.; Antoni, P. W.; Kerzig, C.; Hansmann, M. M. *J. Am. Chem. Soc.* **2024**, *146*, 3416–3426.
- (83) Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 1688–1694.
- (84) Sell, A. C.; Wetzel, J. C.; Schmitz, M.; Maijenburg, A. W.; Woltersdorf, G.; Naumann, R.; Kerzig, C. *Dalton Trans.* **2022**, *51*, 10799–10808.
- (85) Bertrams, M.-S.; Hermainski, K.; Mörsdorf, J.-M.; Ballmann, J.; Kerzig, C. *Chem. Sci.* **2023**, *14*, 8583–8591.
- (86) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401–449.
- (87) MaLauchlan, K. A.; Steiner, U. E. *Mol. Phys.* **1991**, *73*, 241–263.
- (88) Knibbe, H.; Rehm, D.; Weller, A. *Berich. Bunsen Gesell.* **1986**, *72*, 257–263.
- (89) Grellman, K. H.; Watkins, A. R.; Weller, A. *J. Lumin.* **1970**, *1-2*, 678–692.
- (90) Feskov, S. V.; Rogozina, M. V.; Ivanov, A. I.; Aster, A.; Koch, M.; Vauthey, E. *J. Chem. Phys.* **2019**, *150*, 024501–1.
- (91) Mataga, N.; Migita, M.; Nishimura, T. *J. Mol. Struct.* **1978**, *47*, 199–219.
- (92) Neumann, S.; Wenger, O. S.; Kerzig, C. *Chem. Eur. J.* **2021**, *27*, 4115–4123.
- (93) Troian-Gautier, L.; Turlington, M. D.; Wehlin, S. A. M.; Maurer, A. B.; Brady, M. D.; Swords, W. B.; Meyer, G. J. *Chem. Rev.* **2019**, *119*, 4628–4683.
- (94) Prat, D.; Pradigon, O.; Flemming, H.-W.; Letestu, S.; Ducandas, V.; Isnard, P.; Guntrum, E.; Senac, T.; Ruisseau, S.; Cruciani, P.; Hosek, P. *Org. Process Res. Dev.* **2013**, *17*, 1517–1525.
- (95) Clarke, C. J.; Tu, W.-C.; Levers, O.; Böhl, A.; Hallett, J. P. *Chem. Rev.* **2018**, *118*, 747–800.
- (96) Zhou, F.; Hearne, Z.; Li, C.-J. *Curr. Opin. Green Sustain. Chem.* **2019**, *18*, 118–123.
- (97) Kitano, T.; Masuda, K.; Xu, P.; Kobayashi, S. *Chem. Rev.* **1986**, *86*, 401–449.
- (98) Capello, C.; Fisher, U.; Hungerbühler, K. *Green Chem.* **2007**, *9*, 927–934.
- (99) Ishimatsu, R.; Matsunami, S.; Shizu, K.; Adachi, C.; Nakano, K.; Imato, T. *J. Phys. Chem. A* **2013**, *117*, 5607–5612.
- (100) Madani, A.; Anghileri, L.; Heydenreich, M.; Möller, H. M.; Pieber, B. *Org. Lett.* **2022**, *24*, 5376–5380.
- (101) Cortes-Clerget, M.; Yu, J.; Kincaid, J. R. A.; Walde, P.; Gallou, F.; Lipshutz, B. H. *Chem. Sci.* **2021**, *12*, 4237–4266.

-
- (102) Pfund, B.; Steffen, D. M.; Schreier, M. R.; Bertrams, M.-S.; Ye, C.; Börjesson, K.; Wenger, O. S.; Kerzig, C. *J. Am. Chem. Soc.* **2020**, *142*, 10468–10476.
- (103) Aycock, R. A.; Wang, H.; Juli, N. T. *Chem. Sci.* **2017**, *8*, 3121–3125.
- (104) Guo, X.; Okamoto, Y.; Schreier, M. R.; Ward, T. R.; Wenger, O. S. *Chem. Sci.* **2019**, *9*, 5052–5056.
- (105) Wehlin, S. A. M.; Troian-Gautier, L.; Li, G.; Meyer, G. J. *J. Am. Chem. Soc.* **2017**, *139*, 12903–12906.
- (106) Kiran, R. V.; Hogan, C. F.; Jams, B. D.; Wilson, D. J. D. *Eur. J. Inorg. Chem.* **2011**, *31*, 4816–4825.
- (107) Fayad, R.; Bui, A. T.; Shepard, S. G.; Castellano, F. N. *ACS Appl. Energy Mater.* **2020**, *3*, 12557–12564.
- (108) Pannwitz, A.; Saaring, H.; Beztsinna, N.; Li, X.; Siegler, M. A.; Bonnet, S. *Chem. Eur. J.* **2020**, *26*, 17.
- (109) Asthana, D.; Hisamitsu, S.; Morikawa, M.; Duan, P.; Nakashima, T.; Kawai, T.; Yanai, N.; Kimizuka, N. *Org. Mater.* **2019**, *1*, 43–49.
- (110) Jeyaseelan, R.; Utikal, M.; Naesborg, L. *Asian J. Org. Chem.* **2024**, *13*, e2023006.
- (111) Lipshutz, B. H. *Green Chem.* **2024**, *26*, 739–752.
- (112) Anis-Ul-Haque, K. M.; Woodward, C. E.; Day, A. I.; Wallace, L. *Inorg. Chem.* **2020**, *59*, 3942–3953.
- (113) Noto, N.; Hyodo, Y.; M. Yoshizawa; Koika, T.; Akita, M. *ACS Catal.* **2020**, *10*, 14283–14289.
- (114) Maillard, J.; Klehs, K.; Rumble, C.; Vauthey, E.; Heilermann, M.; Fürstenberg, A. *Chem. Sci.* **2021**, *12*, 1352–1362.
- (115) Liu, Y.-C.; Lu, G.-D.; Zhou, J.-H.; Rong, J.-W.; Liu, H.-Y.; Wang, H.-Y. *RSC Adv.* **2022**, *12*, 7405–7412.
- (116) Crabtree, R. H., *Organometallic Chemistry of Transition Metals*, 6th ed.; Wiley: 2014.
- (117) Mara, M. W.; Fransted, K. A.; Chen, L. X. *Coord. Chem. Rev.* **2015**, *282–283*, 2–18.
- (118) Bassan, E.; Gualandi, A.; Cozzi, P. G.; Ceroni, P. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886.
- (119) Maroncelli, M.; MacInns, J.; Fleming, G. R. *Science* **1989**, *243*, 1674–1681.
- (120) Sun, K.; Lv, Q.-Y.; Chen, X.-L.; Qu, L.-B.; Yu, B. *Green Chem.* **2021**, *23*, 232–248.

-
- (121) Cheng, S.; Wang, Y.; Huang, Y.; Zhang, Y.; Deng, P. *ACS Sustainable Chem. Eng.* **2023**, *11*, 2704–2712.
- (122) Coles, M. S.; Quach, G.; Beves, J. E.; Moore, E. G. *Angew. Chem. Int. Ed.* **2020**, *59*, 9522–9526.
- (123) Seo, H.; Katcher, M. H.; Jamison, T. F. *Nat. Chem.* **2017**, *9*, 453–456.
- (124) Okamoto, S.; Kojiyama, K.; Tsujioka, H.; Sudo, A. *Chem. Comm.* **2017**, *52*, 11339–11342.
- (125) Wenger, O. S. *J. Am. Chem. Soc.* **2018**, *140*, 13522–13533.
- (126) Neumann, S.; Kerzig, C.; Wenger, O. S. *Chem. Sci.* **2019**, *10*, 5624–5633.
- (127) Coe, B. J.; Helliwell, M.; Sánchez, S.; Peers, M. K.; Scrutton, N. S. *Dalton Trans.* **2015**, *44*, 15420–15423.
- (128) Glaser, F.; Kerzig, C.; Wenger, O. S. *Angew. Chem. Int. Ed.* **2020**, *59*, 10266–10284.
- (129) Schreier, M. R.; Guo, X.; B.Pfund; Okamoto, Y.; Ward, T. R.; Kerzig, C.; Wenger, O. S. *Acc. Chem. Res.* **2022**, *55*, 1290–1300.
- (130) Hari, D. P.; König, B. *Chem. Comm.* **2014**, *50*, 6688–6699.
- (131) Aguirre-Soto, A.; Kaastrup, K.; Kim, S.; Ugo-Beke, K.; Sikes, H. D. *ACS Catal.* **2018**, *8*, 6394–6400.
- (132) Bryden, M. A.; Millward, F.; Matulaitis, T.; Chen, D.; Villa, M.; Fermi, A.; Cetin, S.; Ceroni, P.; Zysman-Colman, E. *J. Org. Chem.* **2023**, *88*, 6364–6373.
- (133) Du, Y.; Pearson, R. M.; Lim, C.-H.; Sartor, S. M.; Ryan, M. D.; Yang, H.; Damrauer, N. H.; Miyake, G. M. *Chem. Eur. J.* **2017**, *23*, 10962–10968.
- (134) MacKenzie, I. A.; Wang, L.; Onuska, N. P. R.; Williams, O. F.; Begam, K.; Moran, A. ; Dunietz, B. D.; Nicewicz, D. A. *Nature* **2020**, *580*, 76–80.
- (135) Dhara, A. K.; Maity, S.; Dhar, B. B. *Org. Lett.* **2021**, *23*, 3269–3273.
- (136) Yanai, N.; Kimizuka, N. *Chem. Sci.* **2018**, *9*, 6670–6678.
- (137) Zhang, X.-F.; Zhang, I.; Liu, L. *Photochem. Photobiol.* **2010**, *86*, 492–498.
- (138) Lower, S. K.; El-Sayed, M. A. *Chem. Rev.* **1966**, *66*, 200–241.
- (139) Vega-Penaloza, A.; Mateos, J.; Companyó, X.; Escudero-Casao, M.; Dell’Amico, L. *Angew. Chem. Int. Ed.* **2021**, *60*, 1082–1097.
- (140) Cruz, C. D.; Yuan, J.; Climent, C.; Tierce, N. T.; Christensen, P. R.; Chronister, E.; Casanova, D.; Wolf, M. O.; Bardeen, C. J. *Chem. Sci.* **2019**, *10*, 75611–7573.
- (141) McCarthy, B. G.; Pearson, R.; Lim, C.-H.; Sartor, S. M.; Damrauer, N. H.; Miyake, G. M. *J. Am. Chem. Soc.* **2018**, *140*, 5088–5101.

-
- (142) Imran, M.; Sukhanov, A. A.; Wang, Z.; Karatay, A.; Zhao, J.; Mahmood, Z.; Elmali, A.; Voronkova, V. K.; Hayvali, M.; Xing, Y. H.; Weber, S. *J. Phys. Chem. C* **2019**, *123*, 7010–7024.
- (143) Mims, D.; Schmiedel, A.; Holzapfel, M.; Lukzen, N. N.; Lambert, C.; Steiner, U. E. *J. Chem. Phys.* **2019**, *151*, 244308.
- (144) Bassan, E.; Gualandi, A.; Cozzi, P. G.; Ceroni, P. *Chem. Sci.* **2021**, *12*, 6607–6628.
- (145) Kocia, R. *Int. J. Chem. Kinet.* **2019**, *51*, 958–964.
- (146) Yang, X.-J.; Chen, B.; Zheng, L.-Q.; Wu, L.-Z.; Tung, C.-H. *Green Chem.* **2014**, *16*, 1082–1086.
- (147) Ghosh, I.; Ghosh, T.; Bardagi, J. I.; König, B. *Science* **2014**, *346*, 725–728.
- (148) Brandl, F.; Bergwinkl, S.; Allacher, C.; Dick, B. *Chem. Eur. J.* **2020**, *26*, 7946–7954.
- (149) Goetz, M.; Kerzig, C.; Naumann, R. *Angew. Chem.* **2014**, *126*, 10072–10074.
- (150) Gosh, I.; Shaikh, R. S.; König, B. *Angew. Chem. Int. Ed.* **2017**, *56*, 8544–8549.
- (151) Marchini, M.; Bergamini, G.; Cozzi, P. G.; Ceroni, P.; Balzani, V. *Angew. Chem. Int. Ed.* **2017**, *56*, 12820–12821.
- (152) Matsuoka, S.; T.Kohzuki; Pac, C.; Ishida, A.; Takamuku, S.; Kusaba, M.; Nakashima, N.; Yanagida, S. *J. Phys. Chem.* **1992**, *96*, 4437–4442.
- (153) Wei, Y.; Li, Y.; Zheng, M.; Zhou, X.; Zou, Y.; Yang, C. *Adv. Optical Mater.* **2020**, *8*, 1902157.
- (154) Tyson, D. S.; Henbest, K. B.; Bialecki, J.; Castellano, F. N. *J. Phys. Chem. A* **2001**, *105*, 8154–8161.
- (155) Kerzig, C.; Wenger, O. S. *Chem. Sci.* **2018**, *9*, 6670–6678.
- (156) ElRoz, K.; Castellano, F. N. *Chem. Comm.* **2017**, *53*, 117505–11708.
- (157) Schmid, L.; Kerzig, C.; Prescimone, A.; Wenger, O. S. *JACS Au* **2021**, *1*, 819–832.
- (158) Morales, A. F.; Anccorsi, G.; Armarolli, N.; Barigelletti, F.; Pope, S. J. A.; Ward, M. D. *Inorg. Chem.* **2002**, *41*, 6538–6936.
- (159) Wilson, G. J.; Launikonis, A.; Sasse, W. H. F.; Mau, A. W.-H. *J. Phys. Chem. A* **1997**, *101*, 4860–4866.
- (160) Sasaki, Y.; Oshikawa, M.; Bharmoria, P.; Kouno, H.; Hayashi-Takagi, A.; Sato, M.; Ajioka, I.; Yanai, N.; Kimizuka, N. *Angew. Chem. Int. Ed.* **2019**, *58*, 17827–17833.

-
- (161) RoqueIII, J. A.; Barrett, P. C.; Cole, H. D.; Lifshits, L. M.; Shi, G.; Monroe, S.; von Dohlen, D.; Kim, S.; Russo, N.; Deep, G.; Cameron, C. D.; Alberto, M. E.; McFarland, S. A. *Chem. Sci.* **2020**, *11*, 9784–9806.
- (162) Wei, Y.; Li, Y.; Li, Z.; Xu, X.; Cao, X.; Zhou, X.; Yang, C. *Inorg. Chem.* **2021**, *60*, 19001–19008.
- (163) Li, H.; Wang, C.; Glaser, F.; Sinha, N.; Wenger, O. S. *J. Am. Chem. Soc.* **2023**, *145*, 11402–11414.
- (164) Lu, Y.; Wang, J.; McGoldrick, N.; Cui, X.; Zhao, J.; Caverly, C.; Twamley, B.; Máille, G. M. Ó.; Irwin, B.; Conway-Kenny, R.; Draper, S. M. *Ange. Chem. Int. Ed.* **2016**, *55*, 14688–14692.
- (165) Wang, C.; Lystrom, L.; Yin, H.; Hetu, M.; Kilina, S.; McFarland, S. A.; Sun, W. *Dalton Trans.* **2016**, *45*, 16366–16378.
- (166) Flamigni, L.; Baranoff, E.; Collin, J.-P.; Sauvage, J.-P. *Chem. Eur. J* **2006**, *12*, 6339–6715.
- (167) Cordero, M. A. A.; Boden, P. J.; Rentschler, M.; DiMartino-Fumo, P.; Frey, W.; Yang, Y.; Gerhards, M.; Karnahl, M.; Lochbrunner, S.; Tschierlei, S. *Inorg. Chem.* **2022**, *61*, 214–226.
- (168) Doettinger, F.; Yang, Y.; Karnahl, M.; Tschierlei, S. *Inorg. Chem.* **2023**, *62*, 8166–8178.
- (169) Dierks, P.; Pöpcke, A.; Bokareva, O. S.; Altenburger, B.; Reuter, T.; Heinze, K.; Kühn, O.; Lochbrunner, S.; Bauer, M. *Inorg. Chem.* **2020**, *59*, 14746–14761.
- (170) Wang, C.; Wegeberg, C.; Wenger, O. S. *Angew. Chem. Int. Ed.* **2023**, *62*, e202311470.
- (171) Tyson, D. S.; Castellano, F. N. *J. Phys. Chem. A* **1999**, *103*, 10955–10960.
- (172) Riesebeck, T.; Bertrams, M.-S.; Stipurin, S.; Konowski, K.; Kerzig, C.; Strassner, T. *Inorg. Chem.* **2022**, *61*, 15499–15509.
- (173) Wilke, B. M.; Castellano, F. N. *J. Chem. Educ.* **2013**, *90*, 786–789.
- (174) Yan, D.-M.; Chen, J.-R.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2019**, *58*, 378–380.
- (175) Rodeghiero, A. G. G.; Rocca, E. D.; Bertoni, F.; Marchini, M.; Perciaccante, E.; Jansen, T. P.; Ceroni, P.; Cozzi, P. G. *Chem. Commun.* **2018**, *54*, 10044–10047.
- (176) Förster, C.; Heinze, K. *Chem. Phys. Rev.* **2022**, *3*, 041302.
- (177) Kerzig, C.; Wenger, O. S. *Chem. Sci.* **2019**, *10*, 11023–11029.
- (178) Schmermund, L.; Reischauer, S.; Bierbaumer, S.; Winkler, C. K.; Diaz-Rodriguez, A.; Edwards, L. J.; Kara, S.; Mielke, T.; Cartwright, J.; Grogan, G.; Pieber, B.; Kroutil, W. *Angew. Chem. Int. Ed.* **2021**, *60*, 6965–6969.
- (179) Ghosh, I.; König, B. *Angew. Chem. Int. Ed.* **2016**, *55*, 7676–7679.

-
- (180) Li, J.; Luo, Y.; Cheo, H. W.; Lan, Y.; Wu, J. *Chem.* **2019**, *5*, 192–203.
- (181) Svejstrup, T. D.; Chatterjee, A.; Schekin, D.; Wagner, T.; Zach, J.; Johansson, M. J.; Bergonzini, G.; König, B. *ChemPhotoChem.* **2021**, *5*, 808–814.
- (182) Joshi-Pangu, A.; Lévesque, F.; Roth, H. G.; Oliver, S.; Campeau, L.-C.; Nicewicz, D.; DiRocco, D. A. *J. Org. Chem.* **2016**, *81*, 7244–7249.
- (183) Mataga, N.; Chosrowjan, H.; Taniguchi, S. *J. Photochem. Photobiol. C* **2005**, *6*, 37–79.
- (184) Fay, T. P.; Limmer, D. T. *Chem. Sci.* **2024**, DOI 10.1039/D4SC01369G.
- (185) Feskov, S. V.; Ivanov, A. I. *Appl. Magn. Res.* **2022**, *53*, 745–761.
- (186) Michel-Beyerle, M. E.; Haberkorn, R.; Bube, W.; Steffens, E.; Schröder, H.; Neusser, H. J.; Schlag, E. W. *Chem. Phys.* **1976**, *17*, 139–145.
- (187) Orbach, N.; Potashnik, R.; M. Ottolenghi *J. Phys. Chem.* **1972**, *76*, 1089–1230.
- (188) Roth, H. D.; Sauers, R. S. *Photochem. Photobiol. Sci.* **2013**, *12*, 2036–2042.
- (189) Safirovich, V. Y.; Levin, P.; Kuzmin, V. A.; Thorgeirsson, T. E.; Kliger, D. S.; Geacintov, N. E. *J. Am. Chem. Soc.* **1994**, *116*, 63–72.
- (190) Wega, J.; Vauthey, E. *Photochem. Photobiol. Sci.* **2023**, *23*, 93–105.
- (191) Watkins, A. R. *J. Phys. Chem.* **1974**, *78*, 2555–2558.
- (192) Singh-Rachford, T. N.; Castellano, F. N. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.
- (193) Saltiel, J.; Marchand, G. R.; Smothers, W. K.; Stout, S. A.; Charlton, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 7159–7164.
- (194) Bossanyi, D. G.; Sasaki, Y.; Wang, S.; Chekulaev, D.; Kimizuka, N.; Yanai, N.; Clark, J. *JACS Au* **2021**, *13*, 2188–2201.
- (195) Feng, J.; Alves, J.; deClercq, D. M.; Schmidt, T. W. *Annu. Rev. Phys. Chem.* **2023**, *74*, 145–168.
- (196) Cheng, Y. Y.; Fückel, B.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N.; Crossley, M. J.; Schmidt, T. W. *J. Phys. Chem Lett.* **2010**, *1*, 1795–1799.
- (197) Zhou, Y.; Castellano, F. N.; Schmidt, T. W.; Hanson, K. *ACS Energy Lett.* **2020**, *5*, 2322–2326.
- (198) Ye, C.; Gray, V.; Kushwaha, K.; Singh, S. K.; Erhart, P.; Börjesson, K. *Phys. Chem. Chem. Phys.* **2020**, *22*, 1715–1720.
- (199) Parker, C.; Hatchard, C. *Proc. Chem. Soc. London* **1962**, 386–387.

-
- (200) Beery, D.; Schmidt, T. W.; Hanson, K. *ACS Appl. Mater. Interfaces* **2021**, *13*, 32601–32605.
- (201) Nattestad, A.; Cheng, Y. Y.; MacQueen, R. W.; Schulze, T. F.; Thompson, F. Q.; Mozer, A. J.; Füchel, B.; Khoury, T.; Crossley, M. J.; Lips, K.; Wallace, G. G.; Schmidt, T. W. *J. Phys. Chem. Lett.* **2013**, *4*, 2073–2078.
- (202) Huang, L.; Wu, W.; Li, Y.; Huang, K.; Lin, W.; Han, G. *J. Am. Chem. Soc.* **2020**, *142*, 18460–18470.
- (203) Zhou, J.; Liu, Q.; Feng, W.; Sun, Y.; Li, F. *Chem. Rev.* **2015**, *115*, 395–465.
- (204) Idris, N. M.; Gnanasammandhan, M. K.; Zhang, J.; Ho, P. C.; Mahendran, R.; Zhang, Y. *Nat. Med.* **2012**, *10*, 1580–1586.
- (205) Bilger, J. B.; Kerzig, C.; and O. S. Wenger, C. B. L. *J. Am. Chem. Soc.* **2021**, *143*, 1651–1663.
- (206) Wang, X.; Tom, R.; Liu, Y.; Congreve, D. N.; Marom, N. *J. Mater. Chem. C* **2020**, *8*, 10816–10824.
- (207) Nishimura, N.; Gray, V.; Allardice, J. R.; Zhang, Z.; Pershin, A.; Beljonne, D.; Rao, A. *ACS Mater. Lett.* **2019**, *1*, 660–664.
- (208) Harada, N.; Sasaki, Y.; Hosoyamada, M.; Kimizuka, N.; Yanai, N. *Angew. Chem. Int. Ed.* **2021**, *60*, 142–147.
- (209) Olesund, A.; Ghasemi, S.; Moth-Poulsen, K.; Albinsson, B. *J. Am. Chem. Soc.* **2023**, *145*, 22168–22175.
- (210) Zähringer, T. J. B.; Bertrams, M.-S.; Kerzig, C. *J. Mater. Chem. C* **2022**, *10*, 4568–4573.
- (211) Sanders, S. N.; Gangishetty, M. K.; Sfeir, M. Y.; Congreve, D. N. *J. Am. Chem. Soc.* **2019**, *131*, 9180–9184.
- (212) Li, Y.; Chen, G. *Advanced Nano Biomed. Research* **2023**, *14*, 4205–4218.
- (213) Nakadai, Y.; Tsuchiya, S.; Uehara, M.; Umezawa, S.; Motokoi, R.; Umezawa, H.; Ikoma, T.; Yui, T. *J. Phys. Chem. B* **2022**, *126*, 8245–8250.
- (214) Ye, C.; Gray, V.; Martensson, J.; Börjesson, K. *J. Am. Chem. Soc.* **2019**, *141*, 9578–9584.
- (215) Eöhrle, D.; Tausch, M. W.; Stohrer, W.-D.
- (216) Bienz, S.; Bigler, L.; Fox, T.; Meier, H., *Spektroskopische methoden in der organischen Chemie*, 9th ed.; Georg Thieme Verlag: 3026.
- (217) Bevernaegie, R.; Wehlin, S. A. M.; Elias, B.; Troian-Gautier, L. *Chem. Photo. Chem.* **2020**, *5*, 217–234.

-
- (218) Day, J. I.; Teegardin, K.; J. Weaver; Chan, J. *Org. Process. Res. Dev.* **2016**, *20*, 1156–1163.
- (219) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637–1755.
- (220) Elgrishi, N.; Routntree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. *J. Chem. Educ.* **2018**, *95*, 197–206.
- (221) Coe, B. J.; Helliwell, M.; Raftery, J.; Sánchez, S.; Peers, M. K.; Scrutton, N. S. *Dalton Trans.* **2015**, *44*, 20392–20405.
- (222) Arnold, D. R.; maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931–5937.
- (223) Kerzig, C.; Hoffmann, M.; Goetz, M. *Chem. Eur. J.* **2018**, *24*, 3038–3044.
- (224) Treinin, A.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *98*, 3884–3891.
- (225) Funston, A. M.; Lyman, S. V.; Saunders-Price, B.; Czapski, G.; Miller, J. R. *J. Phys. Chem.* **2007**, *111*, 6895–6902.
- (226) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617–2619.
- (227) Ferdermann, P.; Wagner, H. K.; Antoni, P. W.; Mörsdorf, J.-M.; PérezLustres, J. L.; Wadepohl, H.; Motzkus, M.; Ballmann, J. *Org. Lett.* **2019**, *21*, 2033–2038.
- (228) Deetz, A. M.; Troian-Gautier, L.; Wehlin, S. A. M.; Piechota, E. J.; Meyer, G. *J. Phys. Chem. A* **2021**, *125*, 9355–9367.
- (229) Zandoni, K. P. S.; Kariyazaki, B. K.; Ito, A.; Brennmann, M. K.; Meyer, T. J.; Iha, N. Y. M. *Inorg. Chem.* **2014**, *53*, 4089–4099.
- (230) Singh, A.; Teegardin, K.; Kelly, M.; Prasad, K. S.; Krishnan, S.; Weaver, J. D. *J. Organomet. Chem.* **2015**, *776*, 51–59.
- (231) Takizawa, S.-Y.; Aboshi, R.; Murata, S. *Photochem. Photobiol. Sci.* **2011**, *10*, 895–903.
- (232) Lowry, M. S.; Hudson, W. R.; Pascal, R. A.; Bernhard, S. *J. Am. Chem. Soc.* **2004**, *126*, 14129–14135.
- (233) Pellegrin, Y.; Odobel, F. *C. R. Chimie.* **2017**, *20*, 283–295.
- (234) Blum, T. R.; Zhu, Y.; Nordeen, S. A.; Yoon, T. P. *Angew. Chem. Int. Ed.* **2014**, *53*, 11056–11059.
- (235) Gates, B. D.; Dalidowicz, P.; Tebben, A.; Wang, S.; Swenton, J. S. *J. Org. Chem.* **1992**, *57*, 2135–2143.
- (236) Zhang, D.; Yuan, X.; Gong, C.; Zhang, X. *J. Am. Chem. Soc.* **2022**, *144*, 16184–16190.
- (237) Pavlishchuk, V. V.; Addison, A. W. *Inorg. Chim. Acta* **2000**, *298*, 97–102.
- (238) Sunararajan, C.; Falvey, D. E. *Photochem. Photobiol. Sci.* **2006**, *5*, 116–121.

-
- (239) Baek, Y.; Reinhold, A.; Tian, L.; Jeffrey, P. D.; Scholes, G. D.; Knowles, R. *J. Am. Chem. Soc.* **2023**, *145*, 12499–12508.
- (240) Schotten, C.; Nicholls, T. P.; Bourne, R. A.; Kapur, N.; Nguyen, B. N.; Williams, C. E. *Green Chem.* **2020**, *22*, 3358–3375.
- (241) Chen, C.; Wang, C.-X.; Zhang, G.-W.; Wu, M.-Y.; Feng, S. *Adv. Synth. Catal.* **2024**, *366*, 1983–1988.
- (242) Gray, V.; Dzebo, D.; Abrahamsson, M.; Albinsson, B.; Moth-Poulsen, K. *Phys. Chem. Chem. Phys.* **2014**, *16*, 10345–10352.
- (243) Zhao, W.; Castellano, F. N. *J. Phys. Chem. A* **2006**, *110*, 11440–11445.
- (244) Murakami, Y.; Kamada, K. *Phys. Chem. Chem. Phys.* **2021**, *23*, 18268–18282.
- (245) Fallon, K. J.; Churchill, E. M.; Sanders, S. N.; Shee, J.; Weber, J. L.; Meir, R.; Jockusch, S.; Reichmann, D. R.; Sfeir, M. Y.; Congreve, D. N.; Campos, L. M. *J. Am. Chem. Soc.* **2020**, *142*, 19917–19925.
- (246) Doering, J. P. *J. Chem. Phys.* **1969**, *51*, 2866.
- (247) Pittkowski, R.; Strassner, T. *Beilstein J. Org. Chem.* **2018**, *14*, 664–671.
- (248) Stipurin, S.; Strassner, T. *Eur. J. Inorg. Chem.* **2021**, *9*, 804–813.
- (249) Marchetti, A. P.; Kearns, D. R. *J. Am. Chem. Soc.* **1967**, *4*, 768–777.
- (250) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1–250.
- (251) Riesebeck, T.; Strassner, T. *Organometallics* **2023**, *42*, 3275–3282.
- (252) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; V. Barone, B. M.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Jr., J. M.; A., J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J., *Gaussian 09*; Gaussian Inc. Wallingford CT: 2009.
- (253) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515.
- (254) Yi, Y.-Q.-Q.; Yang, W.-C.; Zhai, D.-D.; Zhang, X.-Y.; Li, S.-Q.; Guan, B.-T. *Chem. Comm.* **2016**, *52*, 10894–10897.
- (255) Lavoie, E.; Parhi, A.; Pilch, D. S.; Zhang, Y.; Kaul, M. *ANTIMICROBIAL AGENTS*, WO 2013/106761, 2013.
- (256) Warren, J. J.; Tronic, T. A.; Mayer, J. M. *Chem. Rev.* **2010**, *110*, 6961–7001.

-
- (257) Kerzig, C.; Goetz, M.; Kerzig, C. *Phys. Chem. Chem. Phys.* **2014**, *16*, 25342–25349.
- (258) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005**, *17*, 5712–5719.
- (259) Steenken, S.; Neta, P. *J. Phys. Chem.* **1982**, *86*, 3661–3667.
- (260) Shukla, D.; Schepp, N. P.; Mathivanan, N.; Johnston, L. J. *Can. J. Chem.* **1997**, *75*, 1820–1829.
- (261) Gadosy, T. A.; Shukla, D.; Johnston, L. J. *Angew. Chem. Int. Ed.* **2014**, *53*, 9914–9916.

6 Appendix

The Appendix summarizes general experimental details of chemicals, instrumentation and experimental set ups. Furthermore, the Supporting Information for the publications that were discussed throughout the thesis are provided (Sections 6.7-6.12). The first section (Section 6.1) gives general details on the instrumentation used for all unpublished projects. Section 6.2 contains synthetic procedures and additional data referenced in Section 2.1. Section 6.3 contains thermodynamic considerations and additional data referenced in Section 2.1.2. Section 6.9 contains synthesis and analytical data for the iridium-based metal complexes and dyads discussed in Section 2.3.2 together with additional spectroscopic experiments. Section 6.5 provides additional spectroscopy for Section 2.4.

6.1 General experimental details for unpublished data

The methods and instrumentation within this section were used for analysis and spectroscopic measurements of the presented unpublished data in Section 2.3.2 and 2.4. Sections 2.1, 3.1 and 3.2 present additional data for already-published projects (references [33, 36, 44] respectively) and experimental details are listed in the corresponding supporting information (Sections 6.7, 6.10 and 6.11).

Chemicals:

The chemicals and solvents for individual projects are listed in the corresponding sections of the Appendix (Sections 6.2, 6.9 and 6.5). MilliQ water for spectroscopy and synthesis was used with a specific resistance 18.2 M Ω cm. Argon was used from Nippon Gases (5.0).

Steady-state measurements:

Absorption spectra were measured with a LAMBDA 365 from Perkin Elmer. Emission spectra were measured with a FL 6500 from Perkin Elmer and corrected for the wavelength-dependent sensitivity of the emission spectrometer. Unless noted otherwise, the absorbance was adjusted below 0.1 at the excitation wavelengths and in the overlap area of emission and absorption spectra to avoid filter effects.

Time-resolved measurements:

Laser flash photolysis (LFP) measurements were performed using an LP980-KS apparatus from Edinburgh Instruments. Two lasers (Nd:YAG laser from Quantel, Q-Smart 450 or Lithron, Nano LG 300-10) were employed as excitation source using their frequency-doubled (532 nm) or -tripled (355 nm) output, both with a pulse duration of ~ 5 ns and a frequency of 10 Hz. Typical pulse energies were 10 mJ, unless indicated otherwise in the figure captions. A beam expander (Thorlabs) was used to ensure ho-

mogeneous excitation in the detection volume. Kinetic traces were recorded at a single wavelength with a photomultiplier tube and for measuring transient absorption or emission spectra an iCCD camera from Andor was used. All TA spectra were integrated over 100 ns. Single-wavelength kinetics were recorded using a photomultiplier from Hamamatsu (R298). The temperature was maintained at 20 °C using a cuvette holder that allows temperature control unless indicated otherwise.

For fluorescence lifetimes a mini- τ from Edinburgh Instruments (time-correlated single photon counting TCSPC technique) was used. Excitation was performed with a pulsed LED (EPLD-300, pulse-width 1020.0 ps, average power 40 μ W, λ_{exc} =293 nm) or different lasers (EPL-374, pulse-width 58.3 ps, average power 5 mW, λ_{exc} =371 nm, EPL-450, pulse-width 74.5 ps, average power 5 mW, λ_{exc} =446 nm) and for the detection the built-in band-pass filters were used.

Programs used within the framework of this thesis:

- Data from UV-Vis, fluorescence, TCSPC and transient absorption measurements were plotted with OriginPro9.0.
- MestReNova version 14.3.2-32681 was used for NMR data
- Graphs of this thesis were created using powerpoint
- This thesis was written in $\text{\LaTeX}$ using my personally developed script and the biblatex usepackage for organizing the references

DFT calculations:

For the DFT calculations (structure optimization and frequency analyses), the Gaussian 09 softwarepackage was used with the B3LYP functional and basis set either 6-311+G(d,p) or 6-31+G(d,p).^[252] The minimum structure was confirmed by the lack of negative vibrational frequencies. After optimizing the singlet ground states, the structures were used to calculate the triplet excited state. The triplet energies were obtained by comparing the energies of the optimized ground states to those of the corresponding triplet states.^[33]

^1H NMR spectroscopy and mass spectrometry:

An Avance II 400 multi-nuclear magnetic resonance spectrometer (Bruker, analytic measuring technique, Karlsruhe, Germany) was used for measuring NMR spectra. The solvents used were acetonitrile- d_4 ($\text{MeCN-}d_3$), chloroform- d (CDCl_3), dimethyl sulfoxide- d_6 ($\text{DMSO-}d_6$), water- d_2 (D_2O). Non-deuterated solvent signals were used to calibrate the ^1H NMR spectra^[253] and the chemical shifts are given in δ / ppm. The coupling constants J are given in Hz.

Mass spectrometry was performed on a G6545A Q-ToF (Agilent GmbH, Waldbronn, Germany) using electrospray ionization (ESI).

For all synthesized compounds the ^1H NMR-data is given below the synthetic procedure. The iridium-based dyads are not literature-known, and for that reason also ESI-MS data is provided.

6.2 Additional data and supporting Information for Sensitization-initiated electron transfer with blue light (Section 2.1.1)

6.2.1 General experimental details

Chemicals:

Unless indicated otherwise, chemicals for optical spectroscopy were used as obtained from the supplier (in the highest available purity) without further purification: Acetone (Acros, 99.8 %); 4-Amino-*p*-terphenyl (TCI, >97 %); Amberlite (IRA-410, Sigma-Aldrich); 4-Bromo-*p*-terphenyl (BLD Pharm, 98 %); *n*-Buthyllithium (Acros, 2.5 M in hexane); Diethyl ether (dry, Sigma-Aldrich, 99.5 %); Dry ice (Enotech, 99.7 %) *N,N*-Dimethyl-1-naphthylamine (Alfa Aesar, 99 %); *N,N*-Dimethyl-2-naphthylamine (TCI, 98 %); Disodium decahydrate carbonate (Sigma-Aldrich, >99 %); Ethanol (EtOH, Sigma-Aldrich, 99.5 %); hydrochloric acid (HCl, VWR, AnalaR NORMA PUR, 37 %); Iodomethane (VWR BDH Chemicals, 99 %); $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{dtbpy}]\text{PF}_6$ (Sigma-Aldrich); Methyl *t*-butyl ether (tech.); Methyl trifluoromethanesulfonate (Sigma-Aldrich, >98 %); Monosodium ascorbate (Sigma-Aldrich, >98 %); Sodiumhydroxide (NaOH, Sigma-Aldrich, 97 %); Sodium naphthalene-2-sulfonate (Sigma-Aldrich, >95 %); [1,1':4',1''-Terphenyl]-4,4''-dicarboxylic acid (TDS, BLD Pharm, 95 %); Tetrahydrofuran (THF, dry, Honeywell Chromasolv Plus, $\geq 99\%$).

The sodium salts of $[\text{Ir}(\text{sppy})_3]^{3-}$ and $[\text{Ir}(\text{Fsppy})_3]^{3-}$ were still available from a former study.^[102]

6.2.2 Synthesis and characterization

Synthesis of *N,N,N*-trimethylnaphthylamine-1-ammonium chloride (1-NMA):

The synthesis was performed according to a literature-known procedure.^[254] A schlenk flask was sealed with a septum cap and evacuated and flushed with argon three times. Under inert conditions, diethyl ether (dry, 20 mL) and *N,N*-dimethyl-1-naphthylamine (1.0 mL, 6.1 mmol, 1.0 eq.) were added to the flask. The reaction mixture was stirred under an argon atmosphere and cooled to 0 °C. Methyl trifluoromethanesulfonate (2.0 mL, 18.3 mmol, 3.0 eq.) was added dropwise under constant stirring, which induced the formation of a precipitate. The reaction mixture was stirred for 1.5 h at 0 °C. The cooling bath was removed and the reaction mixture was stirred for 2.0 h at room temperature. The precipitate was filtered, washed with pre-cooled (~ 10 °C) diethyl ether (2×5 mL). The filtrate was redissolved in ethanol (25 mL) and applied to an ion exchange column (Amberlite IRA-410). Ethanol was used to flush the compound from the column and the

solvent was removed under reduced pressure. Recrystallization from acetone yielded 1-NMA (515.7 mg, 2.3 mmol, 38 %) as a colorless powder.

¹H NMR (D₂O, 400 MHz), δ / ppm: 8.4 (dq, J = 9.1, 1.0 Hz, 1H), 8.1 (ddt, J = 7.1, 6.4, 0.9 Hz, 2H), 8.0 (ddd, J = 8.8, 6.9, 1.5 Hz, 1H), 7.7 (ddd, J = 8.0, 6.9, 0.9 Hz, 1H), 7.6 (t, J = 8.2 Hz, 1H), 3.9 (s, 9H).

Synthesis of *N,N,N*-trimethylnaphthylamine-2-ammonium chloride (2-NMA):

The synthesis was performed according to a literature-known procedure.^[254] A schlenk flask was sealed with a septum cap and evacuated and flushed with argon three times. Under inert conditions, diethyl ether (dry, 20 mL) and *N,N*-dimethyl-2-naphthylamine (500 mg, 2.9 mmol, 1.0 eq.) were added to the flask. The reaction mixture was stirred under argon and cooled to 0 °C. Methyl trifluoromethanesulfonate (0.6 mL, 4.9 mmol, 1.7 eq.) was added dropwise under constant stirring, which induced the formation of a precipitate. The reaction mixture was stirred for 1.5 h at 0 °C. The cooling bath was removed and the reaction mixture was stirred for 2.0 h at room temperature. The precipitate was filtered, washed with pre-cooled (~ 10 °C) diethyl ether (2 × 5 mL). The filtrate was redissolved in ethanol (25 mL) and applied to an ion exchange column (Amberlite IRA-410). Ethanol was used to flush the compound from the column and the solvent was removed under reduced pressure. Recrystallization from acetone yielded 2-NMA (231.6 mg, 1.0 mmol, 36 %) as a light-brown powder.

¹H NMR (D₂O, 400 MHz), δ / ppm: 8.4 (d, J = 2.9 Hz, 1H), 8.2 (d, J = 9.3 Hz, 1H), 8.05 (m, 2H), 7.9 (dd, J = 9.3, 2.8 Hz, 1H), 7.7 (m, 2H), 3.7 (s, 9H).

Synthesis of [1,1':4'1'']-terphenyl-4-carboxylic acid (TMC):

The synthesis was performed according to a literature-known procedure.^[102] A schlenk flask was sealed with a septum cap and evacuated and flushed with argon three times. Dry THF (30 mL) and 4-bromo-*p*-terphenyl (1.00 g, 3.23 mmol, 1.0 eq.) were added to the flask and the reaction mixture was kept under inert conditions. The reaction mixture was cooled to -78 °C under constant stirring. *n*-Butyllithium dissolved in hexane (2.5 M, 1.42 mL, 3.56 mmol, 1.1 eq.) was added dropwise. CO₂ from dry ice was bubbled through the reaction solution for 60 min. The cooling bath was removed and after reaching room temperature, aqueous HCL (4 mL, 10 wt%) was added. MTBE (15 mL) was heated to 40 °C and added to the mixture to suspend the crude product. The mixture was filtered, leaving the raw product as filtrate, which was washed with cold MTBE (15 mL). The product was dried under reduced pressure yielding TMC as a colorless solid (479 mg, 1.75 mmol, 54 %).

¹H NMR (DMSO-*d*₆, 400 MHz), δ / ppm: 8.04 (d, *J* = 8.0 Hz, 2H), 7.83 (m, 6H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.56 Hz, 2H), 7.40 (t, *J* = 4.0 Hz, 1H).

Synthesis of *N,N,N*-trimethyl-[1,1':4'1'']-terphenyl]-4-ammonium iodide (TMA):

The procedure was adapted from a patent.^[255] A pressure vial was equipped with a stirring bar, [1,1':4',1'']-terphenyl]-4-amine (300 mg, 1.09 mmol, 1.0 eq.) and iodomethane (8 mL) were added and the vial was sealed. The reaction mixture was stirred and heated to 80 °C for 16 h. The reaction mixture was cooled to room temperature and the residue was washed with diethyl ether (50 mL). The isolated solid was a mixture of the starting material and the mono-, di-, and three-times-methylated amine starting material. The target compound TMA was identified using mass spectrometry and by comparing ¹H NMR data from the patent^[255] with the measured ¹H NMR data in the same solvent, showing some impurities, likely originating from the mono- and di-methyl derivatives.

¹H NMR (DMSO-*d*₆, 400 MHz), δ / ppm: 8.05 (d, *J* = 9.4 Hz, 2H), 7.98 (d, *J* = 9.4 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.76-7.70 (m, 17H), 7.62 (m, 1H), 7.53-7.46 (m, 6H), 7.41 (m, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 4H), 3.65 (s, 9H).

ESI-MS: *m/z* for [M⁺] C₃₄H₂₄N₄Ir⁺ calculated: 288.1747, found: 288.1749.

6.2.3 UV-Vis spectra of iridium-based complexes and naphthalene- and *p*-terphenyl-based organic chromophores

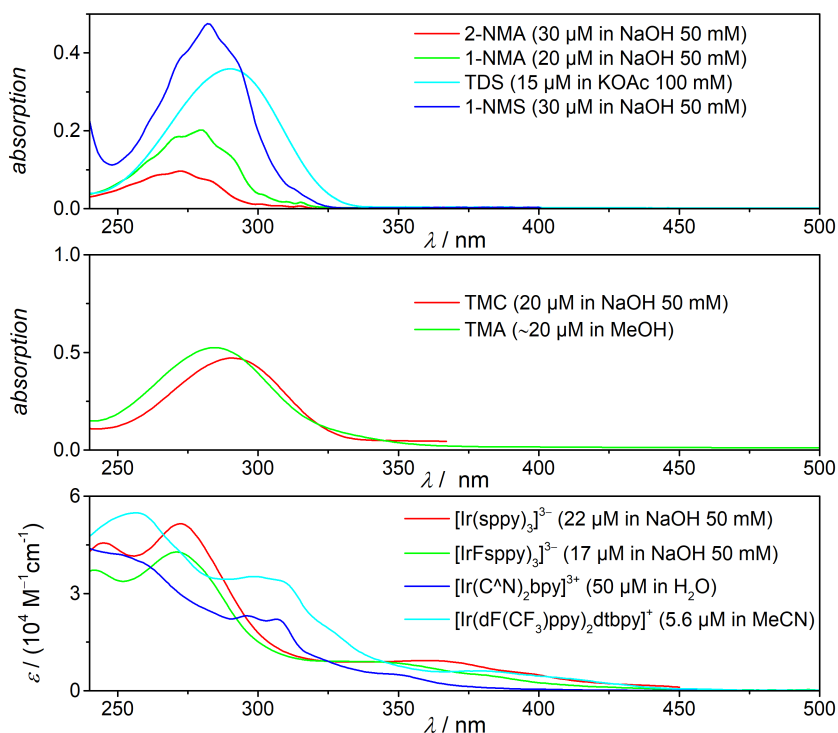


Figure 38: UV-Vis spectra of all naphthalene- and *p*-terphenyl-based organic chromophores (upper and middle panel) and of the iridium-based metal complexes. The concentrations and solvents are color-coded and given in the figure. The molar extinction coefficients of the iridium-based complexes match those found in the literature ($[\text{Ir}(\text{sppy})_3]^{3-}$, ^[102,129] $[\text{Ir}(\text{Fsppy})_3]^{3-}$, ^[102,129] $[\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{bpy}]^{3+}$, ^[127] $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{dtbpy}]^+$ ^[230]).

Figure 38 presents the UV-Vis spectra of the iridium-based metal catalysts and organic chromophores for the blue-light-driven combined electron and energy transfer catalytic cycle. The organic chromophores do not absorb above 350 nm. All of the sensitizers (Figure 38 bottom panel) absorb in the visible region above 400 nm. As a consequence, the laser excitation at 355 nm is selective towards the iridium-based sensitizers.

6.2.4 Potentials of water-soluble naphthalenes and terphenyls

The potentials of the water-soluble naphthalene and *p*-terphenyl derivatives have been rationalized using equation 12, which connects the rate constant for electron transfer k_{ET} to the free energy of the process. Quenching rates slightly below the diffusion limit ($6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in water [48]) are caused by a slightly endergonic ET process.^[80,81] Consequently, Table 4 lists only lower limits for the ground-state potentials assuming a $\Delta G = 0$ and the literature-known potential for $E(\text{Asc}^{\bullet-/2-}) = 0.14 \text{ V vs NHE}$ for the potential of the electron donor.^[5,219,256] For ^3TDS , the reduction was achieved with $\text{Asc}^{\bullet-/}$ = 0.72 V vs NHE .^[118]

Table 11: Parameters for calculating the potential of water-soluble naphthalenes, based on equation 12.

chromophore (C, naphthalene)	$k_{\text{ET}} /$ $10^9 \text{ M}^{-1} \text{ s}^{-1}$	$E_{\text{T}} / \text{eV}^{[\text{a}]}$	$E_{\text{red}} (\text{C/C}^{\bullet-})^{[\text{b}]} /$ V vs NHE
TDS ^c	0.09 ^d	2.60 ^d	< -1.9
2-NMS	1.7	2.50	-2.36
2-NMA	6.3	2.58	-2.44
1-NMA	4.2	2.62	-2.48

^aDFT calculations (B3LYP/6-311+G(d,p)). ^bEstimated using equation 12 with $\Delta G = 0$ and, $E_{\text{ox}}(\text{Asc}^{\bullet-/2-}) = 0.14 \text{ V vs NHE}$ ^[5,219,256], see text for explanation. ^cReduction of the triplet excited state with $E_{\text{ox}}(\text{HAsc}^{\bullet-/}) = 0.72 \text{ V vs NHE}$ ^[118]. ^dDFT calculations (B3LYP/6-31+G(d,p)).

In the estimation for the potentials in Table 11 ionic effects are not taken into account,^[63] which would be an attractive Coulombic interaction between the cationic naphthalene derivatives and the Asc^{2-} . For TDS the electron transfer quenching is well below the diffusion limit, which could be due to the ionic repulsion between the reactants. Assuming $\Delta G = 0$, leads to the potential listed in the table. However, due to the low k_{ET} , and despite the Coulombic repulsion, ΔG is probably slightly positive. Considering the electronic repulsion and the low k_{ET} this potential is to be considered a lower limit. Generally, the potential of naphthalene is below that of *p*-terphenyl, and this is reflected in the calculated potentials for the ionic derivatives.^[48] Eventually, more quenching experiments are required for an exact estimation of the potentials.

6.2.5 Excited state kinetics and transient absorption spectra for catalytic mechanism in Figure 18:

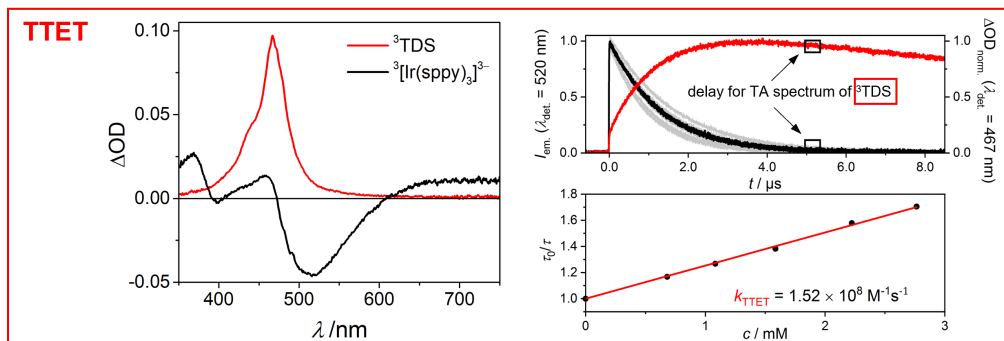


Figure 39: Spectroscopic data for TTET between $^3[\text{Ir}(\text{sppy})_3]^{3-}$ and TDS^{2-} ($[\text{Ir}(\text{sppy})_3]^{3-}$, 50 μM) in KOAc (50 mM). Left: TA spectra of $^3[\text{Ir}(\text{sppy})_3]^{3-}$ (black) and $^3\text{TDS}^{2-}$ (red, 2.5 μM). Right: The kinetic traces for the emission decay of $^3[\text{Ir}(\text{sppy})_3]^{3-}$ (black, measured at $\lambda_{\text{det}} = 550 \text{ nm}$) and formation of $^3\text{TDS}^{2-}$ (red, measured at $\lambda_{\text{det}} = 457 \text{ nm}$) at identical conditions as the TA spectra. The additional gray decay traces present the lifetime of $^3[\text{Ir}(\text{sppy})_3]^{3-}$ at increasing concentrations of TDS. The resulting Stern–Volmer plot together with the k_{TTET} is shown in the lower panel on the right.

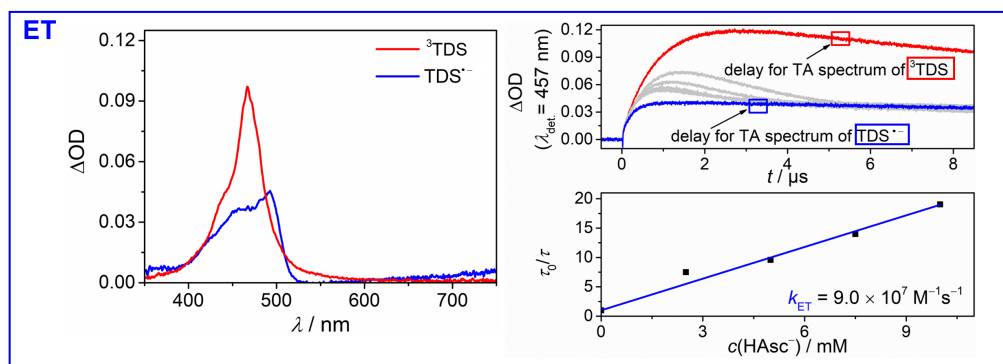


Figure 40: Spectroscopic data for ET between ^3TDS and HAsc^- (10 mM) using $[\text{Ir}(\text{sppy})_3]^{3-}$ (50 μM), TDS (3.0 mM) in KOAc (100 mM). Right: TA spectra of ^3TDS (red, delay 5.5 μs) and $\text{TDS}^{\bullet-}$ (blue, 2.5 μM). Left: The kinetic traces for the decay of ^3TDS (red, measured at $\lambda_{\text{det}} = 457 \text{ nm}$) and formation of $^3\text{TDS}^{\bullet-}$ (blue) were measured at identical conditions as the TA spectra. The additional gray decay traces show the lifetime of ^3TDS at increasing concentrations of HAsc^- . The resulting Stern–Volmer plot together with the k_{ET} is shown at the lower panel on the right.

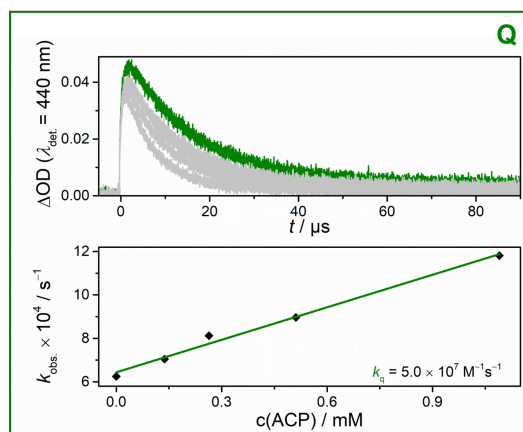


Figure 41: Decay traces of TDS^{*-} (green, measured at $\lambda_{\text{det}} = 440 \text{ nm}$) and at increasing ACP concentrations using $[\text{Ir}(\text{sppy})_3]^{3-}$ ($40 \mu\text{M}$), TDS (4.0 mM), HAsc (30 mM), KOAc (30 mM). The observed quenching rates are plotted below against the respective ACP concentrations and the slope of the linear fit yields the overall quenching rate constant for the substrate activation step.

Unwanted sidereaction 1) quenching of $^3[\text{Ir}(\text{sppy})_3]^{3-}$ with ACP:

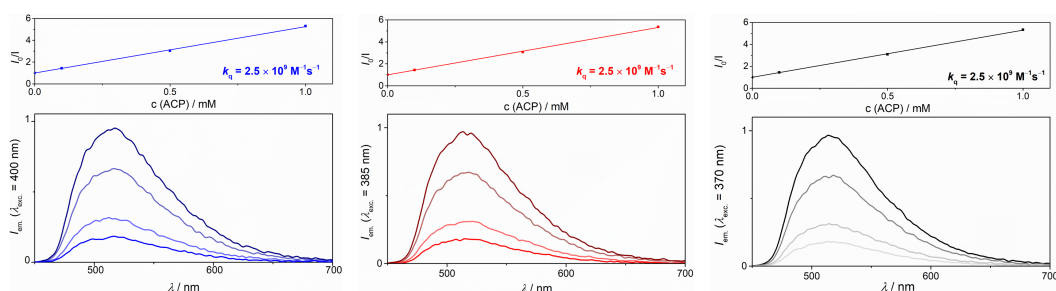


Figure 42: Steady-state quenching of $^3[\text{Ir}(\text{sppy})_3]^{3-}$ with ACP measured with three different excitation wavelengths. The averaged $k_q = 2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (using $\tau_T = 1.7 \mu\text{s}$) outcompetes all other possible and investigated processes (Table 5).

Figure 42 provides the quenching studies of $^3[\text{Ir}(\text{sppy})_3]^{3-}$ with ACP. The corresponding quenching rate ($k_q = 2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) exceeds that for the desired energy transfer between $^3[\text{Ir}(\text{sppy})_3]^{3-}$ and TDS ($k_{\text{TTET}} = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, Table 5). Considering the combined TTET and ET mechanism (Figure 18), this is a competing quenching step.

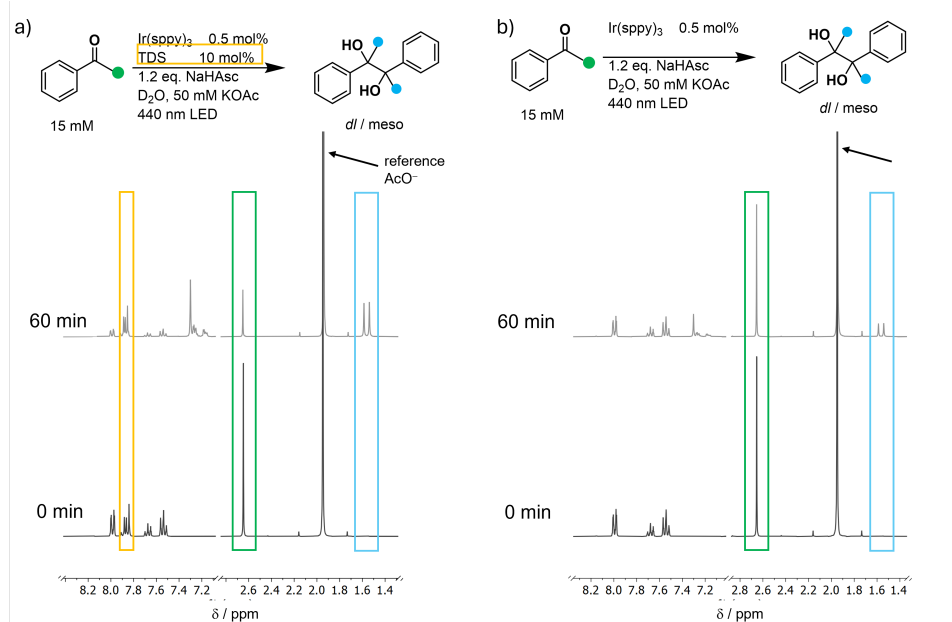


Figure 43: ^1H NMR data for irradiation experiments for pinacol coupling of acetophenone (ACP) with the full catalytic system a) or without TDS b) under otherwise identical conditions.

Comparative ^1H NMR experiments showed a fast conversion of ACP to the pinacol product (pinacol yield of 72 % after 1 h) when using the full catalytic system.¹² In the control experiment without TDS present, a considerable amount of the pinacol product is formed (pinacol yield of 27 % after 1 h), making the full system twice as efficient (by about ~60 %) as the system without TDS. Longer irradiation times resulted in product decomposition for the sample reaction with the full catalytic system (after 2 h, conversion of 100 %, pinacol yield of 89 %). In the control reaction with only the iridium-catalyst present no decomposition was observed, however a product yield of under 50 % was observed (after 2 h, conversion of 40 %, pinacol yield of 40 %). A reasonable explanation for the much slower proceeding of the reaction without TDS present is provided in Figure 44. The figure illustrates the spin allowed bET using the iridium-based complex as photocatalyst as opposed to the $\text{TDS}^{\bullet-}$ generated *via* sensitization and electron transfer (see also Section 1.2.5, Cage escape efficiency of ET reactions).

¹²A pinacol coupling requires two substrate molecules to form one product, which would result in a maximum product yield of 50 %. The yield of the pinacol was multiplied by 2 such that a possible yield of 100 % can be achieved.

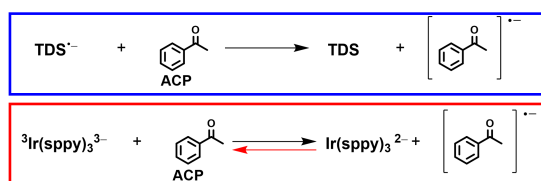


Figure 44: The blue box shows the mechanism for the quenching of $\text{TDS}^{\bullet-}$ with ACP producing the wanted $\text{ACP}^{\bullet-}$, which then further reacts with a second $\text{ACP}^{\bullet-}$ to the pinacol product. The red box shows the proposed reaction for $^3\text{Ir}(\text{sppy})_3^{3-}$ with ACP, which is also an ET reaction producing the oxidized sensitizer and $\text{ACP}^{\bullet-}$. Owing to the heavy atom effect, the bET reaction (red arrow) is not strictly spin forbidden.

Unwanted side reaction 2) quenching of the iridium-based metal complex with the electron donor:

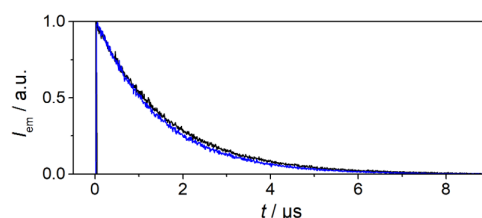


Figure 45: Kinetic traces of $^3\text{Ir}(\text{sppy})_3^{3-}$ (black) and $^3\text{Ir}(\text{sppy})_3^{3-}$ with HAsc^- (60 mM, blue). For both kinetic traces were measured using a KOAc (200 mM) solution of Irspdy (50 μM).

The quenching of $^3\text{Ir}(\text{sppy})_3^{3-}$ with HAsc^- indicated as an unwanted quenching reaction 2) in Figure 18 and Table 5 is slow. Figure 45 shows the lifetime measurements of unquenched $^3\text{Ir}(\text{sppy})_3^{3-}$ and the lifetime in the presence of the electron donor HAsc^- .

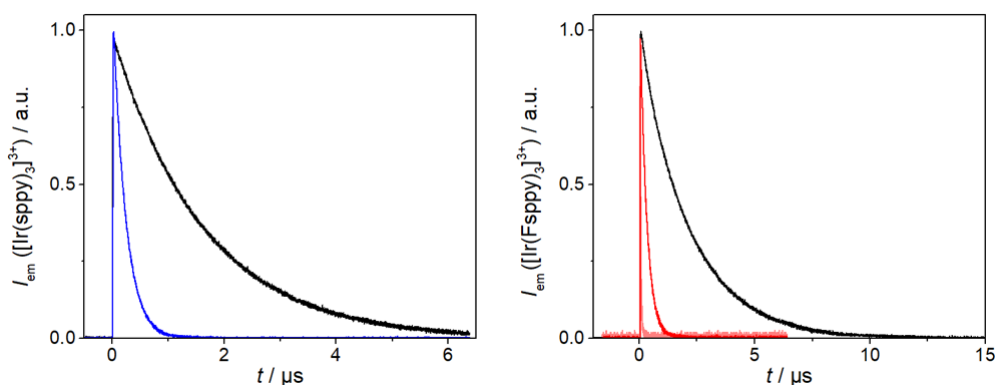


Figure 46: Kinetic decay traces for triplet excited state quenching of $^3\text{Ir}(\text{sppy})_3^{3-}$ (left, 20 μM) and $^3\text{Ir}(\text{Fsppy})_3^{3-}$ (right, 20 μM) in NaOH (150 mM). $^3\text{Ir}(\text{sppy})_3^{3-}$ was quenched with 10 mM NaHAsc (blue) and IrFsppy was quenched with 5 mM (red) and 50 mM (light red) NaHAsc.

The triplet excited states of $[\text{Ir}(\text{sppy})_3]^{3-}$ and $[\text{Ir}(\text{Fsppy})_3]^{3-}$ were also quenched with ascorbate as an electron donor under basic conditions (NaOH, 150 mM). For the reduction of the naphthalene derivatives, the Asc^{2-} is required, which is present at high pH. However, the iridium-based complexes are reduced by this species as well, thereby introducing a competing reaction, slightly below the diffusion limit ($k_{\text{ET}}([\text{Ir}(\text{sppy})_3]^{3-}) \sim 4.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{ET}}([\text{Ir}(\text{Fsppy})_3]^{3-}) \sim 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).

6.2.6 Spectroscopic data for MC–OC systems with enhanced Coulombic interactions:

Stern–Volmer-plots for triplet-triplet energy transfer rates comparing Coulombic attraction and repulsion with water-soluble naphthalene derivatives:

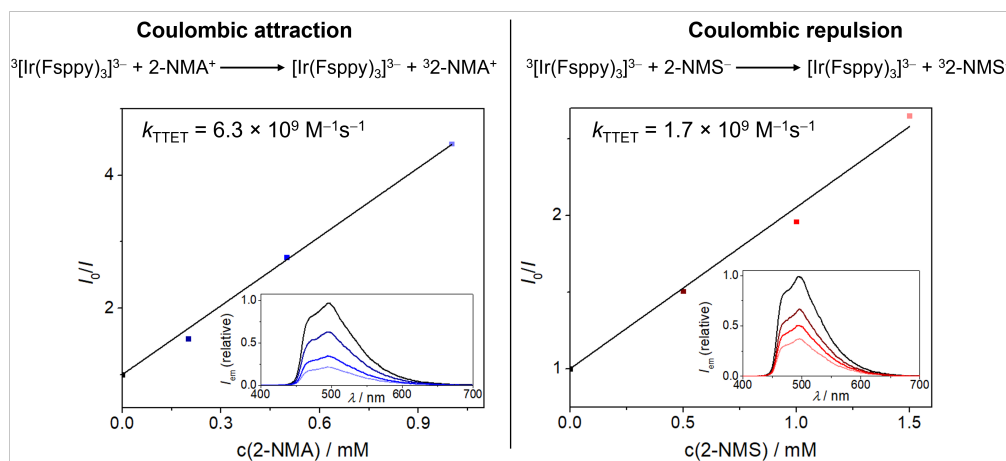


Figure 47: Stern–Volmer-plots for quenching of the anionic $[\text{Ir}(\text{Fsppy})_3]^{3-}$ with water-soluble naphthalenes. Excitation of $[\text{Ir}(\text{Fsppy})_3]^{3-}$ (20 μM) occurred at 375 nm. The corresponding Stern–Volmer plots are provided as inset.

Coulombic attraction to the cationic 2-NMA result in a higher triplet energy transfer rate constant, compared to the anionic 2-NMS. This beneficial Coulombic effect has been exploited for the sensitization-initiated electron transfer with the ruthenium-based metal catalyst (Section 2.1.2).

Transient absorption spectroscopy with cationic naphthalenes as OC:

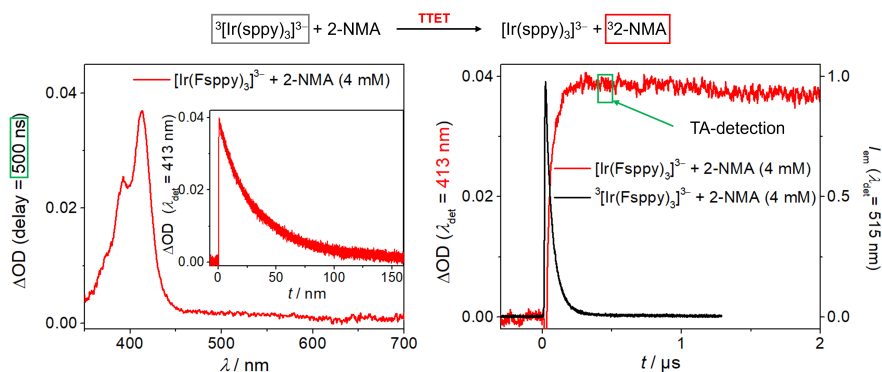


Figure 48: Spectroscopic data for formation of $^32\text{-NMA}$ after TTET from $^3[\text{Ir}(\text{Fsppy})_3]^{3-}$ in aqueous NaOH (50 mM). Left: Transient absorption spectrum of $^32\text{-NMA}$ after a time delay of 1.7 μs with the kinetic decay at a long timescale as inset. Right: Kinetic decay trace of $^3[\text{Ir}(\text{Fsppy})_3]^{3-}$ with 2-NMA (4 mM) present (black) together with the formation kinetic of the $^32\text{-NMA}$ detected at 413 nm. The solution was excited using a pulsed laser (355 nm).

The right part of figure 48 displays the transient absorption spectrum of $^32\text{-NMA}$ after TTET with $^3[\text{Ir}(\text{Fsppy})_3]^{3-}$ (concentration of the sensitizer was chosen such, that an the absorption at the excitation wavelength amounts to 0.1 $\sim$ 40 μM). The shape and shift of the spectrum suits well with that observed for ^3TDS (Figure 40) and with that expected from literature^[145,250]. In the left part of the figure, the kinetic trace of the sensitizer (black) decays on the same time scale as the time resolved transient absorption trace of new species ($^32\text{-NMA}$, red) forms, thereby indicating the direct quenching and energy transfer.

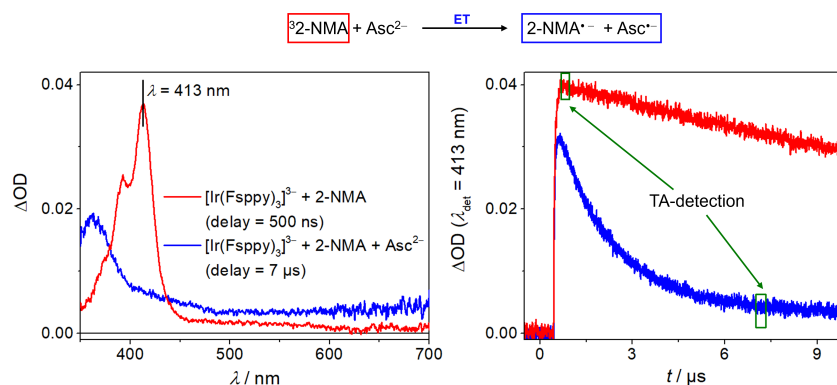


Figure 49: Spectroscopic data for formation of $^32\text{-NMA}$ after ET from Asc^{2-} in aqueous NaOH (50 mM). Left: Transient absorption spectra of $^32\text{-NMA}$ (compare Figure 48, red) and the spectrum detected after the electron transfer (blue, delay = 7 μs). Right: Kinetic traces of the unquenched $^32\text{-NMA}$ (red) and the kinetic after addition of Asc^{2-} (1.0 mM, blue). The solution was excited using a pulsed laser (355 nm).

The transient absorption spectra and kinetic traces in Figure 49 highlight the electron transfer step to obtain $2\text{-NMA}^{\bullet-}$. The same solution as for Figure 48 was used for the spectroscopy with Asc^{2-} (1.0 mM) added (blue data set). After quenching of $^32\text{-NMA}$ with the electron donor, the transient absorption spectrum shows a species with a maximum below 400 nm, which corresponds to the oxidized species of ascorbate ($\text{Asc}^{\bullet-}$).^[257] The absorption band between 400 nm to 500 nm could correspond to the broad absorption that would be expected from the radical anion^[224,225] (Figure 40). Further quenching experiments with a possible substrate were not performed because i) the blue kinetic decay trace indicates that this species is not long lived and therefore not ideal for the sensitization-initiated electron transfer and ii) the weak intensity of this band, together with decomposition throughout the measurement strongly suggest that the species formed is not stable under the selected conditions. This is likely due to decomposition processes, which are known for naphthalene radical anions in protic solvents.^[224,225]

6.3 Additional data and Supporting Information for sensitization-initiated electron transfer with green light (Section 2.1.2)

The potentials of PTS were rationalized using the Rehm–Weller equation, which links the rate constant for electron transfer k_{ET} to the free energy. Quenching rates slightly below the diffusion limit ($6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in water ^[48]) correspond to a slightly endergonic ET process.^[80,81] The potential listed in Table 6 is derived using the table below:

Table 12: Parameters (k_{ET} for quenching of ³PTS with an electron donor (D) and the corresponding redox potentials) for calculating the potential of water-soluble pyrene derivatives, based on Equation 12.

electron donor (D)	$k_{\text{ET}} /$ $10^7 \text{ M}^{-1} \text{ s}^{-1}$	$E_{\text{ox}}(\text{D}^+/\text{D}) /$ V vs NHE	$E_{\text{red}}(\text{PTS}/\text{PTS}^{\bullet-})^{\text{a}} /$ V vs NHE
HAsc [−]	2.3	0.72 ^[118]	−1.08
DMA	~ 2	1.05 ^{b[233]}	−0.72

^a Calculated using Equation 12, lower limit for potential calculated from $\Delta G = 0$, see text for explanation. ^b Calculated from V vs SCE (in MeCN) by adding 0.24V vs NHE.^[71]

The electron transfer rate is significantly below the diffusion limit for the reductive quenching of ³PTS with ascorbate. Therefore, the assumption of $\Delta G = 0$ is an over-estimation of the potential. The quenching rate constant for DMA was only estimated (see experiments for deriving $\Delta \epsilon(\text{PTS}^{\bullet-})$ in reference [36]). Considering both aspects, a reduction potential of $E_{\text{red}}(\text{PTS}/\text{PTS}^{\bullet-}) \sim -0.9 \text{ V vs NHE}$ was assumed.

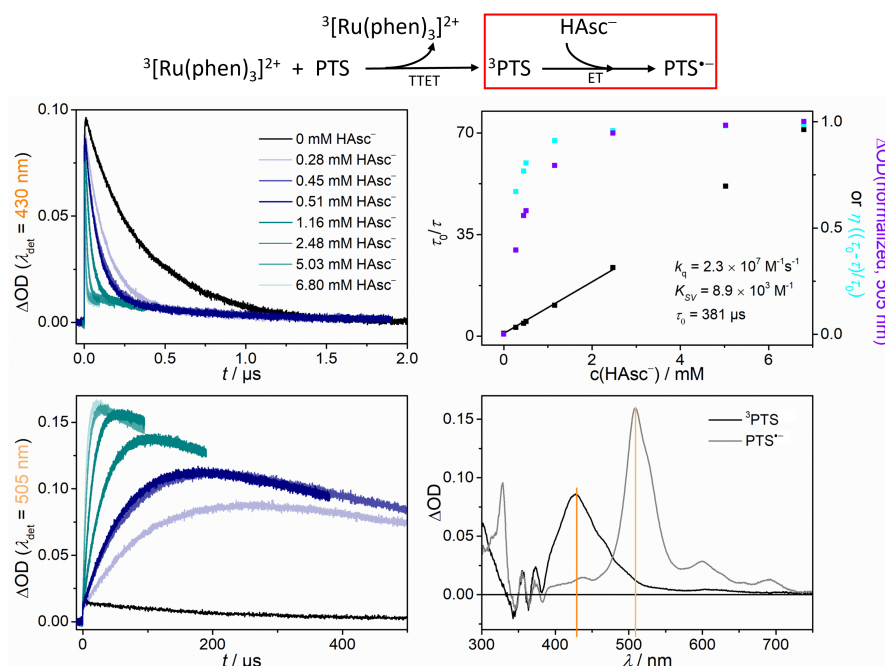


Figure 50: Reaction scheme with the observed ET step highlighted with a red box. The stock solution contained $[\text{Ru}(\text{phen})_3]^{2+}$ ($30 \mu\text{M}$) and PTS ($120 \mu\text{M}$) in water. Upper left shows quenching of ^3PTS with HAsc^- and below the formation $\text{PTS}^{\bullet-}$ (lower left). The top right part of the figure shows the Stern-Volmer plot and the efficiency of the $\text{PTS}^{\bullet-}$ formation. In the lower right part the TA spectra of ^3PTS (same solution without HAsc^- , delay $2.0 \mu\text{s}$) and $\text{PTS}^{\bullet-}$ (5.08 mM HAsc^- , delay $20 \mu\text{s}$).

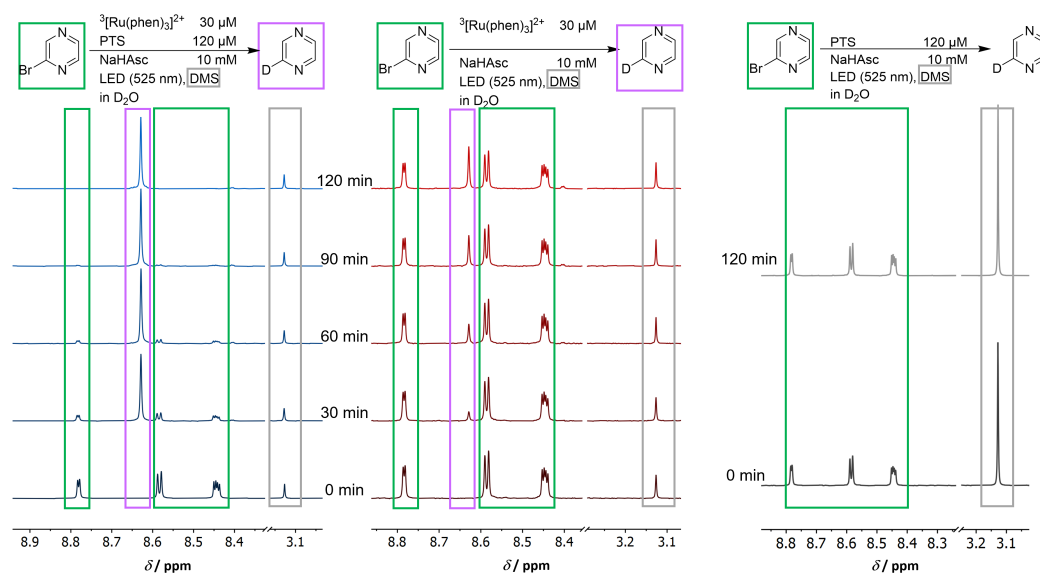


Figure 51: Original ^1H NMR data for the debromination reaction of bromo-pyrazine with the full system (left, blue data), without PTS (middle, red data) or without $[\text{Ru}(\text{phen})_3]^{2+}$ (right, black data). All experiments were conducted under identical conditions and the signals for the starting material, Br-Pz, were marked with a green box, and the debrominated product singlet was marked with a purple box. The signal for the reference compound dimethyl sulfone (DMS) is marked with a gray box.

6.4 Additional data and Supporting Information for Iridium-based dyads (Section 2.3.2)

6.4.1 General experimental details

Chemicals:

Acetonitrile (MeCN, VWR, LC MS grade, 100 %); ammoniumhexafluorophosphate (Thermo Scientific, 99.5 %); dichloromethane (Fisher Scientific, ≥ 99.8 %); diethyl ether (VWR, ≥ 99 %); 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine (BLD Pharm, 97 %); ethylene glycol (Carl Roth, ≥ 99 %); iridium(III)chloride (BLD Pharm, 98 %); 2-methoxyethanol (Thermo Scientific, 99.3 %); 2-methyltetrahydrofuran stab. (2-MeTHF, Alfa Aesar, 98 %); 1,10-phenanthroline (Sigma-Aldrich, ≥ 99 %); 2-phenylpyridine (TCI, ≥ 98 %); sodium sulfate (Acros, 99 %). 5-(Pyren-1-yl)-1,10-phenanthroline was available from previous studies.^[84,85]

General details on spectroscopic measurements:

77 K measurements were performed in 2-MeTHF using the LFP set up. For spectroscopic transient absorption and emission measurements, the following concentrations were chosen, to ensure an optical density of 0.1-0.2 at the excitation wavelength (355 nm): $[\text{Ir}(\text{ppy})_2\text{phen}]^+$ 19 μM to 24 μM $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$ 12 μM to 17 μM to ensure an absorbance between 0.15-0.2 at the excitation wavelength (355 nm).

6.4.2 Synthesis and characterization

Synthesis of *tetrakis*-(2-phenylpyridine)-*bis*-(μ -chloro)-diiridium(III):

The synthesis was performed according to the general literature-known procedure from reference [232]. A mixture of water (10 mL) and 2-methoxyethanol (34 mL) was stirred for 1 h and argon was bubbled through the solvent mixture and the argon atmosphere was maintained throughout the synthesis. Iridium(III)chloride (348.5 mg, 1.1 mmol, 1.0 eq.) and 2-phenylpyridine (341.5 mg, 2.2 mmol, 2.0 eq.) were added. The reaction mixture was, stirred, heated to 120 °C and refluxed (16 h). The reaction mixture was allowed to cool to room temperature and the argon atmosphere was removed. The reaction mixture was filtered and the residue was washed with water (3 $\times$ 8 mL) and diethyl ether (3 $\times$ 5 mL) and let to dry yielding the pure product 404 mg (34 % of the theoretical yield), which was used without further purification.

^1H NMR (CDCl_3 , 400 MHz), δ / ppm: 9.25 (d, 4H), 7.8 (m, 4H), 7.75 (m, 4H), 7.5 (m, 4H), 6.74 (m, 8H), 6.6 (m, 4H), 5.8 (d, 4H).

Synthesis of [(1,10-phenanthroline)-bis-(2-phenylpyridine)-iridium(III)]hexafluorophosphate ([Ir(ppy)₂phen]⁺):

The synthesis was adapted from the general literature-known procedure from the reference [232]. Argon was bubbled through ethylene glycol (8 mL) for 1.0 h. *Tetrakis*-(2-phenylpyridine)-bis-(μ -chloro)-diiridium(III) (160 mg, 0.16 mmol, 1.0 eq.) and 1,10-phenanthroline (58.0 mg, 0.32 mmol, 2.0 eq.) were added and the argon atmosphere was maintained throughout the synthesis. The reaction mixture was heated to 150 °C and stirred for 16 h. The argon atmosphere was removed, the mixture was allowed to cool to room temperature and water (15.0 mL) was added. The reaction mixture was extracted with diethyl ether (3 $\times$ 20 mL). To the aqueous phase, an aqueous solution of ammoniumhexafluorophosphate (saturated) was added until no precipitation was observed (10 mL). The precipitate was filtered off and the pure product was obtained after ether diffusion yielding 92 mg (84 % of the theoretical yield). The compound was obtained pure, according to ¹H NMR.

¹H NMR (MeCN-*d*₃, 400 MHz), δ / ppm: 8.6 (d, 2H), 8.3 (d, 2H), 8.25 (d, 2H), 8.0 (d, 2H), 7.7 (m, 6H), 7.1 (t, 2H), 7.0 (t, 2H), 6.9 (t, 2H), 6.4 (d, 2H).

ESI-MS: m/z for [M⁺] C₃₄H₂₄N₄Ir⁺ calculated: 679.1601, found: 679.1603.

Synthesis of [(5-(Pyren-1-yl)-1,10-phenanthroline)-bis-(2-phenylpyridine)iridium(III)]-hexafluorophosphate ([Ir(ppy)₂Py]⁺):

The synthesis was adapted from the general procedure known from the literature.^[232] Argon was bubbled through ethylene glycol (8 mL) for 1.0 h and the argon atmosphere was maintained throughout the synthesis. *Tetrakis*-(2-phenylpyridine)-bis-(μ -chloro)-diiridium(III) (120 mg, 0.11 mmol, 1.0 eq.) and 5-(pyren-1-yl)-1,10-phenanthroline (88.0 mg, 0.22 mmol, 2.0 eq.) were added to the solvent under constant argon flow. The reaction mixture was heated to 150 °C and stirred for 16 h. The argon atmosphere was removed, the mixture was allowed to cool to room temperature and water (15 mL) was added. The reaction mixture was extracted with dichloromethane (20 mL). Dichloromethane was dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was redissolved in acetonitrile (10 mL) and an aqueous solution of ammoniumhexafluorophosphate (saturated) was added until no further precipitation was observed (10 mL). The precipitate was filtered off, washed with MilliQ water (3 $\times$ 5 mL) and dried to yield 81.8 mg (82 % of the theoretical yield). The compound was obtained pure, according to ¹H NMR.

¹H NMR (MeCN-*d*₃, 400 MHz), δ / ppm: 8.66 (m, 1H), 8.47-8.23 (m, 8H), 8.16-7.97 (m, 6H), 7.87-7.80 (m, 5H), 7.70-7.66 (m, 2H), 7.54-7.47 (m, 2H), 7.07-6.92 (m, 6H), 6.45-6.40 (m, 2H).

ESI-MS: m/z for $[M^+]$ $C_{50}H_{32}N_4Ir^+$ calculated: 879.2227, found: 879.2232.

Synthesis of *tetrakis*-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine-*bis*-(μ -chloro)-diiridium(III):

The synthesis was performed according to the general literature-known procedure from reference [232, 258], using iridium(III)chloride (350 mg, 1.1 mmol, 1.0 eq.) and 2-(2,4-difluoro-phenyl)-5-(trifluoromethyl)pyridine (570 mg, 2.2 mmol, 2.0 eq.). After synthesis and purification according to the literature,^[232] 630 mg, (38 % of the theoretical yield) of the yellow solid was isolated.

1H NMR ($CDCl_3$, 400 MHz), δ / ppm: 9.50 (d, 4H), 8.5 (m, 4H), 8.00 (m, 4H), 6.45 (m, 4H), 5.1 (m, 4H).

Synthesis of [(1,10-phenantrolin)-*bis*-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine]-iridium(III)]hexafluorophosphat ($[Ir(dF(CF_3)ppy)_2phen]^+$):

The synthesis was adapted from the general literature-known procedure that can be found in references [232, 258]. Argon was bubbled through ethylene glycol (8 mL) for 1.0 h and the argon atmosphere was maintained throughout the synthesis. *Tetrakis*-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine-*bis*-(μ -chloro)-diiridium(III) (200 mg, 0.13 mmol, 1.0 eq.) and 1,10-phenanthroline (47.0 mg, 0.26 mmol, 2.0 eq.) were added to the solvent under constant argon flow. The reaction mixture was heated to 150 °C and stirred for 16 h. The argon atmosphere was removed, the mixture was allowed to cool to room temperature and water (15 mL) was added. The reaction mixture was extracted with diethyl ether (3 $\times$ 20 mL). To the aqueous phase, an aqueous solution of ammoniumhexafluorophosphate (saturated) was added until no further precipitation was observed (10 mL). The precipitate was filtered off, rinsed with water (5.0 mL) and the raw product was redissolved in acetonitrile (5.0 mL). Ether diffusion afforded the pure product (98 mg, 85 % of the theoretical yield). The compound was obtained pure according to 1H NMR.

1H NMR ($MeCN-d_3$, 400 MHz), δ / ppm: 8.75 (d, 2H), 8.5 (m, 2H), 8.4 (d, 2H), 8.3 (s, 2H), 8.1 (d, 2H), 7.9 (m, 2H), 7.5 (s, 2H), 6.75 (m, 2H), 5.9 (m, 2H).

ESI-MS: m/z for $[M^+]$ $C_{36}H_{18}F_{10}N_4Ir^+$ calculated: 887.0972, found: 887.0984.

Synthesis of [(5-(Pyren-1-yl)-1,10-phenanthroline)-*bis*-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine]-iridium(III)]hexafluorophosphat ($[Ir(dF(CF_3)ppy)_2Py]^+$):

The synthesis was adapted from the general literature-known procedure that can be found in reference [232]. Argon was bubbled through ethylene glycol (8 mL) for 1.0 h.

Tetrakis-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine-*bis*-(μ -chloro)-diiridium(III) (194 mg, 0.13 mmol, 1.0 eq.) and 5-(pyren-1-yl)-1,10-phenanthroline (100 mg, 0.26 mmol, 2.0 eq., available from a previous study^[85]) were added to the solvent under constant argon flow. The reaction mixture was heated to 150 °C and stirred for 16 h. The reaction mixture was allowed to cool to room temperature and water (15 mL) and acetonitrile (10 mL) were added. The reaction mixture was extracted with dichloromethane (3 $\times$ 20 mL). To the aqueous phase, an aqueous solution of ammoniumhexafluorophosphate (saturated) was added until no precipitation was observed (10 mL). The solvent was removed under reduced pressure and the residue was chopped using a pestle and a mortar. The residue was suspended in water (5 mL) and the suspension was sonicated for 1 h. The mixture was filtered and the filtrate was washed with water (3 $\times$ 5 mL) and dried to yield 110 mg (77 % of the theoretical yield). According to ¹H NMR, the compound contained <10 % of an impurity

¹H NMR (MeCN-*d*₃, 400 MHz), δ / ppm: 8.81-8.79 (m, 1H), 8.53-8.36 (m, 7H), 8.31-7.96 (m, 10H), 7.74-7.73 (m, 1H), 7.68-7.55 (m, 3H), 6.87-6.78 (dd, 2H), 6.04-5.96 (m, 2H).

ESI-MS: m/z for [M⁺] C₅₂H₂₆F₁₀N₄Ir⁺ calculated: 1087.1598, found: 1087.1619.

6.4.3 UV-Vis spectra in aqueous solution

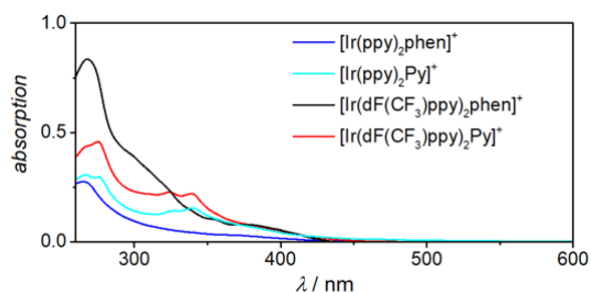


Figure 52: UV-Vis spectra of the iridium-based metal complexes and dyads in aqueous solution (all saturated). The fluorinated complex was measured in pure water (black, [Ir(dF(CF₃)ppy)₂phen]⁺), water with 10 % MeCN (blue, [Ir(ppy)₂phen]⁺; red, [Ir(dF(CF₃)ppy)₂Py]⁺) or water with 20 % MeCN (turquoise, [Ir(ppy)₂Py]⁺).

The UV-Vis spectra of the PF₆-salts of the iridium-based metal complexes and dyads in Figure 52 are recorded either in neat water ([Ir(dF(CF₃)ppy)₂phen]⁺) or in a water acetonitrile mixture ([Ir(ppy)₂phen]⁺ and both iridium-based dyads). Using Cl[−] as counterion instead of PF₆, is expected to increase the water solubility. This measurement is

intended to demonstrate that water as a solvent is possible for the sensitizers presented in Section 2.3.2. Exact concentrations have not been determined, as all solutions were saturated.

6.4.4 Lifetimes of the excited states and E_T energies

The triplet energies of the two complexes were determined differently (Figure 53). The emission spectrum of $[\text{Ir}(\text{ppy})_2\text{phen}]^+$ is broad and for that reason, the excited state energy was estimated at 10 % intensity compared to the maximum on the low-energy side of the spectrum. At low temperature (77 K) the spectrum shifts significantly. Such shifts have been observed for this complex and are characteristic of a charge transfer character of the excited state.^[106] The emission spectrum of the fluorinated complex also shows a slightly blurred fine structure at room temperature, which becomes more refined at 77 K. The triplet energy was therefore taken from the sharp emission maximum of the 77 K measurement.

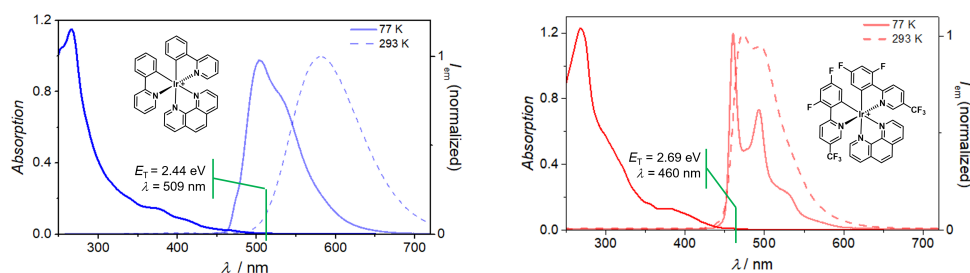


Figure 53: Absorption and normalized emission spectra at room temperature (light, dotted spectra) and at 77 K (light, solid spectra) and E_T of the iridium-based metal complexes $[\text{Ir}(\text{ppy})_2\text{phen}]^+$ (blue spectra, left side) and $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$ (red spectra, right). The emission spectra were recorded using a pulsed laser (355 nm, 10 mJ) for excitation Left: $[\text{Ir}(\text{ppy})_2\text{phen}]^+$ (19 μM) was dissolved in acetonitrile for the absorption spectrum. The emission spectrum at room temperature (16 μM $[\text{Ir}(\text{ppy})_2\text{phen}]^+$ in acetonitrile) was recorded 20 ns after the laser pulse and integrated over 600 ns. The emission spectrum at 77 K was measured 100 ns after the laser pulse and integrated over 5.0 μs . Right: $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$ (15 μM) was dissolved in acetonitrile for the absorption spectrum. The emission spectrum at room temperature (15 μM in acetonitrile) was recorded 20 ns after the laser pulse and integrated over 100 ns. The emission spectrum at 77 K was measured 100 ns after the laser pulse and integrated over 1.0 μs

Table 13: Summary of the lifetimes (τ_T) and energies (E_T) of the triplet excited states of the iridium-based metal complexes and dyads.

complex	$\tau_T / \mu\text{s}^a$	E_T / eV
$[\text{Ir}(\text{ppy})_2\text{phen}]^+$	0.74 ± 0.02	2.4^b
$[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$	2.59 ± 0.2	2.6^c
$[\text{Ir}(\text{ppy})_2\text{phenPy}]^+$	81.3 ± 4.7	$\sim 2.0^d$
$[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phenPy}]^+$	118	$\sim 2.0^d$

^a Details for lifetimes are given in the text below and corresponding figures. ^b Triplet energy from wavelength at 10 % intensity of the emission maximum at room temperature. ^c Triplet energy from maximum at 77 K. ^d Triplet energy slightly below ³pyrene.^[48,84]

The lifetimes of the two iridium complexes were determined as average out of one emission trace and three absorption traces and agree well with the lifetimes reported in literature.^[229,230] No emission was observed for the dyads and therefore the lifetime of $[\text{Ir}(\text{ppy})_2\text{Py}]^+$ was averaged from three absorption decays. The substantial lifetime increase for both dyads is highly sensitive to small amounts of quencher molecules and oxygen could be a suitable quencher. For that reason, the quality of argon bubbling and its influence on the lifetime was investigated. Measuring the excited state lifetime of $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Py}]^+$ after different times of argon bubbling showed equal lifetimes after 5 min and 7 min. As a result, the atmosphere was sufficiently inert for measurements after 5 min of argon bubbling and this time was used as a standard for all measurements in this project.

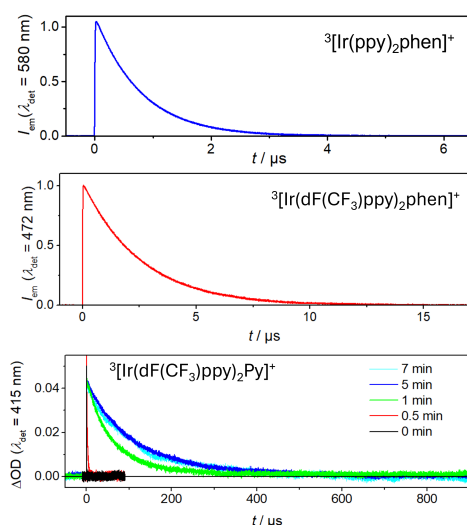


Figure 54: Additional kinetic decay traces excited states of the iridium-based chromophores (see also Figure 27). For the metal complexes, $\text{Ir(ppy)}_2\text{phen}^+$ and $[\text{Ir(dF(CF}_3\text{)ppy)}_2\text{phen}]^+$ upper and middle panel the kinetic decay of the emission is displayed detected (emission spectra in Figure 53). For the fluorinated dyad, the lifetime was determined after different times of argon bubbling (color-coded in the figure). For measurement conditions see transient absorption data in Figure 27, because the same solutions were used for the measurements.

6.4.5 Energetic considerations for potentials of the dyads

The estimation for the potential of the iridium-based dyads ($E_{\text{red}}([\text{Ir-Py}]^+ / [\text{Ir-Py}]^0)$) is based on equation 12 together with the following assumptions:

i) The most reducing electron donor is DMA with a potential of 1.05 V vs NHE, which is consequently used as $E_{\text{ox}}(\text{D/D}^{*+})$ for calculating the lower limit for the reduction potential of the dyads.

ii) The energy of the triplet excited state is estimated to be slightly below that of $^3\text{pyrene}^{[48,84]}$ and therefore $E_{\text{T}} = 2.0 \text{ eV}$.

iii) Owing to the fact, that no reductive quenching was observed (Figures 28, 55 and 56), the driving force for this reaction has to be zero or positive. Since this is only an estimation for the limiting case, it is assumed that $\Delta G = 0$.

Assumptions i)-iii) applied to equation 12 results in a ground state potential of $E_{\text{red}}([\text{Ir-Py}]^+ / [\text{Ir-Py}]^0) \approx -1 \text{ V vs NHE}$ and an excited state potential of $E_{\text{red}}^*(^3[\text{Ir-Py}]^+ / [\text{Ir-Py}]^0) \approx 1 \text{ V vs NHE}$.

6.4.6 Additional quenching experiments

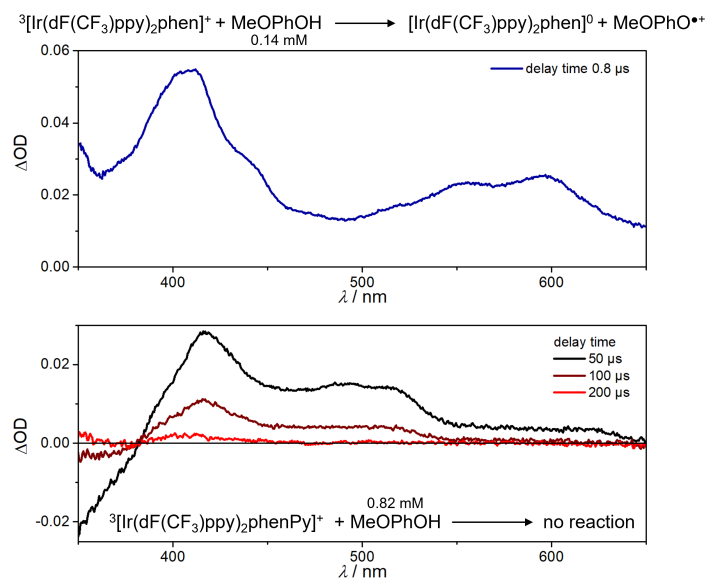


Figure 55: TA spectra of $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$ (upper) and $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Py}]^+$ (lower) in MeCN with MeOPhOH (0.14 mM for the metal complex and 0.82 mM for the dyad) including the corresponding delay times and quencher concentrations. A 355 nm pulsed laser was used for excitation at 10 mJ to 15 mJ.

After quenching the fluorinated ^3MC and $^3\text{dyad}$ (Figure 55) with MeOPhOH the TA-spectra show a new species forming for the MC, whereas the dyad seems to be unaffected by the quencher (no new species observed in the delayed TA spectra). The newly formed species can be assigned to the $\text{MeOPhOH}^{\bullet+}$ ^[259,260] and the reduced iridium^[239]. After oxidation, the radical cation $\text{MeOPhOH}^{\bullet+}$ ($\lambda_{\text{max}} = 440 \text{ nm}$) can be deprotonated to form the radical species $\text{MeOPhO}^\bullet$ ($\lambda_{\text{max}} = 410 \text{ nm}$), in MeCN.^[259–261] Most likely, both species are in equilibrium under the chosen conditions, however, this needs further confirmation.

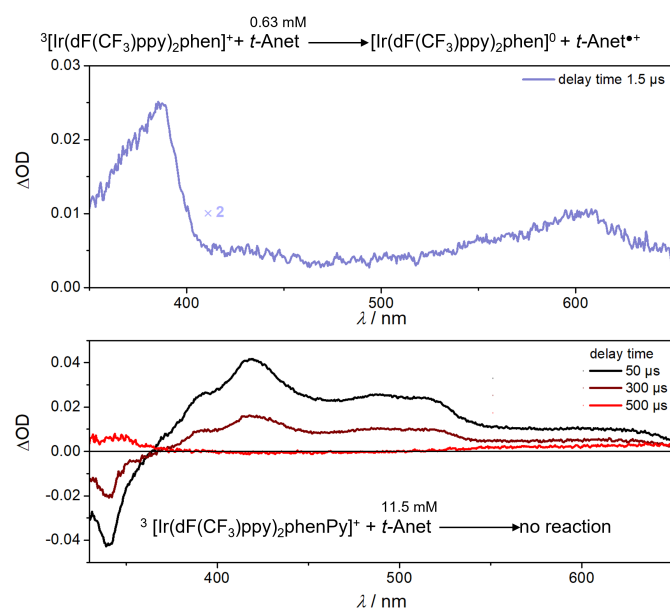


Figure 56: TA spectra of $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{phen}]^+$ (upper) and $^3[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Py}]^+$ (lower) in MeCN with *trans*-anethole (0.63 mM for the metal catalyst and 11.5 mM for the dyad) including the corresponding delay times and quencher concentrations. A 355 nm pulsed laser was used for excitation at 10 mJ to 15 mJ.

6.5 Additional data and Supporting Information for back electron transfer-induced triplet formation (Section 2.4)

The solutions for transient absorption measurements were prepared such, that the optical density of P-H^{2+} at the excitation wavelength is between 0.1-0.15, which corresponds to concentrations from $30\text{ }\mu\text{M}$ to $50\text{ }\mu\text{M}$. For comparative studies in Figures 57, 60, 61, 62 and 63 one stock solution was employed throughout the measurements for the individual data sets within the respective figures.

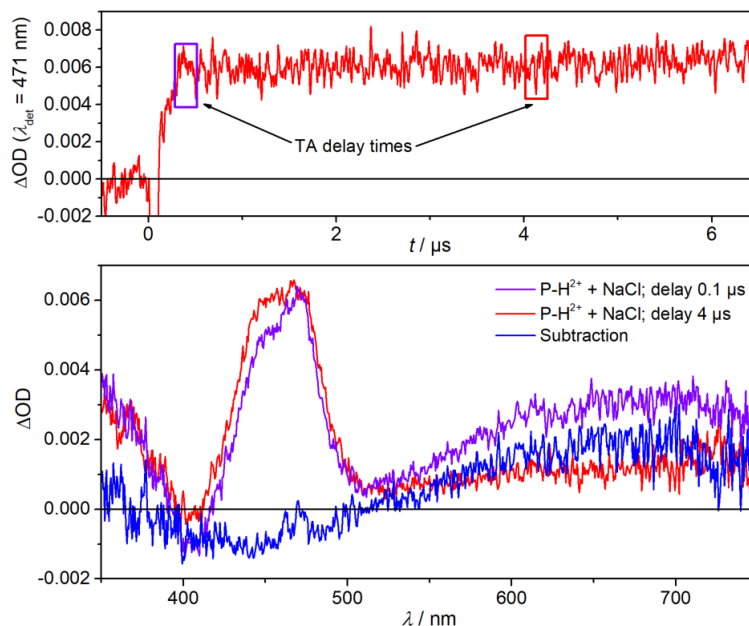


Figure 57: Kinetic trace for P-H^{2+} and NaCl (identical to Figure 29) and TA spectra at different delay times (red 0.1 μs and purple 4.0 μs) and the subtracted spectrum (blue).

Figure 57 shows time-gated ns-transient absorption data for quenching of $^1\text{P-H}^{2+}$ with NaCl. After a long delay time (4 μs) the expected bands for the triplet species are observed (red spectrum in Figure 57 and compare Section 2.3). Shortly after the laser pulse (0.1 μs), the bands in the spectrum (violet spectrum in Figure 57) differ slightly and subtraction (blue) of the two results in a broad absorption band around 650 nm. In this area, the spectral features for the one-electron-reduced $\text{P-H}^{\bullet+}$ are expected. The initial emission from the singlet excited state is intense ($\phi_{\text{F}} = 87\%$ ^[85]) and probably causes the slightly negative part of the subtraction (400 nm to 500 nm).

6.5.1 Additional transient absorption spectra with reductive quenchers

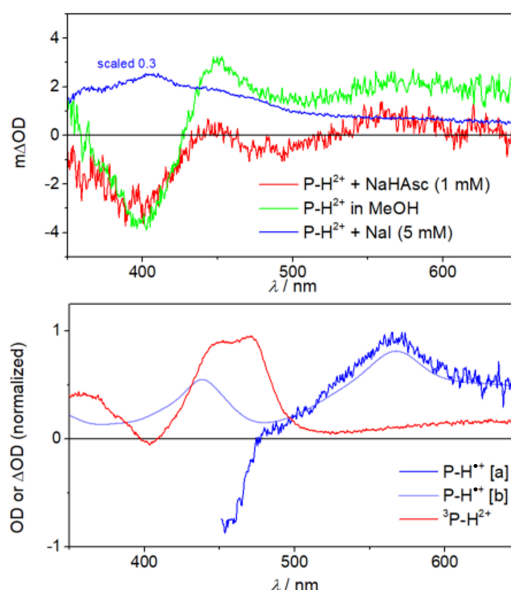


Figure 58: Control quenching experiments of $^1\text{P-H}^{2+}$ with different electron donors. The upper panel shows: red spectrum for P-H^{2+} in water in the presence of NaHAsc (1 mM) excited with 355 nm (pulse energy ~ 10 mJ, time delay 150 ns); green spectrum for P-H^{2+} in methanol (MeOH) and excited with 355 nm (pulse energy ~ 20 mJ, time delay 500 ns); blue spectrum for P-H^{2+} in water in the presence of NaI (5 mM) and excited with 355 nm (pulse energy ~ 10 mJ, time delay 100 ns). The lower panel shows reference spectra of the triplet $^3\text{P-H}^{2+}$ (see Figure 29 for details) in red, the radical spectrum $\text{P-H}^{\bullet+}$ and $[\text{Ru}(\text{bpy})_3]^+$ [a] in blue, or the measured spectrum from spectro-electro chemistry in light blue [b] see Section 6.9 for details.

The spectra in Figure 58 show additional ns-TA data for the quenching of singlet excited P-H^{2+} (see also Table 9). For the quenching with NaHAsc and MeOH (red and green spectrum), the expected bands between 450 nm to 650 nm can be observed. The time delay (150 ns) in the case of ascorbate quenching is comparatively short and remaining singlet emission ($\phi_F = 87\%^{[85]}$) is still present causing the negative signal at 500 nm in the red spectrum. Quenching with iodine shows a broad and intense absorption between 350 nm to 500 nm. Those signals could arise from iodide-derived species (I_2 , $\text{I}_2^{\bullet-}$ or I_3^-), which show intense ($\Delta\epsilon \sim 7500 \text{ M}^{-1} \text{ cm}^{-1}$ to $8600 \text{ M}^{-1} \text{ cm}^{-1}$) bands in that spectral region. As a consequence, the identification of the comparatively weak signals originating from the one-electron-reduced $\text{P-H}^{\bullet+}$ can not be assigned unambiguously. The exact assignment of those quenching products requires further investigations.

6.5.2 Additional data for triplet formation after reductive quenching with Br^-

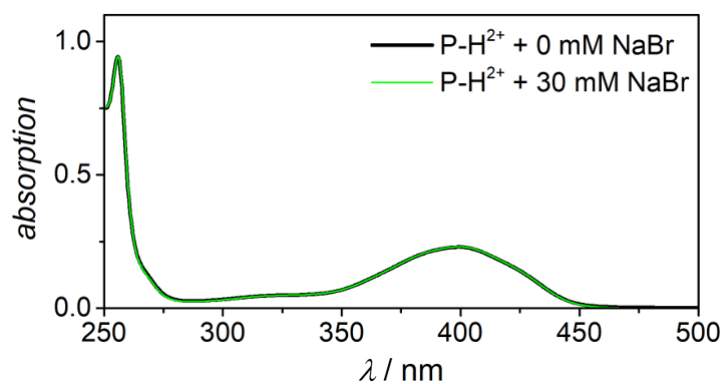


Figure 59: UV-Vis control measurements for quenching reactions displayed in Figure 60. The spectra show P-H^{2+} ($27 \mu\text{M}$) in aqueous H_2SO_4 (50 mM) without (black) or with NaBr (30 mM, green) added.

The UV-Vis spectra displayed in Figure 59 are identical, regardless of the concentration of quencher added. As a consequence, preassociation effects or reactions from the ground state can be neglected.

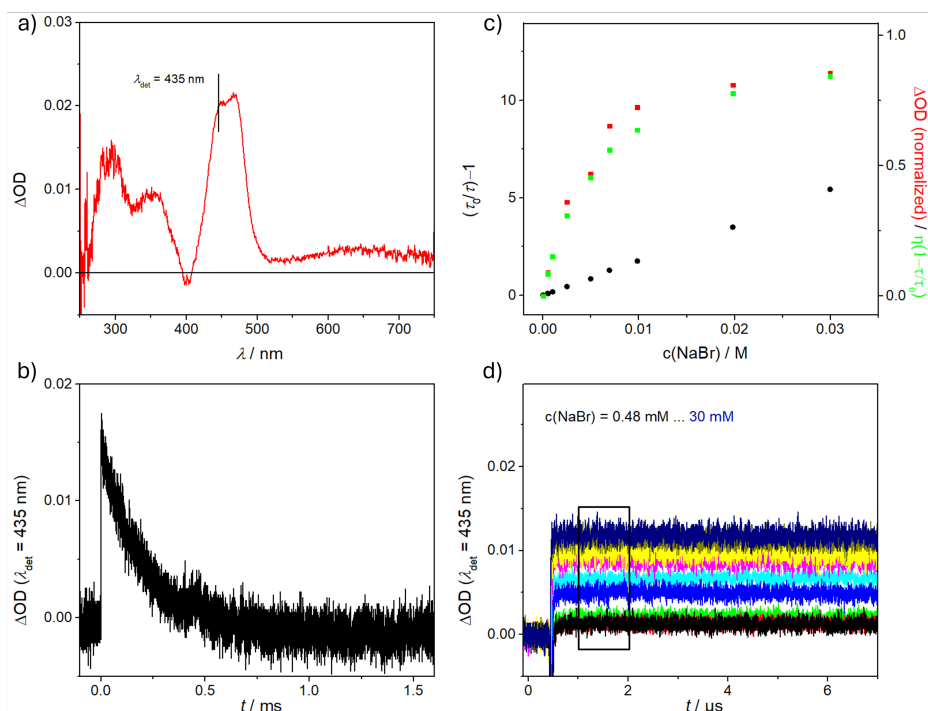


Figure 60: Measurements comparing the formation of ${}^3\text{P-H}^{2+}$ to the efficiency of the singlet quenching. P-H^{2+} was excited directly (355 nm, 7 mJ). a) Shows a transient absorption spectrum with 30 mM NaBr present after 2.0 μs time delay. b) Shows the kinetic decay of ${}^3\text{P-H}^{2+}$ on a long time scale at $\lambda_{\text{det}} = 435$ nm (emission quenching data are in the supporting information of reference [85] and Section 6.9). c) Black and green data points are derived from kinetic quenching studies of the singlet excited ${}^1\text{P-H}^{2+}$ and the original kinetic traces can be found in Section 6.9. The red data set is derived from averaging the signal intensity of ${}^3\text{P-H}^{2+}$ in part d) (1.0 μs to 2.0 μs , black rectangle) at increasing quencher concentration. d) Kinetic traces detected at $\lambda_{\text{det}} = 435$ nm between 1.0 μs to 7.0 μs . The black rectangle indicates the data used for averaging the ΔOD (part c)) at increasing NaBr concentration.

Figure 60 shows the transient absorption spectrum and the decay of ${}^3\text{P-H}^{2+}$ (parts a) and b)) after recombination-induced triplet formation (similar to the data in Figure 29). Part c) of the figure shows the Stern–Volmer plot for singlet quenching with increasing NaBr concentrations (black data points, $(\tau_0/\tau) - 1$), the derived quenching efficiency (green data points, $\eta(1 - \tau/\tau_0)$) and the increase of the signal intensity of ${}^3\text{P-H}^{2+}$ at $\lambda_{\text{det}} = 435$ nm (red data points, $\Delta\text{OD}(\text{normalized})$). A correlation of singlet quenching efficiency (green data points) and triplet formation (red data points) shows nearly identical behaviour for the different NaBr concentrations, confirming a direct correlation between the two processes, singlet quenching and triplet formation. Part d) shows the original kinetic TA traces detected at $\lambda_{\text{det}} = 435$ nm and for increasing NaBr concentration and the black box indicates the window (1.0 μs to 2.0 μs) that was employed for data aver-

aging. The effect of the bromide concentration on the triplet lifetime is detailed in the following section and Figure 61.

6.5.3 Additional quenching experiments related to the external heavy atom effect

Spectroscopy with NaBr as quencher for $^1\text{P}-\text{H}^{2+}$:

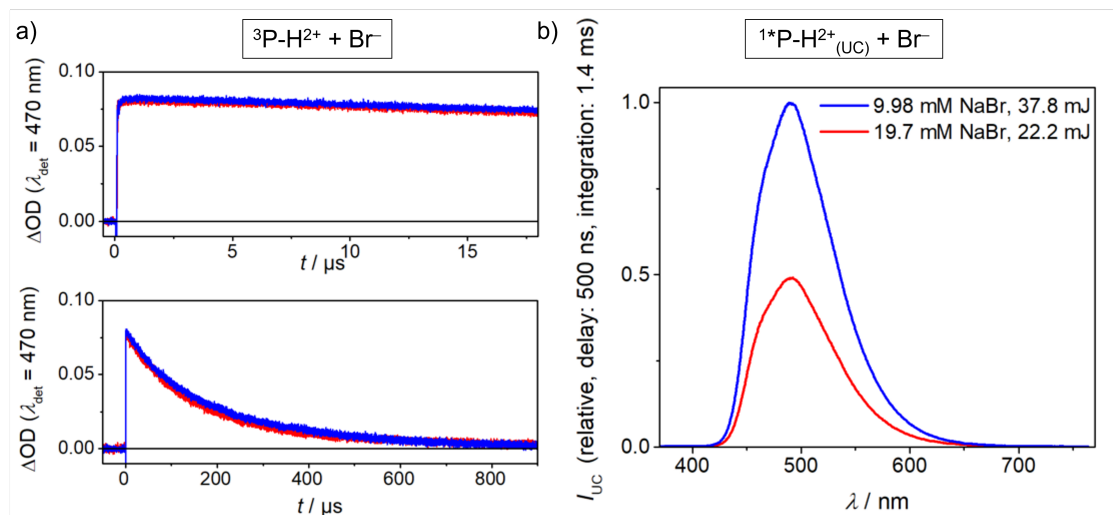


Figure 61: Effects of bromide concentration on $^3\text{P}-\text{H}^{2+}$ part a) and on the upconverted emission part b). The solutions contained $\text{P}-\text{H}^{2+}$ (0 mM) in H_2SO_4 (50 mM) and NaBr (9.98 mM, blue data or 19.7 mM, red data). The laser intensity was adjusted such that for both bromide concentrations the triplet concentration is initially identical (37.8 mJ for the blue data set and 22.2 mJ for the red data set). a) Presents the kinetic decay of $^3\text{P}-\text{H}^{2+}$ at the two bromide concentrations for a short (upper) and long (lower) time scale. b) Presents the delayed emission spectra for both bromide concentrations, detected 500 ns after the laser pulse and integrated over 1.4 ms.

The effects of heavy atoms on the triplet decay and upconverted emission are addressed in Figure 61. Part a) presents kinetic traces of $^3\text{P}-\text{H}^{2+}$ next to the intensity of the upconverted emission (I_{UC}) of $^1\text{P}-\text{H}^{2+}$ after annihilation in part b) for two different Br^- concentrations. To minimize the effects of the annihilation process firstly high excitation energies were chosen such that the annihilation-derived kinetic effects are nearly identical. Furthermore, the excitation intensities were adjusted to provide identical concentration of the $^3\text{P}-\text{H}^{2+}$. An external heavy atom effect would impact ISC as well as the reverse process (bISC). Hence, the decay of the triplet species exposed to higher heavy atom concentrations should be faster. The kinetic traces in part a) of Figure 61 are essentially identical on short and on long time scales indicating that $^3\text{P}-\text{H}^{2+}$ is not impacted by the concentration of bromide ions in solution at the chosen conditions, which is not

in line with a supposed heavy atom effect. In contrast to that, the upconverted emission originating from the $^1\text{P}-\text{H}^{2+}$ is diminished significantly at the high bromide concentration. This effect is likely caused by quenching effects of the upconverted emission by bromide ions. The ratio of the upconversion emission intensities ($\frac{I_{\text{UC}}(9.98\text{mMNaBr})}{I_{\text{UC}}(19.7\text{mMNaBr})}$) is ~ 0.5 , which is similar to the lifetime-based ratio resulting from the singlet excited state quenching after direct excitation (based on Figure 60 in part c), $k_q = 1.22 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ the ratio of lifetimes amounts to ~ 0.6).¹³

Both measurements confirm that mainly the singlet excited state is affected by the heavy atom, whereas the triplet decay remains unchanged.

Spectroscopy with NaCl or CsCl as quencher for $^1\text{P}-\text{H}^{2+}$:

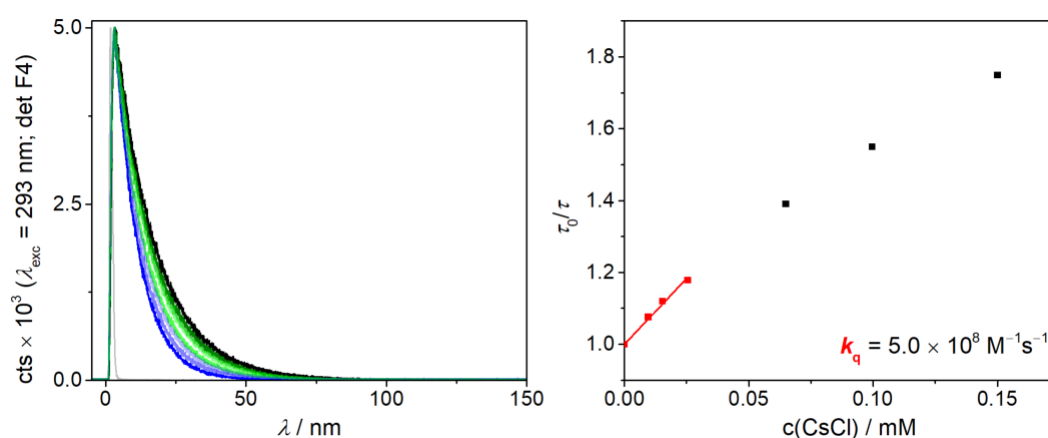


Figure 62: Kinetic traces (left side) and the resulting Stern–Volmer plot (right side) for the quenching of $^1\text{P}-\text{H}^{2+}$ with different CsCl concentrations.

Figure 62 shows the Stern–Volmer plot and corresponding kinetic data for quenching of $^1\text{P}-\text{H}^{2+}$ with CsCl. The resulting quenching rate $k_q = 5.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is almost identical to the quenching with NaCl ($k_q = 5.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).^[85] Hence, the initial quenching step is nearly unaffected by the heavier counterion. Only the first four data points were used for the fitting, because at higher concentrations, ionic effects impede the linearity of the plot. Similar effects were encountered for the Stern–Volmer plot with NaCl (Section 6.9).^[85]

¹³The signal intensity of the upconverted emission and the corresponding integral are based on the measurement presented in part b) of Figure 61. The measurement for those spectra was optimized to exclude any residual emission from direct excitation (delay 500 ns). As a consequence some of the initially formed upconversion emission is cut off. The ratio of upconversion emission at different bromide concentrations is therefore an estimated value and its purpose is to provide a rough estimate for comparison with ratio of the derived lifetimes for singlet quenching after direct excitation.

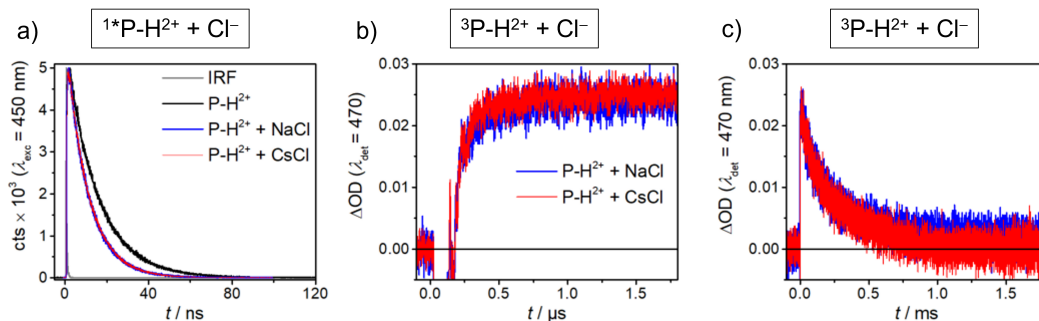


Figure 63: Comparison of $^1\text{P-H}^{2+}$ quenching with NaCl or CsCl. The aqueous solutions (H_2SO_4 , 50 mM) contained P-H^{2+} (0 mM, black trace in a)) and NaCl (98.0 mM, blue traces) or CsCl (90.0 mM, red traces). Part a) presents the quenching of $^1\text{P-H}^{2+}$ with the two chloride salts, resulting essentially identical lifetimes ($\tau(\text{NaCl}) = 10.2 \text{ ns}$, $\tau(\text{CsCl}) = 10.3 \text{ ns}$). Parts b) and c) present the traces for $^3\text{P-H}^{2+}$ decay of the two solutions after excitation with a 355 nm pulsed laser (41.7 mJ). The kinetic traces show the triplet at a short (left, b)) or long (right, c)) time scale.

In Figure 63, the kinetic traces of $^3\text{P-H}^{2+}$ are compared, for an increased heavy atom effect introduced by the counter ion of the quencher. This was realized by employing chloride as sodium or caesium salt and the respective concentration was adjusted such that the initial singlet quenching efficiency is identical (see part a) of the figure). For measuring the kinetic traces of $^3\text{P-H}^{2+}$ both samples were excited using the same laser intensity (41.7 mJ) at 355 nm and detected under identical conditions. The relative intensity of the signals are shown at a short time scale (part b) of the figure) as well as the decay over a long periode of time (part c) of the figure). Both are essentially identical again indicating no effect of the heavier counterion.

6.6 Additional data and Supporting Information for Molybdenum complex as triplet sensitizer for upconversion and as photoredox catalyst (Section 3.1)

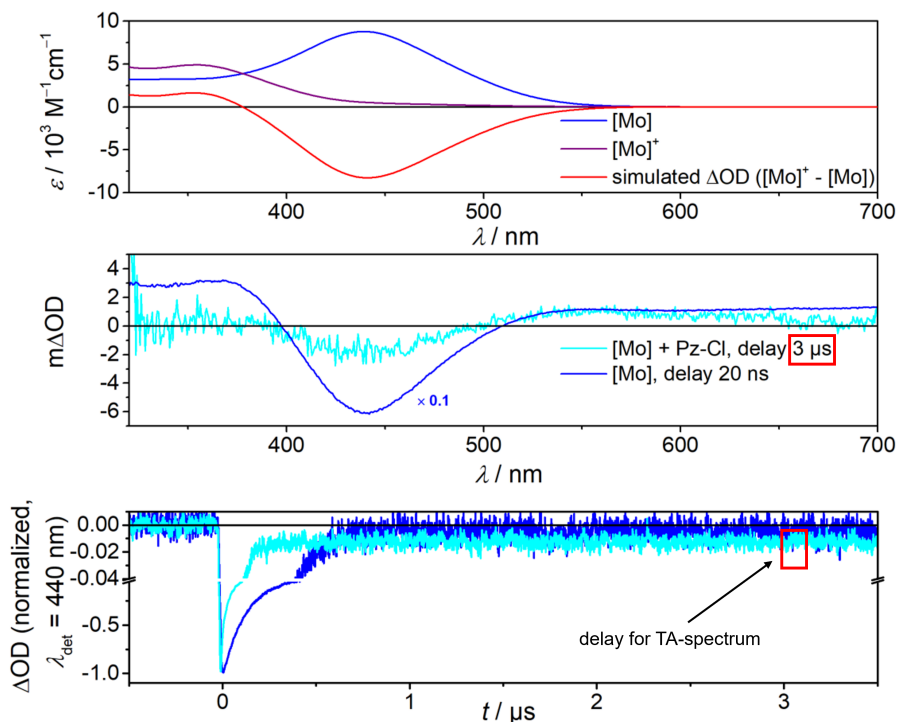


Figure 64: Overview of spectroscopic data for oxidative electron transfer reactivity of $^3[\text{Mo}(\text{CO})_3\text{tpe}]$. The upper panel presents the absorption spectra of molybdenum(0) (blue), the oxidized molybdenum(I) (violet) and the subtraction of the two to simulate the expected bands in transient absorption spectroscopy (red). In the middle and lower panel, the transient absorption spectra and kinetic traces of unquenched $^3[\text{Mo}(\text{CO})_3\text{tpe}]$ (blue) in acetonitrile and a solution of the complex with chloropyrazine (Pz-Cl, 48 mM, turquoise) added are shown. Both solutions were excited using a pulsed laser (532 nm) with 23 mJ pulse energy. The TA spectra (middle panel) are recorded 20 ns for the $^3[\text{Mo}(\text{CO})_3\text{tpe}]$ or 3 μs (red box) for the quenched solution. The corresponding kinetic decay traces in the lowest panel follow the same color code.

Figure 64 presents additional transient absorption spectra supporting the electron transfer reactivity of $^3[\text{Mo}(\text{CO})_3\text{tpe}]$. The simulated TA-spectrum (upper panel, red) derived from UV-Vis data of molybdenum(0) and spectr-electro chemistry of the oxidized form predicts a broad bleach from 400 nm to 500 nm for the TA spectrum of the oxidized complex (spectra taken from reference [44], Section 3.1 and the corresponding supporting information, Section 6.10). The kinetic traces (lowest panel) confirm the initial quenching of the triplet excited molybdenum(0) ($\tau=124$ ns) upon addition of chloropyrazine ($\tau=38$ ns). Additionally, the turquoise trace (solution with the quencher added)

does not return to zero indicating the formation of a new and long-lived species. A transient absorption spectrum of this species is shown in the middle panel (turquoise spectrum, delay 3 μ s, red box), which coincides with the band of the simulated TA-spectrum. The spectrum of $^3[\text{Mo}(\text{CO})_3\text{tpe}]$ (blue spectrum in the middle panel) is provided for comparison.

6.7 Supporting Information for Sensitization-initiated electron transfer with green light (Section 2.1.2)

Supporting Information for

Efficient Energy and Electron Transfer Photocatalysis with a Coulombic Dyad

Matthias Schmitz ^a, Maria-Sophie Bertrams ^a, Arne C. Sell ^a, Felix Glaser ^{a,b} and Christoph Kerzig ^a

^a Department of Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10–14, 55128 Mainz, Germany.

^b Present Address: Université catholique de Louvain (UCLouvain), Institute of Condensed Matter and Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Place Louis Pasteur 1, bte L4.01.02, 1348 Louvain-la-Neuve, Belgium

E-Mail: ckerzig@uni-mainz.de

Table of contents

S1 General experimental details and methods.....	3
S2 Additional steady-state experiments	6
S2.1 NMR titration experiment with Ruphen and PTS.....	6
S2.2 Benesi–Hildebrand plot for Ruphen and PTS.....	9
S2.3 Steady-state emission quenching of ³ Ruphen by PTS.....	10
S2.4 pH-dependent ground state absorption spectrum of PTS	10
S3 Additional experiments for determining the quenching efficiency by oxygen and stability measurements	11
S3.1 Singlet oxygen assay according to the RNO method	11
S3.2 Kinetic simulation of the lifetime dependency of quenching efficiency	12
S3.3 Oxygen quenching efficiency at 50 °C.....	13
S3.4 Comparison of expected and observed performance for photocatalytic ¹ O ₂ formation and photostability measurements	14
S4 Influence of Coulombic interactions on static quenching and quenching efficiency.....	16
S5 Irradiation experiments	19
S5.1 General procedure	19
S5.2 Photooxygenation of 5-HMF	20
S5.2.1 Variation of catalyst loading and excitation wavelength	21
S5.2.2 Comparison of H ₂ O and D ₂ O as solvent.....	22
S5.2.3 Determination of oxygen concentration during irradiation.....	22
S5.2.4 Kinetic simulation for quenching efficiency depending on quencher concentration	24
S5.2.5 Photooxygenation with sunlight.....	25
S5.2.6 Gram-scale photooxygenation	26
S5.2.7 Control experiments	26
S5.2.8 Photooxygenation under alkaline conditions	27

S5.3 Photooxygenation of TAN.....	28
S5.4 Debromination of 2-BP	29
S5.4.1 LED irradiation	29
S5.4.2 Irradiation using sunlight.....	30
S5.4.3 Control experiments	31
S5.5 Pinacol coupling of 2-FBA.....	31
S5.5.1 LED irradiation	31
S5.5.2 Irradiation using sunlight.....	33
S5.6 Additional pinacol coupling reactions.....	34
S6 Stern–Volmer quenching experiments.....	39
S6.1 Quenching of $^3\text{Ruphen}$ by HAsc^-	39
S6.2 Quenching of ^3PTS by HAsc^-	39
S6.3 Quenching of $\text{Ruphen}^{\cdot-}$ by 2-BP	40
S6.4 Quenching of $\text{PTS}^{\cdot-}$ by 2-BP.....	41
S6.5 Quenching of $\text{Ruphen}^{\cdot-}$ by 2-FBA.....	41
S6.6 Quenching of $\text{PTS}^{\cdot-}$ by 2-FBA.....	42
S7 Determination of extinction coefficients.....	43
S7.1 Extinction coefficient of PTS in water	43
S7.2 $^3\text{Ruphen}$ difference extinction coefficient in water	43
S7.3 ^3PTS difference extinction coefficient in water	44
S7.4 $\text{Ruphen}^{\cdot-}$ difference extinction coefficient in water.....	46
S7.5 Estimation of the difference extinction coefficient of $\text{PTS}^{\cdot-}$	47
S8 Determination of efficiencies	49
S8.1 Energy transfer efficiency of the initial step.....	49
S8.2 Cage escape efficiency for the reduction of $^3\text{Ruphen}$ by HAsc^-	50
S8.3 Cage escape efficiency for the reduction of ^3PTS by HAsc^-	51
S8.3 Additional investigations.....	52
S8.3.1 Static and dynamic quenching observed by time-resolved emission and absorption	52
S8.3.2 Estimation of the back energy transfer rate between ^3PTS and Ruphen	53
S8.3.3 Ionic strength dependent formation of the key species ^3PTS and $\text{PTS}^{\cdot-}$	54
9 Identification of other Coulombic dyads.....	56
9.1 Osmium-based Coulombic dyad	56

9.2 Ruthenium-based Coulombic dyad in an organic solvent	59
S10 Miscellaneous	61
S10.1 77 K phosphorescence spectrum of PTS	61
S10.2 DFT calculations	61
S10.3 Supplementary data	63
S10.4 NMR spectrum of methyl phenyl sulfoxide	64

S1 General experimental details and methods

Materials

Unless noted otherwise, all chemicals for optical spectroscopy and irradiation experiments were obtained commercially in high purity and used as received (acetonitrile, 99.9%, VWR Chemicals; bis(2,2'-bipyridine)(5-pyrenyl-1,10-phenanthroline)ruthenium(II) dichloride (**RuphenPy**), still available from a former project¹; 2-bromopyrazine (**2-BP**), 98%, BLDpharm; chloroform, 99.5%, Titolchimica; chloroform-d₁, 99.8%, Deutero; deuterium oxide, 99.9%, Deutero; *N,N*-dimethyl-4-nitrosoaniline, 98%, Fisher Scientific; dichloromethane, 99.8%, fisher scientific; dimethyl sulfone, 98%, Sigma-Aldrich; eosin Y disodium salt, >98%, Alfa Aesar; ethanol, absolute, VWR Chemicals; ethyl acetate, ≥99.8%, Fisher Scientific; ethylene glycol, ≥99%, Carl Roth; 2-fluorobenzaldehyde (**2-FBA**), 97%, Sigma-Aldrich; 4-fluorobenzaldehyde, 98%, Sigma-Aldrich; 5-(hydroxymethyl)furfural, 98%, abcr (**5-HMF**); hydroxypropyl- β -cyclodextrin (**HPCD**), TCI; imidazole, >98%, TCI; maleic acid, >99%, TCI; methyl phenyl sulfoxide, ≥97%, Sigma-Aldrich; methyl viologen dichloride hydrate, 98%, Sigma-Aldrich; methylene blue, ≥97%, Sigma-Aldrich; 3,4,9,10-perylenetetracarboxylic 3,4,9,10-dianhydride, 97%, Sigma-Aldrich; potassium hexachloroosmate(IV), >99%, Sigma-Aldrich; potassium hydroxide, 85–100%, Honeywell; pyrene (**Py**), 98%, Fisher Scientific; 1-pyrenemonosulfonic acid monosodium salt (**PMS**), ≥97%, Sigma-Aldrich; 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt hydrate (**PTS**), ≥98%, Sigma-Aldrich; rose bengal disodium salt, 95%, Sigma-Aldrich; [Ru(phen)₃](PMS)₂, still available from a former project²; sodium L-ascorbate (**NaHAsc**), 98%, Sigma-Aldrich; sodium chloride, ≥99.5%, Fisher Scientific; sodium hydroxide, ≥98%, Sigma-Aldrich; sodium sulfate, 99%, Acros Organics; sulfuric acid, 98%, Sigma-Aldrich; thioanisole (**TAN**), >99%, TCI; trifluoroacetic acid, 99%, Acros Organics; 2-(trifluoromethyl)benzaldehyde, 98%, Sigma-Aldrich; 4-(trifluoromethyl)benzaldehyde, 98%, Sigma-Aldrich; tris(bipyridine)ruthenium(II) chloride hexahydrate (**Rubpy**), 99.95%, Sigma-Aldrich; tris(1,10-phenanthroline)ruthenium(II) dichloride hydrate, 98%, Sigma-Aldrich (**Ruphen**). Aqueous solutions were prepared using ultrapure Millipore MilliQ water with a specific resistance of 18.2 M Ω cm (20 °C). Prior to all spectroscopic measurements and irradiation experiments under oxygen-free conditions, argon from Nippon Gases (5.0) was bubbled

through the sample solutions for at least 10 minutes to remove dissolved oxygen. Unless otherwise stated, the solutions for optical spectroscopy were sealed in 10 mm pathlength cuvettes (quartz glass) equipped with septum caps.

Steady-state measurements

Absorption spectra were recorded using a Perkin Elmer LAMBDA 365 instrument. Emission measurements were performed with a Perkin Elmer FL-6500 spectrometer. This instrument provides reliable values (*i.e.* sensitivity-corrected spectra) up to 660 nm. All steady-state absorption and emission measurements were carried out at room temperature (20 ± 2 °C). Very low concentrations of the emitting substances were used to avoid filter effects.

Laser flash photolysis

For the recording of transient absorption spectra or time-resolved absorption or emission traces, an LP980KS setup from Edinburgh Instruments was used with either an Nd:YAG laser from Litron (Nano LG 300-10) with frequency-tripled output (355 nm) or an Nd:YAG laser from Quantel (Q-smart 450) with frequency-doubled output (532 nm). For both lasers, the laser pulse duration was about 10 ns and the pulse frequency was 10 Hz. The excitation energy was adjusted with a mechanical attenuator (Litron) or by modifying the Q-switch delay (Quantel). Pulse energy measurements were conducted using a pyroelectric detector equipped with a broadband absorber sourced from gentec-eo (QE25LPS-MB-QED-D0). Unless otherwise specified, the intensity when using 532 nm as the excitation wavelength was ~50 mJ per laser pulse. To ensure a uniform excitation throughout the detection volume, beam expanders (Thorlabs) were employed. The beam diameter in front of the cuvette window was approximately 1.2 cm (Litron) and 0.8 cm (Quantel). This allowed accurate determination of the concentrations of the excited states in the cuvette and provided reliable kinetic analyses. Transient absorption spectra were detected using an iCCD camera from Andor. Unless otherwise stated, transient absorption spectra were integrated over 100 ns. Single-wavelength kinetics were recorded using a Hamamatsu photomultiplier tube (R928). Spectroscopic experiments were performed using a temperature-controlled cell holder. Unless otherwise stated, LFP measurements were performed at 20 °C.

77 K phosphorescence measurements

The 77 K measurements were performed with the LP980KS setup, replacing the standard cuvette holder with a dewar containing a 4 mm thick sample glass tube surrounded by liquid nitrogen (L-G03 Liquid Nitrogen EPR Dewar).

LED irradiation experiments

Application-related irradiation experiments were conducted with a 525 nm LED (Kessil Science, PR160L) with 100% output power. The emission spectrum is shown in Figure S1.

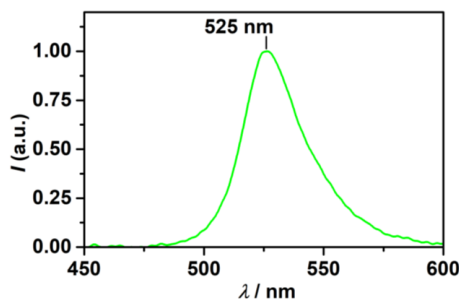


Figure S1 Emission spectrum of the used 525 nm LED. The spectrum was measured by irradiation a water-containing cuvette in the FL-6500 instrument, recording the Rayleigh scattered light. The light source was installed in a 90° angle with respect to the detector.

NMR spectroscopy

NMR spectroscopic studies were performed on a 300 MHz Avance III HD multi nuclear magnetic resonance spectrometer (Bruker, analytic measuring technique, Karlsruhe, Germany). The solvents were chloroform- d_1 and water- d_2 (Deutero GmbH, Kastellaun, Germany). The ^1H NMR spectra were calibrated using the residual non-deuterated solvent.³ In ^{19}F NMR spectroscopy, chemical shifts were referenced to trifluoroacetate ($\delta = -76.2$ ppm).^{4,5} Chemical shifts are given as δ values in ppm and all coupling constants are given in Hertz (Hz). All conversions and product yields were determined by ^1H NMR using an internal standard (see section S5).

Quantum chemical computations

Density Functional Theory (DFT) calculations were performed using the program Orca 5.0.4.⁶ Unless otherwise stated, the functional B3LYP and the basis set def2-SVP were used for the computations. After each geometry optimization, vibration frequencies were calculated. For **PTS^{•-}**, atom-pairwise dispersion correction with the Becke–Johnson damping scheme (D3BJ) was included.⁷ In every case, no imaginary vibration frequencies were obtained, indicating convergence on minimum structures. The lowest triplet states were calculated starting from the energy-minimized singlet ground state geometries. Triplet state energies were determined by comparing the energies of the optimized structures of the singlet ground state and triplet state for each compound.^{8,9} To determine electronic excitation energies and oscillator strengths of the lowest 30 transitions (unless otherwise stated), TD-DFT calculations were performed with previously geometry-optimized structures at the same level of theory. Additional single-point calculations were carried out to obtain the spin densities of the optimized triplet states based on Mulliken population analyses. The structures, and spin densities (iso value: 0.005) were displayed using the software Avogadro1.2.0.¹⁰ The color code for the atoms in the ball and stick representation is as follows: carbon (black), hydrogen (white), oxygen (red), sulfur (yellow). In the depiction of spin

densities, blue-colored surfaces denote positive spin densities, whereas red-colored surfaces denote negative spin densities.

S2 Additional steady-state experiments

S2.1 NMR titration experiment with Ruphen and PTS

The ground state association between **Ruphen** and **PTS** was investigated by ^1H NMR spectroscopy. Similar to the absorbance changes in the UV-vis study shown below (see Figure S5), changes in the chemical shift of the signals of **Ruphen** occur when **PTS** is added. In a so-called NMR titration, **PTS** (guest compound) was added in varying amounts at a constant **Ruphen** concentration (0.5 mM, host compound). The corresponding ^1H NMR spectra are shown in Figure S2. It can clearly be seen that the chemical shifts of **PTS**, which can be regarded as the mean value of all **PTS** molecules, shift with changing **PTS** concentrations. The chemical shifts of the signals of **Ruphen** (δ_1 – δ_4) for different **PTS**:**Ruphen** ratios are shown in Figure S3.

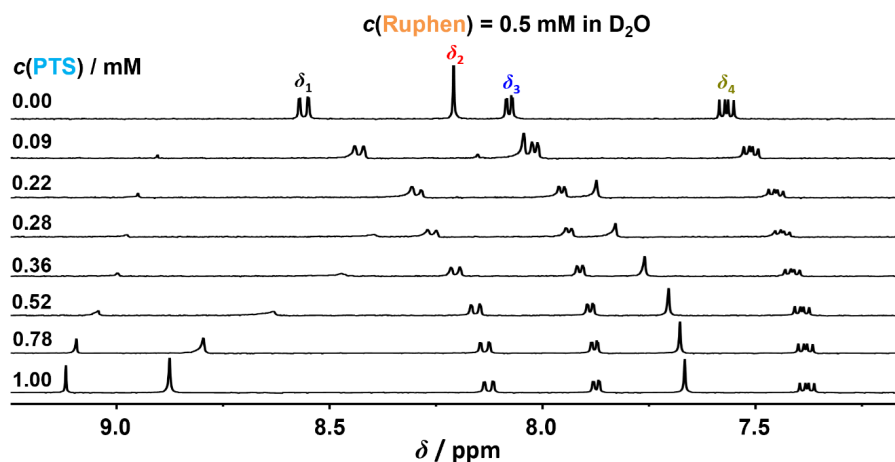


Figure S2 ^1H NMR spectra of **Ruphen** (signals labeled with δ_1 – δ_4) in the presence of **PTS** at different concentrations in D_2O at 20 °C.

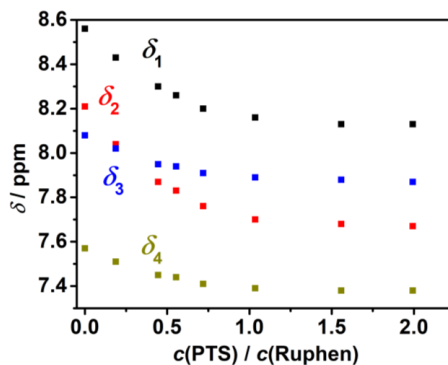


Figure S3 Chemical shifts of the ^1H NMR spectra of **Ruphen** (signals labeled with δ_1 – δ_4) at different guest:host ratios ($c(\text{PTS})/c(\text{Ruphen})$) in D_2O at $20\text{ }^\circ\text{C}$.

The well-established program BindFitV0.5^{11–17} from the Thordarson group was used to analyze the data. This allows the selection of different fitting models, allowing a distinction between a 1:1, 1:2 or 2:1 aggregation (host:guest) as well as mixed aggregation models.¹¹ A 1:2 aggregation (**Ruphen:PTS**) is not considered meaningful due to the very high charge of **PTS** with -4 compared to **Ruphen** with +2.

Initially, a fit based on a 1:1 aggregation model was made, which results in an inappropriate fit with large errors. According to the recommendations of the Thordarson group,¹² the fit as well as the raw and metadata can be accessed via the following link:

<http://app.supramolecular.org/bindfit/view/b82a6c82-38b2-4ad3-8d00-09acabeb23fb>

In contrast, a fit based on a mixed 1:1 and 2:1 aggregation model (see also Figure S4) provides a very good agreement with the measurement data:

<http://app.supramolecular.org/bindfit/view/d4144d5b-5cdf-499c-9823-a922e965eb18>

The corresponding complexation constants of the 1:1 and 2:1 association are:

$$K_{11} = (2.2 \pm 1.1) \cdot 10^4 \text{ M}^{-1}$$

$$K_{21} = (37 \pm 5) \text{ M}^{-1}.$$

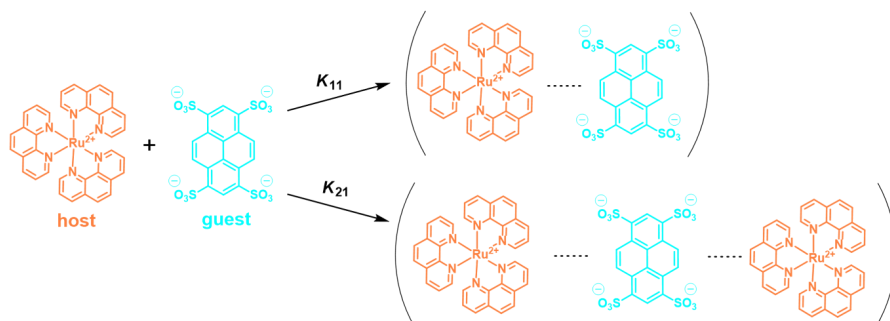


Figure S4 Schematic representation of 1:1 and 2:1 (host:guest) complexation between **Ruphen** (host) and **PTS** (guest) in aqueous solution.

K_{11} is 3 orders of magnitude higher than K_{21} . This already implies that the 1:1 association is much more significant than the 2:1 association. Via the links shown above, the proportion of free **Ruphen**, **(Ruphen)(PTS)** and **(Ruphen)₂(PTS)** can also be displayed in the form of a mole fraction. For each host:guest ratio, a 2:1 aggregate is present less than 1%, which means that it has practically no relevance. In contrast, at **PTS:Ruphen** ratios of 1 and 2, 70% and 90%, respectively, of the **Ruphen** molecules are in a 1:1 aggregate with **PTS**, which is consistent with the results of the static quenching efficiency of the LFP studies (see main part, Figure 3 (a)). K_{11} and K_S are of the same order of magnitude, with K_{11} being lower by a factor of 2.7. This difference can be explained by the fact that the concentrations of chromophores in the NMR titration were higher, which results in an intrinsically higher salt effect. Additionally, the experiments were performed in D₂O, whereas in the LFP studies the experiments were performed in MilliQ water.

S2.2 Benesi–Hildebrand plot for Ruphen and PTS

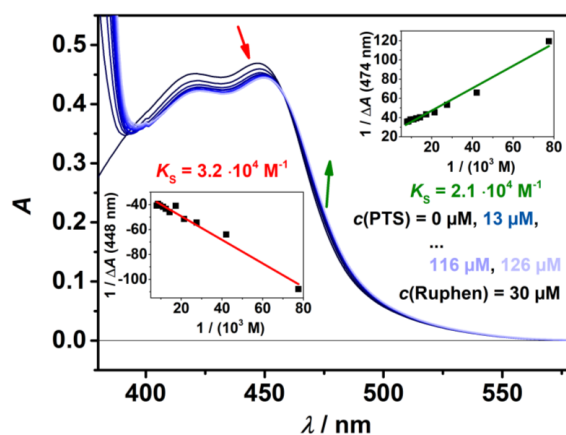


Figure S5 UV-vis spectra of aqueous solutions with different **PTS** concentrations in the presence of a constant **Ruphen** concentration (30 μM). Insets: Benesi–Hildebrand-type plots based on the changes in the absorbance at 448 nm and 474 nm.

A bathochromic shift of the MLCT absorption band with an isosbestic point at $\lambda = 460$ nm indicates a ground state interaction between the inorganic and organic chromophore. The differences in the absorbance of the different solutions at the laser excitation wavelength 532 nm are well below 5%, which means that no correction factors are necessary when performing quantitative measurements using the LFP setup.

The Benesi–Hildebrand-type¹⁸ plots show a linear trend for the wavelengths at which the largest change in absorbance can be seen (448 and 474 nm), supporting the outcomes of the ^1H NMR titration (see section S2.1), which indicate a 1:1 complexation between **Ruphen** and **PTS**. The obtained values for the association constant are of the same order of magnitude as for the laser measurements and the NMR titration experiment. However, we regard the NMR method^{11,12} shown in section S2.1 as more meaningful given that some simplifications in the Benesi–Hildebrand analysis are made that rely on a clear excess of one component.

S2.3 Steady-state emission quenching of ³Ruphen by PTS

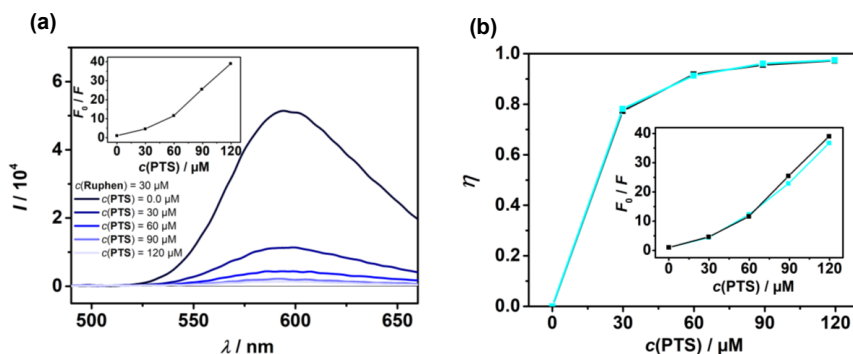


Figure S6 (a) Main plot: Stationary emission of ³Ruphen ($c(\text{Ruphen}) = 30 \mu\text{M}$, $\lambda_{\text{exc}} = 460 \text{ nm}$) in Ar-saturated water in the presence of PTS at different concentrations. Inset: Corresponding Stern–Volmer plot based on the reduced emission intensity (integral from 525 to 660 nm). (b) Main plot: Comparison of quenching efficiencies obtained from total time-resolved emission intensity (cyan, see Figure 3 (a) in the main part) and steady-state emission (black). Inset: The corresponding Stern–Volmer plot with its characteristic quadratic concentration dependence.¹⁹

The steady-state and kinetic emission measurements provide comparable Stern–Volmer plots and an almost identical quenching efficiency of ³Ruphen in the presence of PTS. Therefore, time-resolved measurements are essential for a clear separation of static and dynamic quenching (see Figure 3 (a) in the main part and the corresponding discussion for further details).

S2.4 pH-dependent ground state absorption spectrum of PTS

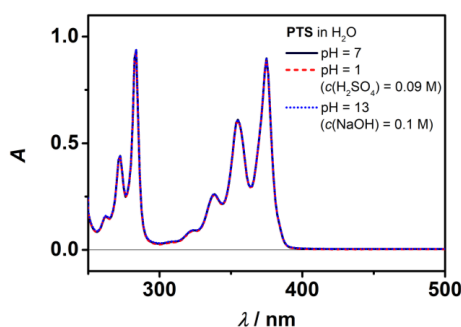


Figure S7 Ground state absorption spectrum of PTS in water ($c(\text{PTS}) = 24 \mu\text{M}$) at different pH values. At a pH of 1, the UV-vis spectrum is unchanged compared to neutral or alkaline conditions, indicating that PTS is present in the fully deprotonated form under acidic conditions in water, *i.e.* also during the **5-HMF** oxidation, in which the pH is gradually reduced as a result of formic acid release.¹

S3 Additional experiments for determining the quenching efficiency by oxygen and stability measurements

S3.1 Singlet oxygen assay according to the RNO method

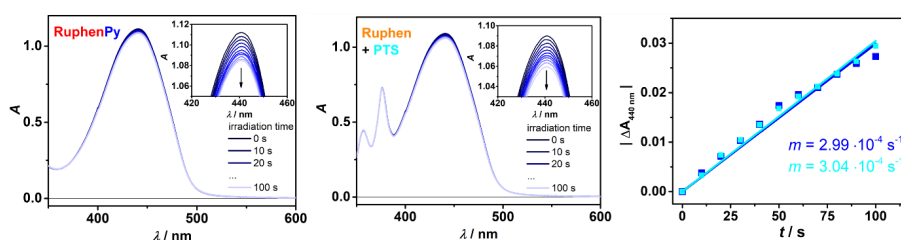


Figure S8 (left, middle) UV-vis spectra of air-saturated aqueous solutions of RNO (140 μM), imidazole (8 mM) and the respective sensitizer (system) (60 μM) before and during irradiation (LED, $\lambda_{\text{exc,max}} = 525 \text{ nm}$). (right) Changes in the absorption band at 440 nm during irradiation with their respective slope.

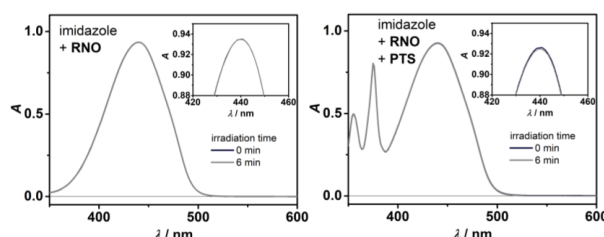


Figure S9 UV-vis spectra of control experiments for the $^1\text{O}_2$ assay in water before and after irradiation. The same concentrations and LED intensity were used as in the experiments shown in Figure S8.

The **RNO** method initially developed by Kraljić and Mohsni is a reliable method to selectively observe $^1\text{O}_2$ formation in water.^{1,20} After $^1\text{O}_2$ is generated, a corresponding endoperoxide is formed together with imidazole, which selectively oxidizes the **RNO**, in this case *N,N*-dimethyl-4-nitrosoaniline, to the corresponding nitro compound. The decrease of the **RNO** compound can be observed via the decrease of its absorption band at 440 nm. Thus, the relative rate of decrease of the absorption band can be directly related to the relative rates of $^1\text{O}_2$ formation. To allow a direct comparison of the results of the $^1\text{O}_2$ assay with those of the **5-HMF** photooxygenation, the same catalyst concentrations were used. Cuvettes with a path length of 0.2 cm were chosen to perform the measurement in the linear range of the absorbance measurement of the spectrometer. The cuvette was filled with 550 μL of air-saturated solution and tightly sealed with a teflon stopper. To ensure the same photon flux, each cuvette was irradiated frontally with a 525 nm LED located at a distance of 10 cm and set at 25% power. After an irradiation period of 10 seconds, a UV-vis spectrum was recorded in each case. A low overall conversion was selected in

order to remain within the linear range of the reaction progress and to ensure an approximately constant oxygen concentration. The decrease of the absorption band at 440 nm could be clearly observed for the complete photocatalysis systems. In addition, the control experiments show that no conversion of **RNO** is found in the absence of the sensitizer or imidazole, so that interfering side reactions can be excluded.

S3.2 Kinetic simulation of the lifetime dependency of quenching efficiency

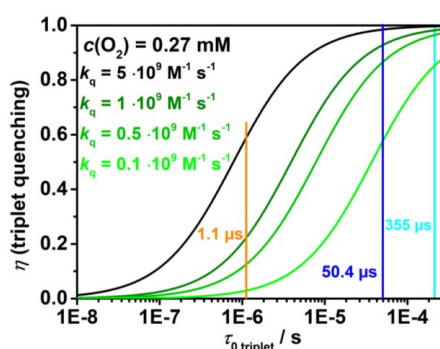


Figure S10 Simulated quenching efficiencies at a standardized quencher concentration of 0.27 mM (which corresponds to the solubility of dissolved oxygen in air-saturated water²¹) as a function of the unquenched lifetime of the photosensitizer using four different quenching rate constants. The simulation is based on well-known kinetic equations for bimolecular quenching of excited states.²²

The solubility of dissolved oxygen and various other potential energy acceptors in aqueous solutions is typically low. This characteristic combined with short excited-state lifetimes often leads to inefficient energy transfer processes and low quantum yields of many reactions. Figure S10 presents a kinetic simulation that demonstrates the necessity of extended triplet lifetimes for sensitizers in reactions that cannot be performed at high concentrations of acceptor and substrate. Even when utilizing sensitizers like **Ruphen** (with a triplet lifetime of 1.1 μ s) with second-order rate constants approaching the diffusion limit, the quenching efficiencies remain below 60% for sensitizing oxygen. In contrast, employing long-lived triplet-excited species as sensitizers enables energy transfer with efficiencies close to unity, even at considerably slower bimolecular rate constants. Furthermore, in this regard, the Coulombic dyad outperforms the molecular dyad, due to the higher triplet lifetime achieved in the Coulomb-matched pair resulting from less back energy transfer ($\Delta E_T \approx 0.4$ eV) to the inorganic chromophore, as already explained in the main paper.

S3.3 Oxygen quenching efficiency at 50 °C

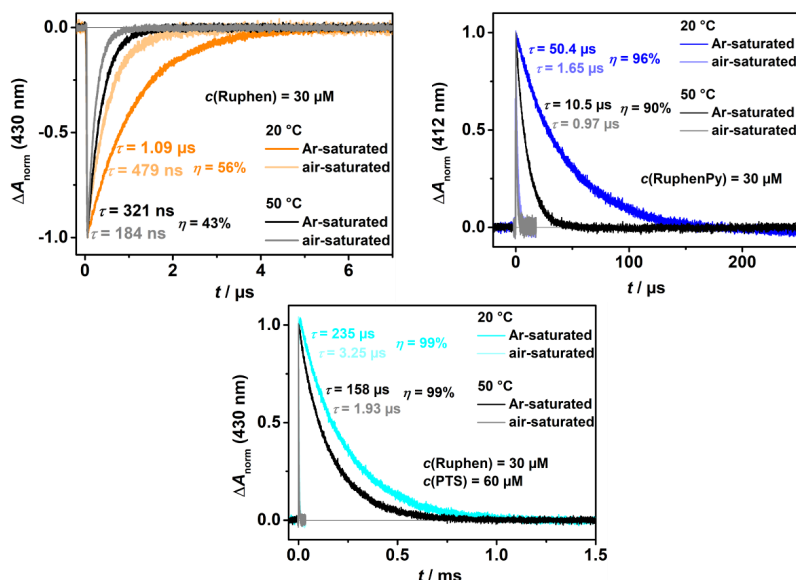


Figure S11 Time-resolved absorption measurements to determine the lifetimes of the triplet excited **Ruphen** (top left), **RuphenPy** (top right) and **PTS** (bottom) at 20 °C and 50 °C in air- or Ar-saturated solutions with the corresponding quenching efficiencies by molecular oxygen.

The lifetimes of ³**Ruphen** and ³**RuphenPy** show a pronounced temperature dependence. In the case of ³**Ruphen**, thermally activated population of the ³MC state can take place, which reduces the lifetime of the ³MLCT state.²³ For ³**RuphenPy** it is known that deactivation via the metal complex unit is more efficient at elevated temperatures.¹ In contrast, the lifetime of ³**PTS** seems to be more robust towards increased temperatures.

Since ³**Ruphen** has a lifetime of only about 300 ns at 50 °C, the quenching efficiency by dissolved O₂ drops below 50%. Despite suffering from a high lifetime reduction, the quenching efficiency of ³**RuphenPy** by O₂ is with 90% still very high. Since a lifetime of more than 100 μs is achieved for ³**PTS** even at elevated temperatures, the quenching efficiency by O₂ stays close to 100%, making ³**PTS** an attractive energy transfer catalyst.

The quenching efficiency of ³**Ruphen** by **PTS** also depends on temperature. For a **PTS** concentration of 60 μM , ³**Ruphen** is quenched with an efficiency as high as 92% at 20 °C and 83% at 50 °C, which globally has little effect on the overall quantum yield of the reaction.

S3.4 Comparison of expected and observed performance for photocatalytic $^1\text{O}_2$ formation and photostability measurements

Table S1 Expected and observed performance for $^1\text{O}_2$ formation in water with the photocatalysts used (see also Figure 5 (b) in the main part, ++ means excellent, whereas -- means poor) based on the molar extinction coefficient at the LED peak wavelength ($\epsilon_{525\text{ nm}}$), the unquenched triplet lifetime ($\tau_{\text{T},0}$), the intersystem crossing quantum yield (Φ_{ISC}), the quenching efficiency by dissolved oxygen ($\eta_{\text{q},\text{O}_2}$) and the quantum yield of singlet oxygen formation (Φ_{Δ}).

Compound	$\epsilon_{525\text{ nm}}$	$\tau_{\text{T},0}$	Φ_{ISC}	$\eta_{\text{q},\text{O}_2}$	Φ_{Δ}	Expected performance in $^1\text{O}_2$ formation	Observed performance in $^1\text{O}_2$ formation
Ruphen	-	$1.10\ \mu\text{s}^{[\text{a}]}$	~ 1	$\sim 0.54^{[\text{a}]}$	$\sim 0.25^{24}$	-	+
RuphenPy	-	$50.4\ \mu\text{s}^{[\text{a}]}$	~ 1	$\sim 1^{[\text{a}]}$	$\sim 0.60^1$	+	+
Ruphen and PTS	-	$355\ \mu\text{s}^{[\text{a}]}$	~ 1	$\sim 1^{[\text{a}]}$	$\sim 0.60^{[\text{c}]}$	+	++
eosin Y	++	$\sim 190\ \mu\text{s}^{25}$	$\sim 0.8^{25}$	$\sim 1^{[\text{b}]}$	$\sim 0.57^{26}$	+	--
methylene blue	+	$>400\ \mu\text{s}^{27}$	$\sim 0.52^{28}$	$\sim 1^{[\text{b}]}$	$\sim 0.52^{29}$	+	--
rose bengal	++	$\sim 104\ \mu\text{s}^{30}$	$\sim 0.86^{31}$	$\sim 1^{[\text{b}]}$	$\sim 0.76^{32}$	++	--

[a] From this work; [b] Assuming $k_{\text{q}} = 1 \cdot 10^9\ \text{M}^{-1}\text{s}^{-1}$ as a lower limit and $c(\text{O}_2) = 0.27\ \text{mM}^{21}$; [c] From this work, same result compared to the dyad, see section S3.1

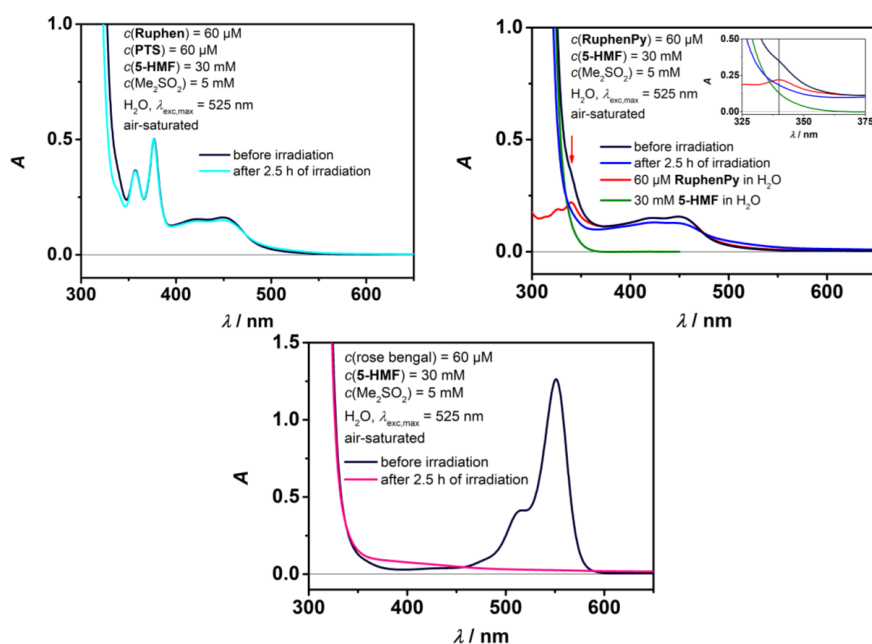


Figure S12 UV-vis spectra (recorded in 2 mm quartz glass cuvettes) of the solutions used for photocatalysis before and after 2.5 h of irradiation (525 nm LED) under the standard reaction conditions (see Figure 5 (b) in the main part and section S5.1) using the catalysts **Ruphen** and **PTS** (top left), **RuphenPy** (top right) and **rose bengal** (bottom).

As demonstrated in Figure S12, there are only minor changes in the characteristic MLCT band of **Ruphen** and the π - π^* band of **PTS** in the UV-vis spectrum during irradiation, which demonstrates the high photostability of the Coulombic dyad.

In contrast, more pronounced changes in the MLCT band and a disappearance of the characteristic π - π^* band of pyrene (in the form of a shoulder marked with a red arrow) are observed for the molecular dyad **RuphenPy**. More than half of the absorption intensity observed for the freshly prepared reaction mixture at 340 nm is attributed to the absorption of the molecular dyad (Figure S12 top right, inset). As we found, the observed decrease of the absorption by 50% after irradiation is a result of two effects: First, a minor absorption decrease at 340 nm can be expected owing to the conversion of ~40% **5-HMF** into a less-absorbing product. Second, a substantial amount of the dyad photocatalyst has vanished. A careful analysis allows us to set a lower limit for this photodegradation process – more than 50 % of the molecular dyad molecules underwent degradation after 2.5 h of green-light irradiation.

For all organic sensitizers, we observed pronounced changes of their intense colors with the naked eye after a few minutes of photoirradiation. The organic photocatalyst rose bengal shows a very poor photostability, which can be observed by the complete disappearance of the characteristic absorption band after 2.5 h of irradiation. The low photostabilities of the molecular dyad and the organic photocatalyst explain the lower experimental $^1\text{O}_2$ formation performance compared to the expectations based on literature values (see Table S1 and Figure 5 (b) in the main part).

S4 Influence of Coulombic interactions on static quenching and quenching efficiency

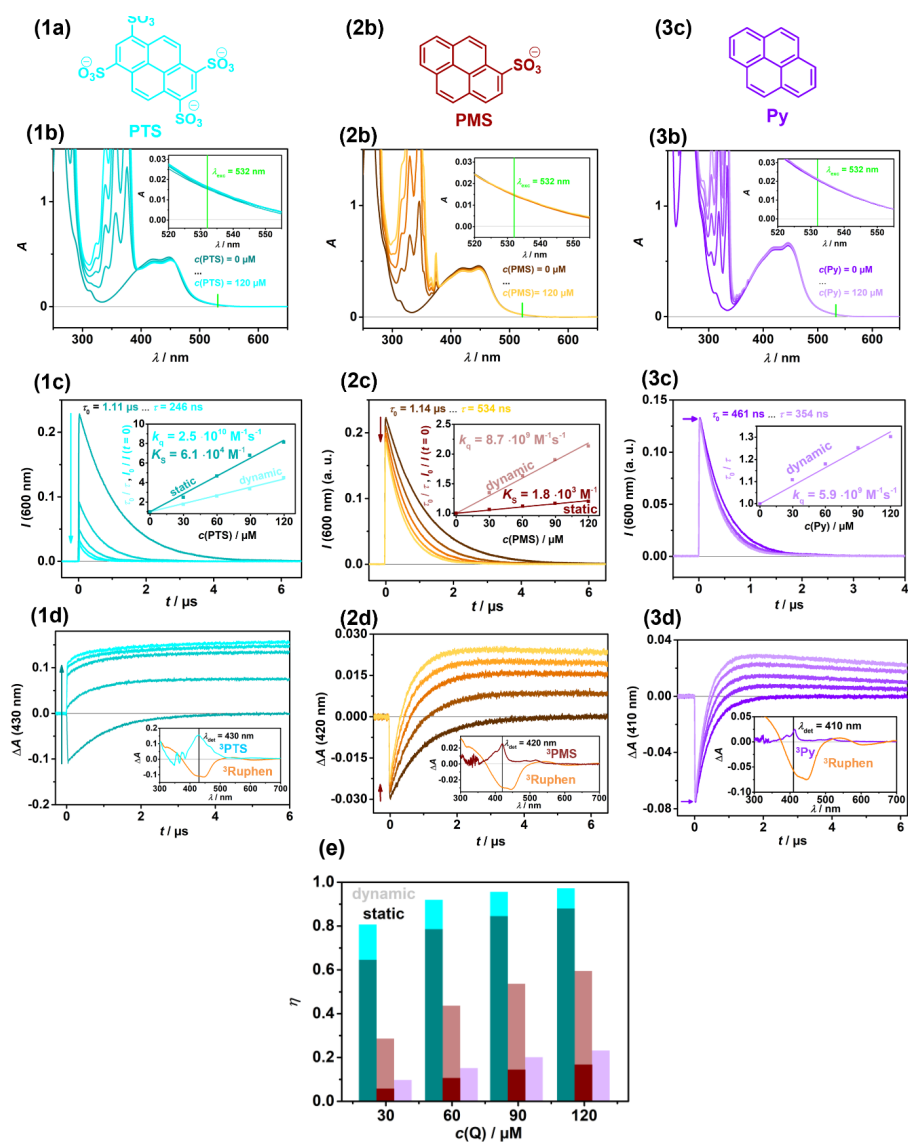


Figure S13 Elucidation of charge effects for static energy transfer in solution between ³Ruphen and differently charged pyrene derivatives. (a) Molecular structures of PTS, PMS and Py. (b) Main plot: UV-vis spectra of solutions containing ³Ruphen (30 μM) and the corresponding pyrene derivative (c = 0, 30, 60, 90, 120 μM) in Argon-saturated water (1b and 2b) or acetonitrile (3b). Inset: Enlarged image to show the absorbance at the excitation wavelength. (c) Main plot: Respective time-resolved emission after laser excitation (λ_{exc} = 532 nm) with arrows indicating static energy transfer for (1c) and (2c). Inset: Stern-Volmer plots for static and/or dynamic

quenching. (d) Main plot: Time-resolved transient absorption a detection wavelength, which was chosen such that there is both a clear ground state bleach due to $^3\text{Ruphen}$ formation after the laser pulse ($\lambda_{\text{exc}} = 532 \text{ nm}$) and a strongly pronounced excited state absorption due to the respective pyrene triplet after the quenching process. Arrows indicate static quenching for (1d) and (2d). Inset: TA spectra for $c(\text{pyrene derivative}) = 0 \text{ }\mu\text{M}$ ($^3\text{Ruphen}$ is formed only, delay = 50 ns) and $c(\text{pyrene derivative}) = 30 \text{ }\mu\text{M}$ (1d) or $120 \text{ }\mu\text{M}$ (2d, 3d) (showing the pyrene triplet, (1d) delay = 2 μs , (2d) delay = 2 μs , (3d) delay = 3 μs). (e) Proportion of static and dynamic quenching of $^3\text{Ruphen}$ ($c(\text{Ruphen}) = 30 \text{ }\mu\text{M}$) by **PTS** (cyan, in water), **PMS** (brown, in water) or **Py** (purple, in acetonitrile) for different quencher concentrations in Ar-saturated solution.

The extent to which Coulombic interactions have an influence on static quenching was investigated. For this purpose, in comparison to the tetrasulfonated pyrene (**PTS**), the monosulfonated pyrene (**PMS**) was used as well. Since sulfonic acids are typically very strong acids, these compounds most likely exist as tetra- and monoanions in neutral water respectively. In addition, unsubstituted pyrene (**Py**) and the PF_6 salt (for solubility reasons) of **Ruphen** were investigated in acetonitrile, to observe the quenching behavior in the absence of Coulombic interactions between the photosensitizer and the quencher.

Initially, the changes in UV-vis spectra (part b of Figure S13) were observed with increasing quencher concentrations. In the case of charged quenchers, slight spectral changes are seen in the region of the MLCT absorption bands, indicating complexation between the two chromophores. In the absence of Coulombic attraction, such a change is not present. For the subsequent laser measurements, the absorbances at the excitation wavelength are relevant. For the solutions with **PTS**, the absorbance varies by less than 5%. For the solutions with **PMS** and **Py**, the absorbance of the Ru complex remains almost constant at 532 nm.

Using the time-resolved emission at 600 nm after the laser pulse (part c of Figure S13), the phosphorescence of $^3\text{Ruphen}$ and thus its quenching by the pyrene derivatives can be observed. Based on the initial amplitude under otherwise identical conditions, the static quenching as a result of the complexation between the inorganic and organic chromophore can be quantified. Very pronounced static quenching is observed for the tetraanion **PTS**, yielding a complexation constant of $6.1 \cdot 10^4 \text{ M}^{-1}$. In addition, dynamic quenching with a quenching constant of $2.5 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ is well above the diffusion limit in water ($6.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at $20 \text{ }^\circ\text{C}$)²¹, which can also be attributed to attractive interactions between **Ruphen** and **PTS**. Weak static quenching is observable for **PMS**, resulting in a complexation constant of $1.8 \cdot 10^3 \text{ M}^{-1}$. Dynamic quenching occurs with a constant of $8.7 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$. When quenching $^3\text{Ruphen}$ by **Py** in acetonitrile (whose viscosity is about 2.5 times lower compared to water, allowing much faster diffusion-based reaction rates), no decrease in initial amplitude is seen, excluding static quenching. The constant of dynamic quenching was estimated to $5.9 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Additional time-resolved measurements of the transient absorption signals were performed (part d of Figure S13). Here, the detection wavelength was chosen such that both ^3PTS and $^3\text{Ruphen}$ give clear signals (excited state absorption of ^3PTS and ground state bleach of $^3\text{Ruphen}$). When **PTS** is used as a quencher, the quasi-instantaneous formation of ^3PTS (in static quenching typically on a sub-ns time

scale) is very clearly seen under the simultaneous recovery of the **Ruphen** ground state (*i.e.* the expected **Ruphen** ground state bleach cannot be observed). In the case of the monoanion **PMS**, static quenching occurs to a smaller extent. This leads to the fact that with increasing **PMS** concentration less ³**Ruphen** and ³**PMS** is formed initially. In total, this results in slightly more positive transient absorption signals. For the uncharged quencher, that the initial transient absorption is independent of the **Py** concentration, which also indicates the absence of static quenching.

The summary of the quenching efficiencies for the pyrene derivatives and the differentiation into static and dynamic contributions (part e of Figure S13) allows two conclusions: i) The overall quenching efficiency under the chosen conditions increases with increasing Coulombic interaction and ii) the proportion of static quenching is more pronounced in the presence of attractive Coulombic interactions. It can be concluded that Coulombic interactions are in charge for the pronounced static quenching and the beneficial properties of our Coulombic dyad consisting of ³**Ruphen** and **PTS**.

S5 Irradiation experiments

S5.1 General procedure

For photooxygenations, a cylindrical glass vessel with a total volume of 20 mL and a diameter of 2.3 cm was used. It was filled with 5 mL of the respective reaction solution and closed with a septum. A water bath was used to ensure a constant reaction temperature (room temperature). For reactions at 50 °C, the water bath was kept at this temperature using a hot plate. The irradiation was carried out with a 525 LED, which was located at a distance of one centimeter from the reaction vessel and operated at 100% power. The gas space of the reaction vessel was connected via a cannula to a pressure-controlled vacuum pump (Büchi V-500 vacuum pump and Büchi Vacuum Controller V-800) and a slight vacuum of 25 ± 10 mbar below the ambient pressure was adjusted. A second cannula, which reaches to the bottom of the reaction vessel and is connected to the outside air, ensures a constant air flow and thus a constant oxygen concentration (see Figure S14).

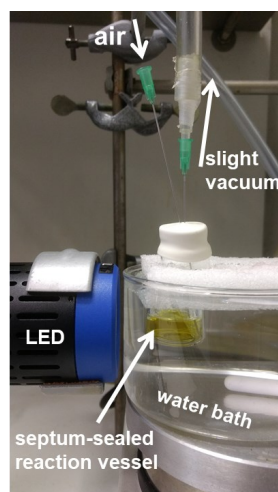


Figure S14 Reaction setup used for photooxygenations.

The reactions were carried out in MilliQ water. For reaction control, ^1H NMR spectra were recorded from a mixture of 0.25 mL reaction solution and 0.35 mL D_2O . A very intense signal is obtained for water, centered at 4.79 ppm and extending approximately from 5.2–4.2 ppm. This has been cut out for clarity in the ^1H NMR spectra shown.

Debromation and Pinacol coupling reactions were performed in septum-sealed NMR tubes filled with 0.7 mL reaction solution under an argon atmosphere. The NMR tube was also placed in a water bath for maintaining the temperature during irradiation. Only one NMR tube was irradiated with one LED at a time.

To quantify the reactant and products, the corresponding signals were compared to the signal from the internal standard.

S5.2 Photooxygenation of 5-HMF

5-HMF is one of the most promising platform chemicals derived from sugars, which can be processed into building blocks for biopolymers, biofuels, fine chemicals or large-scale chemicals.^{33,34}

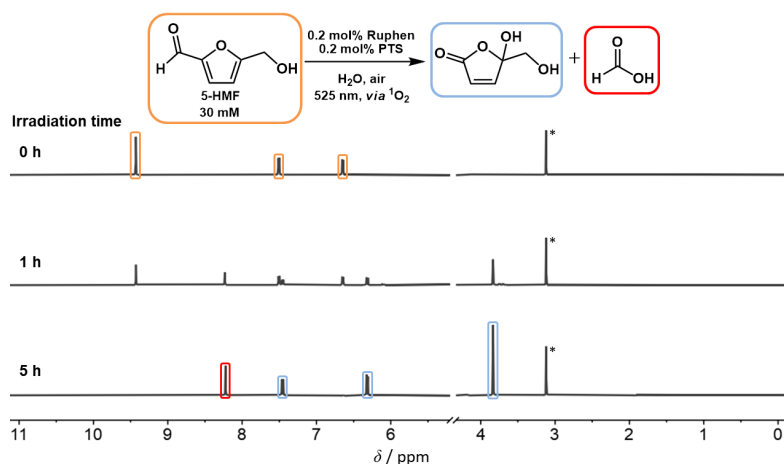


Figure S15 Reaction equation of **5-HMF** photooxygenation with the corresponding ¹H NMR spectra and assignment of reactant and product signals (color-coded) after different irradiation times (525 nm LED). The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone (c = 5 mM).

Figure S15 shows the photooxygenation of **5-HMF** with the corresponding ¹H NMR spectra under optimized conditions. A clean and nearly complete conversion of **5-HMF** to the two products is obtained in this reaction. The signals could be clearly assigned to the products.^{1,34} In the absence of a suitable sensitizer, neither product formation nor substrate conversion are observed. For the time and catalyst dependent product yields, see Figure 5 (b) of the main part. **Ruphen** and **PTS** are so low in concentration that they are not visible in the NMR. Additionally, no by-products could be observed.

Formic acid: $^1\text{H NMR}$ (300 MHz, $\text{H}_2\text{O}+\text{D}_2\text{O}$): δ [ppm] = 8.22 (s, 1H).

5-Hydroxy-5-(hydroxymethyl)furan-2(5H)-one: $^1\text{H NMR}$ (300 MHz, $\text{H}_2\text{O}+\text{D}_2\text{O}$): δ [ppm] = 7.46 (d, J = 5.8 Hz, 1H), 6.32 (d, J = 5.7 Hz, 1H), 3.83 (s, 2H).

S5.2.1 Variation of catalyst loading and excitation wavelength

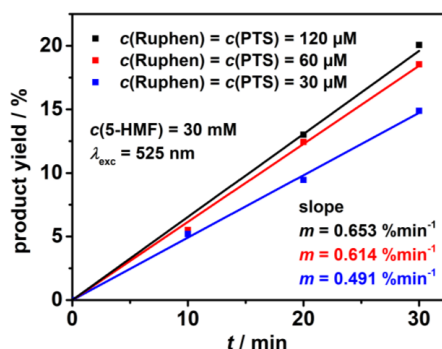


Figure S16 Comparison of the reaction rates for the photooxygenation of 5-HMF with different **Ruphen** and **PTS** concentrations in air-saturated solution.

In the molecular dyad, the inorganic and organic chromophore are present in a 1:1 ratio. To have a direct comparison with the Coulombic dyad, **Ruphen** and **PTS** were also used at the same concentration for most experiments. At twice the sensitizer concentration, twice as many photons from the light source are absorbed, which can be assumed given the layer thickness used and the moderate absorbance at the excitation wavelength. Since twice the amount of $^3\text{Ruphen}$ (and therefore ^3PTS) is obtained in the process as well, it is ultimately assumed that the rate of $^1\text{O}_2$ formation is twice as high. Additionally, when the **PTS** concentration is increased from 30 μM to 60 μM , the quenching efficiency of $^3\text{Ruphen}$ by **PTS** is slightly increased (from just below 80% to over 90%). When the catalyst concentrations are increased from 30 to 60 μM , the reaction rate is increased by 25%. When the catalyst concentrations are further doubled, there is very little increase in reaction rate. At a concentration of 60 μM the upper limit of the reaction rate seems to be reached. Therefore, this concentration was chosen for the irradiation reactions. Based on this result it is assumed that with this catalyst concentration the oxygen uptake rate of the solution is the rate determining step of the photooxygenation.

S5.2.2 Comparison of H₂O and D₂O as solvent

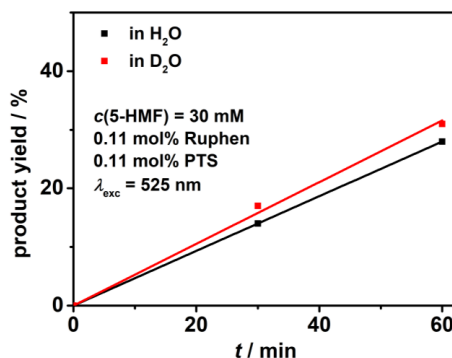


Figure S17 Product formation rates during the photooxygenation of **5-HMF** with **Ruphen** and **PTS** in air-saturated H₂O or D₂O.

Furthermore, it was tested whether the [2+4] cycloaddition was the rate-determining step in the reaction. A catalyst loading was selected at which the rate is not yet limited by the oxygen uptake into the solution. In D₂O, ¹O₂ has a lifetime that is about twenty times longer than in H₂O (~67 μs vs ~3.5 μs).³⁵ If the reaction rate is limited by the [2+4] cycloaddition, a much higher reaction rate would be observed in D₂O. Since an almost identical reaction rate is obtained, it is assumed that **5-HMF** reacts very rapidly with ¹O₂. Thus, the reaction is likely limited by the rate of oxygen uptake into solution.

S5.2.3 Determination of oxygen concentration during irradiation

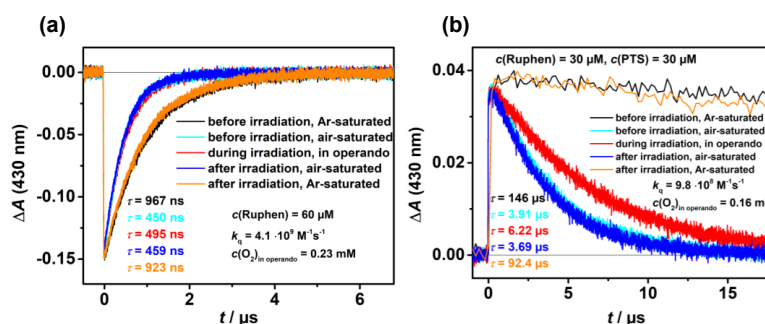


Figure S18 Time-resolved absorbance measurements of aqueous reaction solutions containing **5-HMF** (30 mM) and dimethyl sulfone (5 mM) with the catalysts **Ruphen** (60 μM) (a) and **Ruphen** (60 μM) and **PTS** (60 μM) (b), respectively, before and after irradiation (10 min with 525 nm LED) in air- and argon-saturated solution and “in operando”. Details and calculations are presented in the text.

Assuming that the oxygen uptake into the solution is the rate-determining step during the photooxygenation of **5-HMF**, the question arises as to what equilibrium concentration of oxygen is

reached (in operando). For this purpose, a cuvette (1 cm layer thickness, 3.5 mL total volume) containing 3.0 mL of reaction solution was irradiated for 10 minutes with a 525 nm LED in the same way as in the general procedure, passing air through it with a canula. Before irradiation, the lifetime of the triplet state in air- and Ar-saturated solution was determined via time-resolved absorption measurements. Immediately after the LED was turned off, the air flow was interrupted and the lifetime of ³**Ruphen** or ³**PTS** was determined again. Together with the lifetime measurements in air- and Ar-saturated solution after irradiation, the oxygen concentration in operando can be estimated.

The lifetimes of the triplet states of **Ruphen** and **PTS** are slightly lower in the reaction solution than in the pure solvent. Also, after irradiation, the lifetimes in Ar-saturated solution are noticeably lower than before irradiation. In the case of **PTS**, the decrease in lifetime is particularly pronounced. It is conceivable that a certain pH dependence or ionic strength due to the formic acid produced has an influence on the lifetime.³⁶ Nevertheless, the determined **PTS** lifetime of about 100 μs in this case is sufficiently high for an efficient reaction.

The rate constant of the quenching of the triplet state in the reaction solution after irradiation can be determined from the corresponding lifetimes in air- and Ar-saturated solution. For this purpose, the rearranged Stern–Volmer equation is required. A maximum O₂ concentration of 0.27 mM in air-saturated water is assumed.²¹ The same color code as in Figure S18 is used in the following equations,

$$k_q = \frac{\frac{\tau}{\tau} - 1}{(0.27 \text{ mM}) \cdot \tau}$$

Assuming that the same rate constant is present in operando, the equilibrium concentration of oxygen can be calculated.

$$c(\text{O}_2)_{\text{in operando}} = \frac{\frac{\tau}{\tau} - 1}{\tau \cdot k_q}$$

The oxygen concentration when **PTS** is used is significantly lower (0.16 mM) than when **Ruphen** alone is used (0.23 mM), indicating faster O₂ conversion, which is consistent with the higher rate of ¹O₂ formation.

Due to the fact that the triplet lifetimes are shorter in the actual reaction mixture and a lower oxygen concentration is present, the quenching efficiency for the triplet state decreases. This can be calculated with the knowledge of k_q , τ and $c(\text{O}_2)_{\text{in operando}}$.

$$\eta = 1 - \frac{1}{1 + k_q \cdot \tau \cdot c(\text{O}_2)_{\text{in operando}}}$$

For **Ruphen**, a low quenching efficiency of 46% is calculated. The triplet state of **PTS**, on the other hand, is still quenched almost quantitatively with 93%, although both the lifetime and the quencher

concentration have decreased. The relationship between quencher concentration and quenching efficiency is shown for the two triplet states with the observed lifetimes and values for k_q in a simulation (Figure S19).

S5.2.4 Kinetic simulation for quenching efficiency depending on quencher concentration

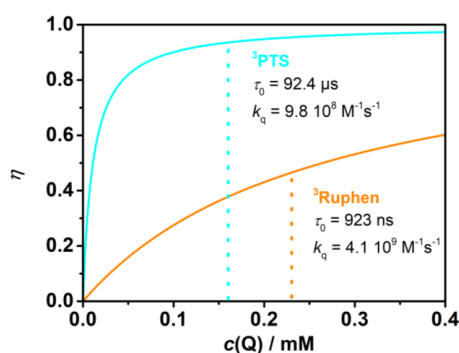


Figure S19 Kinetic simulation for the quenching efficiency η of ^3PTS and $^3\text{Ruphen}$ depending on the quencher concentration for the values of k_q and τ_0 obtained in the irradiation experiment in section S5.2.3 ($c(\text{5-HMF}) = 30 \text{ mM}$, $c(\text{dimethylsulfone}) = 5 \text{ mM}$, $c(\text{Ruphen}) = 60 \mu\text{M}$ and $c(\text{PTS}) = 60 \mu\text{M}$, 10 minutes of irradiation with $\lambda_{\text{exc,max}} = 525 \text{ nm}$).

Figure S19 clearly shows the importance of a long triplet lifetime when quenchers can only be used in a low concentration. The 100-fold higher lifetime of ^3PTS leads to a relatively constant quenching efficiency above 90% in the range in which the oxygen concentration varies during irradiation. Even at a concentration of $c(\text{Q}) = 50 \mu\text{M}$, an efficiency of over 80% is possible. In contrast, for much shorter lifetimes, as is the case for $^3\text{Ruphen}$, the quenching efficiency is sensitively dependent on the quencher concentration. A decrease of $c(\text{Q})$ leads to a significant reduction of η .

S5.2.5 Photooxygenation with sunlight

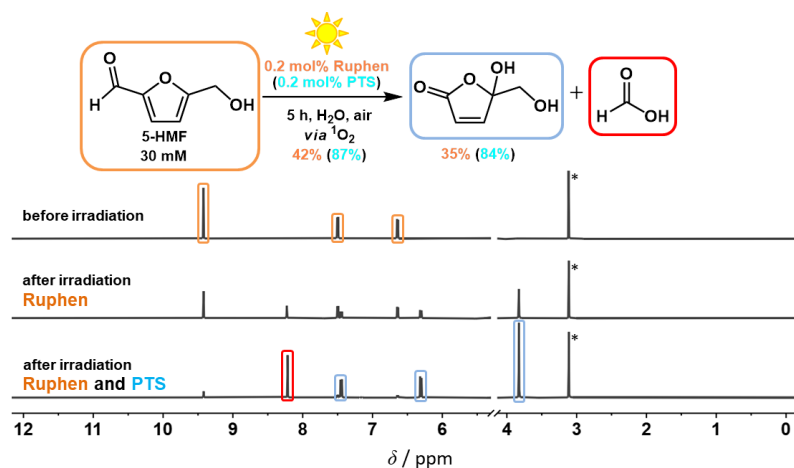


Figure S20 Reaction equation of **5-HMF** photooxygenation with the corresponding ¹H NMR spectra and assignment of reactant and product signals after irradiation with sunlight for 5 h. The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone (*c* = 5 mM).

The reaction vessel, which was placed in a water bath, was irradiated with sunlight without being sealed. Oxygen input from the surrounding air was ensured by stirring vigorously with a stirring bar driven by a magnetic stirring plate. Due to the irradiation with the (almost) complete solar spectrum, the reaction temperature (25–30 °C) was slightly above room temperature (typically 20 °C). A 400 nm long pass filter was placed in front of the reaction vessel to avoid direct excitation of **PTS** by solar UV radiation. The solar irradiation was carried out on 05/31/2023 between 9:30 am and 2:30 pm in Mainz.

S5.2.6 Gram-scale photooxygenation

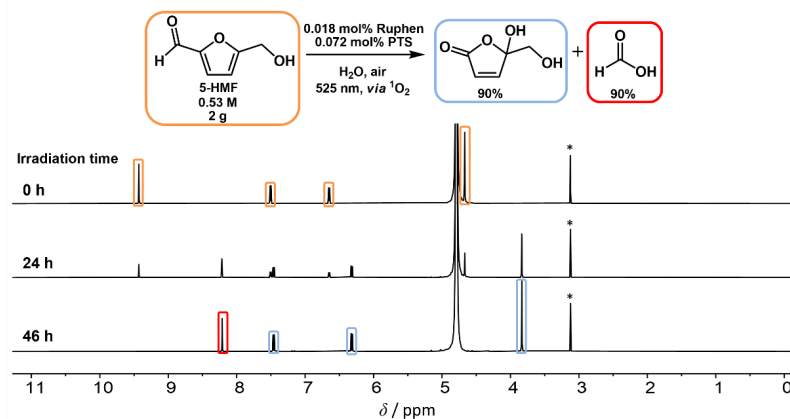


Figure S21 Reaction equation of **5-HMF** photooxygenation with the corresponding ^1H NMR spectra and assignment of reactant and product signals (color-coded) after different irradiation times (525 nm LED). The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone ($c = 81 \text{ mM}$).

The set-up used for the photooxygenation of **5-HMF** on a gram-scale was similar to that shown in Figure S14, except that a 50 mL round bottom flask was used as the reaction vessel. After complete conversion, the solution was saturated with NaCl and extracted 8 times with 15 mL ethyl acetate each. The collected organic phases were dried with sodium sulfate and then filtered. The solvent was removed under reduced pressure. This yielded 1.57 g of a yellow oil containing 75 wt. % of 5-hydroxy-5-(hydroxymethyl)furan-2(5H)-one, as well as internal standard and formic acid (determined by ^1H NMR). Further attempts to separate this mixture were not carried out.

S5.2.7 Control experiments

Table S2 Control experiments for the photooxygenation of **5-HMF** with **Ruphen** and **PTS** after 5 h of irradiation in air-saturated water.

Ruphen (60 μM)	PTS (60 μM)	Air	Irradiation (525 nm LED)	Conversion / %	Yield / %^[a]
+	+	+	+	99	93
+	-	+	+	61	61
-	+	+	+	0	0
+	+	- ^[b]	+	1	0
+	+	+	-	2	0

^[a] Yield of the lactone. ^[b] Argon instead of air was bubbled through the solution.

S5.2.8 Photooxygenation under alkaline conditions

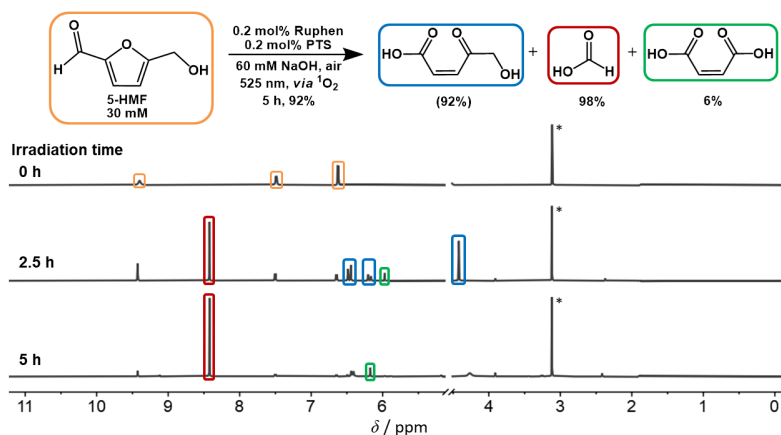


Figure S22 Reaction equation of 5-HMF photooxygenation under basic conditions with the corresponding ¹H NMR spectra (in D₂O) and assignment of reactant and product signals after different irradiation times (525 nm LED). The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfoxide (*c* = 5 mM).

By simply switching to alkaline pH conditions (compare with Figure S15), a completely different C5 building block can be obtained, which can serve as a monomer for biobased polymers.^{1,34} Even under these conditions, a highly efficient reaction with the Coulombic dyad is possible. In addition to formic acid as a co-product, maleic acid was clearly identified by the addition of a commercially available sample. Since it is a diprotic acid, the ¹H NMR signal of maleic acid is strongly dependent on the pH of the solution. The fact that the yield of formic acid exceeds the conversion suggests that the ring-opened product is further oxidized, leading to the release of another equivalent formic acid and maleic acid.¹ After 5 h of irradiation, hardly any signals of the ring-opened product are observed in the ¹H NMR spectrum. This is due to oligomerization and decomposition of this compound, which leads to broadening of the NMR signals.¹ The decrease of the monomer can be inhibited by cooling the reaction mixture.¹

cis-5-Hydroxy-4-keto-2-pentenoic acid: ¹H NMR (300 MHz, H₂O+D₂O): δ [ppm] = 6.46 (d, *J* = 12.2 Hz, 1H), 6.18 (d, *J* = 12.1 Hz, 1H), 4.42 (s, 2H).

S5.3 Photooxygenation of TAN

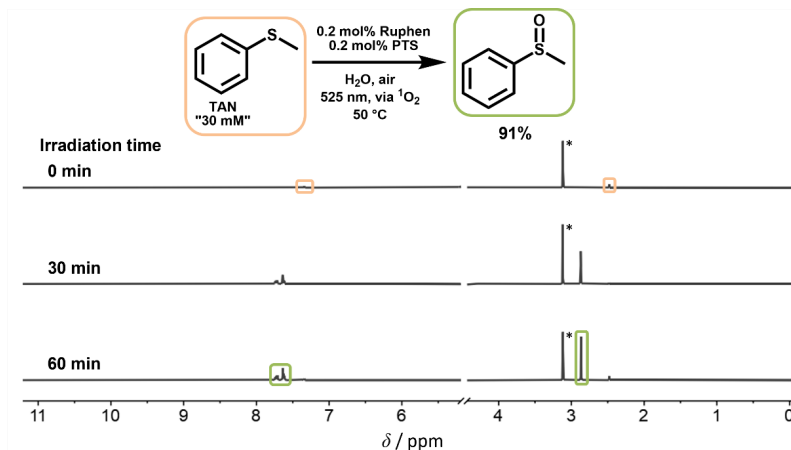


Figure S23 Reaction equation of TAN photooxygenation in air-saturated water at 50 °C with the corresponding ^1H NMR spectra (in D_2O) and assignment of reactant and product signals after different irradiation times (525 nm LED). The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone ($c = 15 \text{ mM}$).

Water can only solve a small amount of **TAN** at room temperature. At higher temperatures, a sufficiently high concentration can be achieved so that efficient photocatalysis is possible. The product is much better soluble in water than the reactant, so that this can be reliably observed in the ^1H NMR spectrum. The reaction mixture thus consists of a suspension of the aqueous solution and the undissolved **TAN**. The air flow through the solution ensures constant mixing and thus a high contact surface between the liquid components, so that a steady concentration of **TAN** is reached in the reaction solution.

Since no reference ^1H NMR for methyl phenyl sulfoxide in pure water is known in the literature, we recorded one with a commercially available sample (see Figure S63). The signals of the reference substance match perfectly those recorded in the irradiation reaction. Since no other signals are observed, it is assumed that **TAN** is selectively converted to methyl phenyl sulfoxide. The corresponding sulfone, which can be obtained during the conversion of **TAN**, is not observed.³⁷

After 60 min of irradiation, a yield of 91% is already achieved. In the case of the **5-HMF** photooxygenation, only a yield of 44% was observed after this time. The reaction rate was significantly influenced by the oxygen uptake rate in solution, such that a higher reaction rate is not plausible. The reaction rate, which is about twice as high, can be explained by the fact that two **TAN** molecules can be oxidized with one $^1\text{O}_2$ molecule. $^1\text{O}_2$ reacts with a **TAN** molecule to form a persulfoxide, which is able to oxidize a further sulfide to a sulfoxide, resulting in a total of two equivalents of the sulfoxide.^{38–41} A temperature effect probably plays a minor role.

Methyl phenyl sulfoxide: ^1H NMR (300 MHz, $\text{H}_2\text{O}+\text{D}_2\text{O}$): δ [ppm] = 7.75–7.61 (m, 5H), 2.88 (s, 3H).

S5.4 Debromination of 2-BP

S5.4.1 LED irradiation

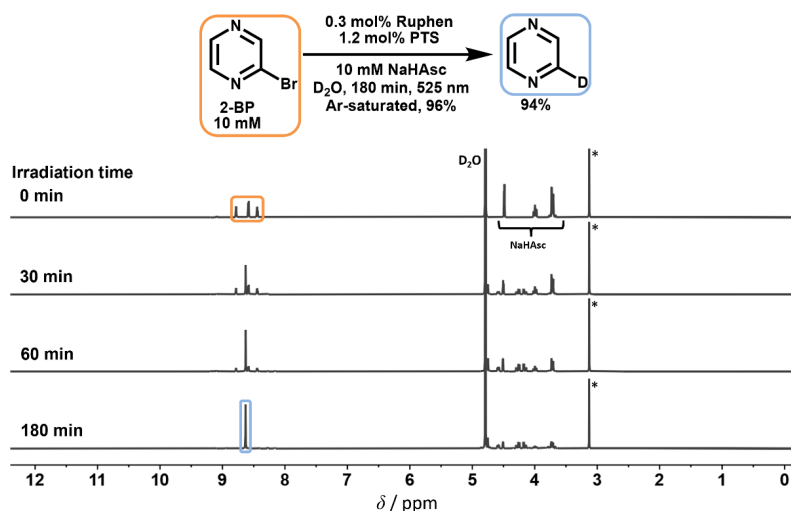


Figure S24 Reaction equation of the photocatalyzed dehalogenation of **2-BP** in Ar-saturated D₂O with the corresponding ¹H NMR spectra and assignment of reactant and product signals after different irradiation times (525 nm LED). The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone (*c* = 2 mM).

Dehalogenation of **2-BP** yields pyrazine, which shows a sharp singlet at 8.63 ppm in the ¹H NMR spectrum in D₂O.^{42,43}

During the irradiation reaction, the total integral of reactant and product signals in the ¹H NMR remains the same, indicating an equal number of ¹H atoms in both molecules. Therefore, it is assumed that the resulting sigma radical is saturated with a deuterium atom after bromide cleavage. Presumably, the sigma radical at the aromatic structure abstracts a hydrogen atom from ascorbate, which has exchanged the most reactive, in other words most acidic, ¹H atoms for D atoms with the solvent D₂O.⁴⁴ The ³*J*_{H,D} coupling in pyrazine is in fact very low, making the signal appear as a sharp singlet.⁴⁵

Pyrazine-d1: ¹H NMR (300 MHz, D₂O): δ [ppm] = 8.63 (s, 3H).

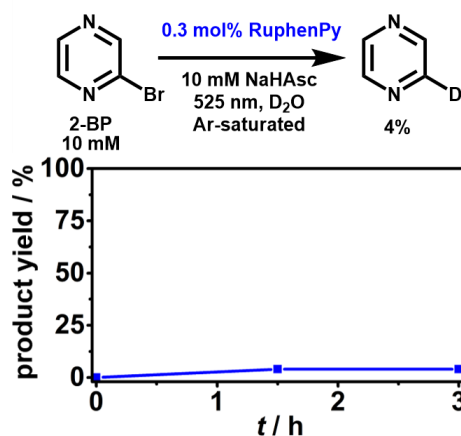


Figure S25 Reaction equation with pertinent conditions and time-resolved product yield of the dehalogenation of **2-BP** (10 mM) with 0.3 mol% **RuphenPy** upon LED irradiation ($\lambda_{\text{max,exc}} = 525 \text{ nm}$) in Ar-saturated water at 20 °C (see also Figure 7 (c) of the main part) for related experiments.

S5.4.2 Irradiation using sunlight

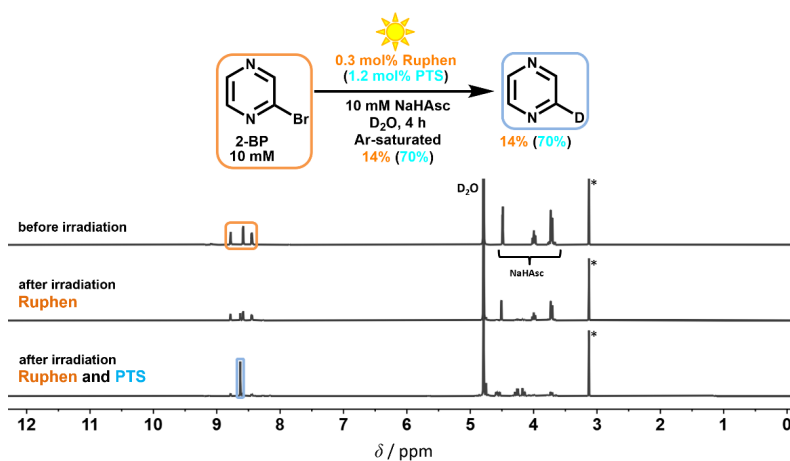


Figure S26 Reaction equation of the photocatalyzed dehalogenation of **2-BP** in Ar-saturated D₂O at RT with the corresponding ¹H NMR spectra and assignment of reactant and product signals in the absence or presence of **PTS** before and after exposing the solution to sunlight. The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone ($c = 2 \text{ mM}$).

Due to the irradiation with the (almost) complete solar spectrum, the reaction temperature (25–30 °C) was slightly above room temperature (typically 20 °C). A 400 nm long pass filter was placed in front of

the reaction vessel to avoid direct excitation of **PTS** by solar UV radiation. The solar irradiation was carried out on 06/16/2023 between 10:30 am and 2:30 pm in Mainz.

S5.4.3 Control experiments

Table S3 Control experiments for the dehalogenation of **2-BP** with **Ruphen**, **PTS** and **NaHAsc** after 3 h of irradiation in Ar-saturated D₂O.

Ruphen (30 μ M)	PTS (120 μ M)	NaHAsc (10 mM)	Irradiation (525 nm LED)	Conversion / %	Yield / %
+	+	+	+	96	94
+	-	+	+	22	16
-	+	+	+	0	0
+	+	-	+	0	0
+	+	+	-	0	0

S5.5 Pinacol coupling of 2-FBA

S5.5.1 LED irradiation

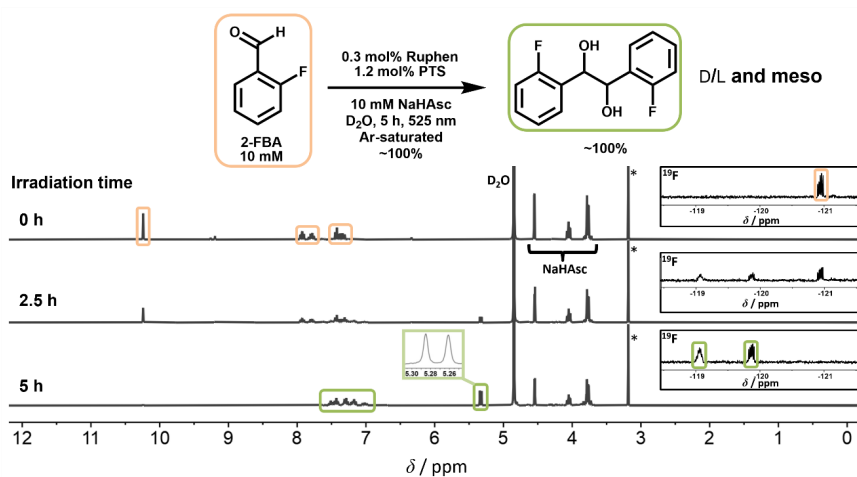


Figure S27 Main plot: Reaction equation of the photocatalyzed pinacol coupling of **2-FBA** in Ar-saturated D₂O at RT with the corresponding ¹H NMR spectra and assignment of reactant and product signals after different irradiation times (525 nm LED). The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfoxide (*c* = 3 mM). Insets on the right: Corresponding ¹⁹F NMR spectra.

The C atom at which the C-C bond linkage between two **2-FBA** molecules takes place is prochiral. In other words, two stereocenters are formed in the molecule after bond formation. Since working in an

otherwise achiral environment, an equal distribution of *R* and *S* centers in the product is expected. When two *R* or two *S* centers are formed, it is also referred to as the D or L compound. If there is one *S* and one *R* center each, the molecule is achiral. These two forms are summarized as meso compounds. In the achiral setting, the chiral D/L compounds give the identical signal in NMR. Furthermore, the D/L and the meso compounds are diastereomeric to each other and therefore give a separate signal. The coexistence of two diastereomeric compounds in a 1:1 ratio is observable from the two singlets at 5.29 and 5.26 ppm. The same can be observed in ^{19}F NMR, supporting the proposed mechanism.

1,2-bis(2-Fluorophenyl)ethane-1,2-diol: ^1H NMR (300 MHz, D_2O): δ [ppm] = 7.52–6.88 (m, 16H, from D/L and meso), 5.29 (s, 2H, from meso or D/L), 5.26 (s, 2H, from meso or D/L).

^{19}F NMR (282 MHz, D_2O): δ [ppm] = -119.06 (m, 2F, from meso or D/L), -119.87 (m, 2F, from meso or D/L).

Since no reference ^1H NMR in water is known in the literature, the reaction solution was extracted with chloroform, the solvent of the extract was removed under reduced pressure, and a ^1H NMR spectrum of the residues was measured in chloroform- d_1 . This gives almost perfectly the chemical shifts of both the D/L and meso pinacol products described in the literature.⁴⁶

In the context of pinacol coupling, a non-linear or even quadratic correlation between the overall reaction rate and the concentration of the **2-FBA** radical (anion) is expected. Based on our quantitative LFP measurements (section S8), reaction rates being faster by one order of magnitude could in principle result with the Coulombic dyad. However, the substantial but less pronounced difference in reaction rates, a factor of 3.3 within the first hour of photoirradiation (Figure 8 (b) in the main part), can be attributed to the slow decomposition of **PTS** in this particular example as confirmed by NMR experiments. Nevertheless, the catalyst decomposition products do not cause significant problems and the addition of inexpensive **PTS** evidently leads to a reactivity boost.

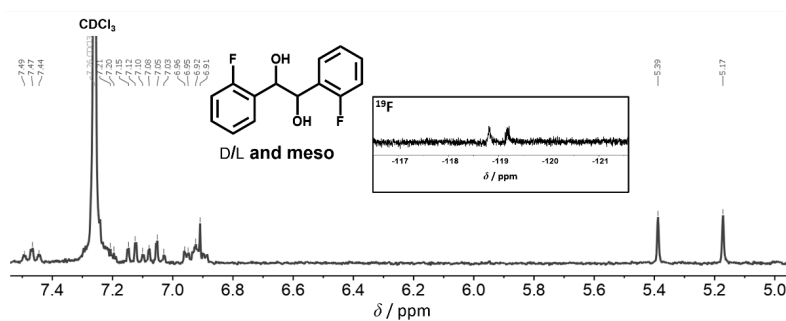


Figure S28 Main plot: ^1H NMR spectrum in CDCl_3 of the extracted reaction mixture containing the photoproduct(s) of the **2-FBA** pinacol coupling reaction (from Figure S27), showing the signals of the pinacol product. Inset: Corresponding ^{19}F NMR spectrum.

1,2-bis(2-Fluorophenyl)ethane-1,2-diol: ^1H NMR (300 MHz, CDCl_3): δ [ppm] = 7.49–7.44 and 7.26–7.03 (m, 16H, from D/L and meso), 5.39 (s, 2H, from meso or D/L), 5.17 (s, 2H, from meso or D/L).

^{19}F NMR (282 MHz, CDCl_3): δ [ppm] = -118.82 (m, 2F, from meso or D/L), -119.21 (m, 2F, from meso or D/L).

S5.5.2 Irradiation using sunlight

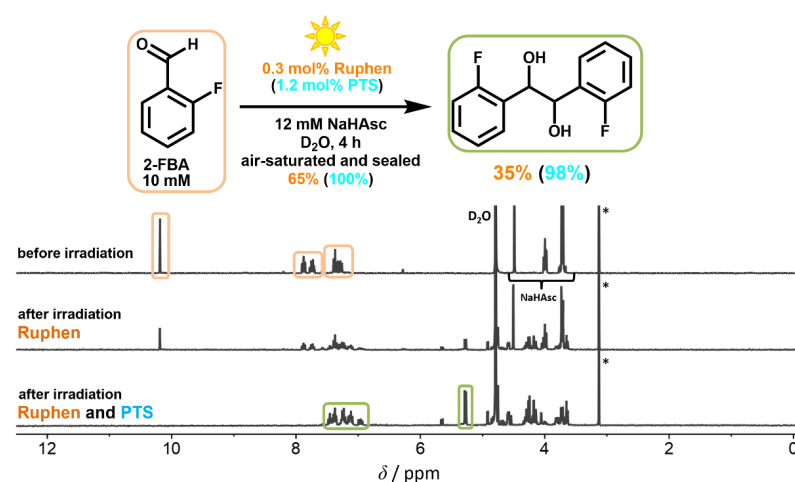


Figure S29 Reaction equation of the photocatalyzed pinacol coupling of **2-FBA** in air-saturated D_2O with the corresponding ^1H NMR spectra and assignment of reactant and product signals in the absence or presence of **PTS** before and after placing the solution in the sun. The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone ($c = 3$ mM).

The pinacol coupling of **2-FBA** was performed under sunlight conditions. For this purpose, the reaction solution was irradiated with sunlight for 4 h. A 400 nm long pass filter was placed in front of the reaction vessel to avoid direct excitation of **PTS** by solar UV radiation. In addition, dissolved oxygen was not removed from the solution. Instead, 0.2 equivalents of additional **NaHAsc** were added because it has the ability to react readily with dissolved oxygen, giving a similar result like purging the solution with Argon gas.⁴⁷ Due to the irradiation with the (almost) complete solar spectrum, the reaction temperature (25–30 °C) was slightly above room temperature (typically 20 °C). The solar irradiation was carried out on 04/04/2023 between 8:30 am and 12:30 pm in Mainz.

S5.6 Additional pinacol coupling reactions

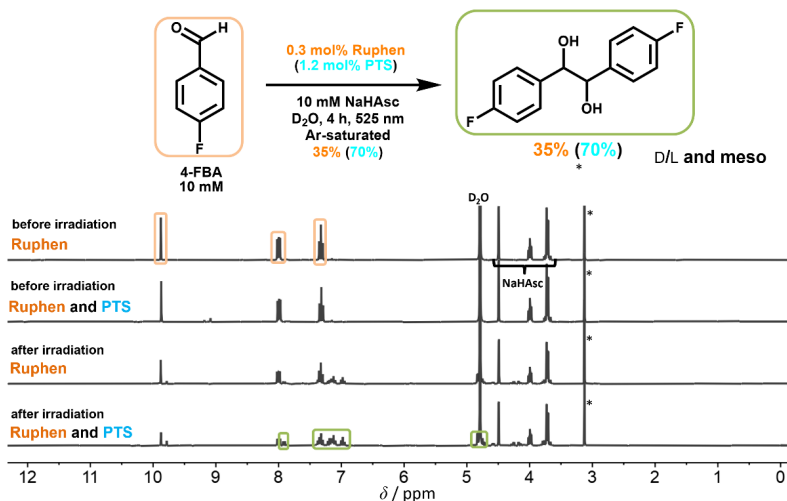


Figure S30 Reaction equation of the photocatalyzed pinacol coupling of 4-fluorobenzaldehyde (**4-FBA**) in Ar-saturated D₂O at RT with the corresponding ¹H NMR spectra and assignment of reactant and product signals after 4 h of irradiation (525 nm LED). The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone (*c* = 2 mM).

Since no reference spectrum of the pinacol product in D₂O exists in literature, the reaction mixture containing **PTS** was extracted with chloroform after irradiation. The solvent of the extract was removed under reduced pressure and a ¹H and a ¹⁹F NMR spectrum in chloroform-d₁ was measured from the residue. The signals of the obtained product are identical to the literature-known signals of 1,2-bis(4-fluorophenyl)ethane-1,2-diol.⁴⁸

1,2-bis(4-Fluorophenyl)ethane-1,2-diol: ¹H NMR (300 MHz, D₂O): δ [ppm] = 7.96–7.86 (m, 4H, from meso and D/L), 7.45–6.87 (m, 12H, from meso and D/L), 4.84 (s, 2H, from meso or D/L), 4.82 (s, 2H, from meso or D/L).

¹⁹F NMR (282 MHz, D₂O): δ [ppm] = -115.45 (m, 2F, from meso or D/L), -115.69 (m, 2F, from meso or D/L).

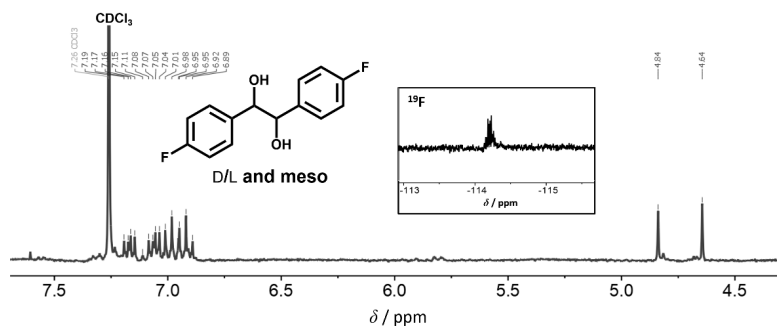


Figure S31 Main plot: ^1H NMR spectrum in CDCl_3 of the extracted reaction mixture containing the photoproduct(s) of **4-FBA** (from Figure S30), showing the signals of the pinacol product. Inset: Corresponding ^{19}F NMR spectrum.

1,2-bis(4-Fluorophenyl)ethane-1,2-diol: ^1H NMR (300 MHz, CDCl_3): δ [ppm] = 7.22–6.85 (m, 16H, from D/L and meso), 4.84 (s, 2H, from meso or D/L), 4.64 (s, 2H, from meso or D/L).

^{19}F NMR (282 MHz, CDCl_3): δ [ppm] = -114.21 (m, 4F, from meso and D/L).

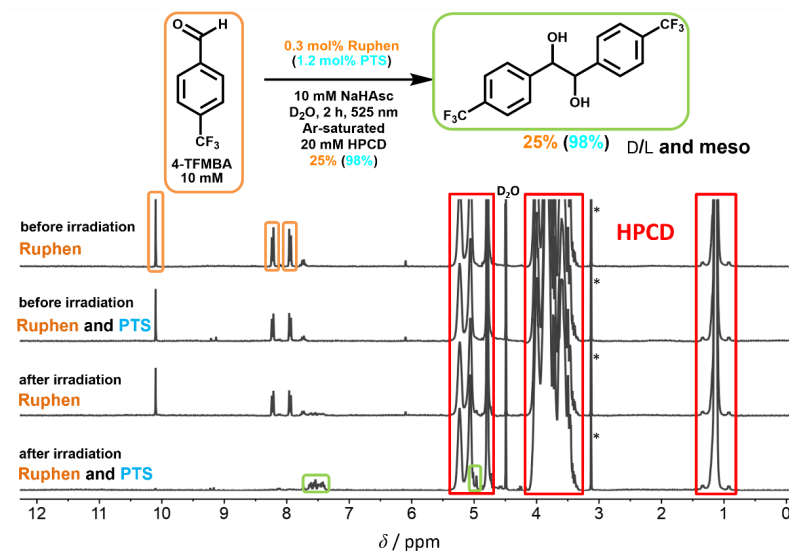


Figure S32 Reaction equation of the photocatalyzed pinacol coupling of **4-TFMB** in Ar-saturated D_2O with 20 mM HPCD at RT with the corresponding ^1H NMR spectra and assignment of reactant and product signals after 2 h of irradiation (525 nm LED). The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone ($c = 2$ mM).

Due to the low solubility of 4-trifluoromethyl benzaldehyde (**4-TFMBA**) in pure water, hydroxypropyl- β -cyclodextrin (**HPCD**, 20 mM) was added, which is capable of incorporating the reactant. Thus, all components were present in dissolved form. The signals of the benzylic H atoms can be seen at 5.01 ppm and 4.96 ppm and they are superimposed by those of HPCD (compare, lower spectrum in Figure S32).

Since no reference spectrum of the pinacol product in D₂O exists in literature, the reaction mixture containing **PTS** was extracted with chloroform after irradiation. The solvent of the extract was removed under reduced pressure and a ¹H and a ¹⁹F NMR spectrum in chloroform-d₁ was measured from the residue. The signals of the obtained product are identical to the literature known signals of 1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-diol.^{49,50}

1,2-bis(4-(Trifluoromethyl)phenyl)ethane-1,2-diol: ¹H NMR (300 MHz, D₂O): δ [ppm] = 7.67–7.37 (m, 16H, from meso and D/L), 5.01 (s, 2H, from meso or D/L), 4.96 (s, 2H, from meso or D/L).

¹⁹F NMR (282 MHz, D₂O): δ [ppm] = -62.81 – -62.97 (m, 12F, from D/L and meso).

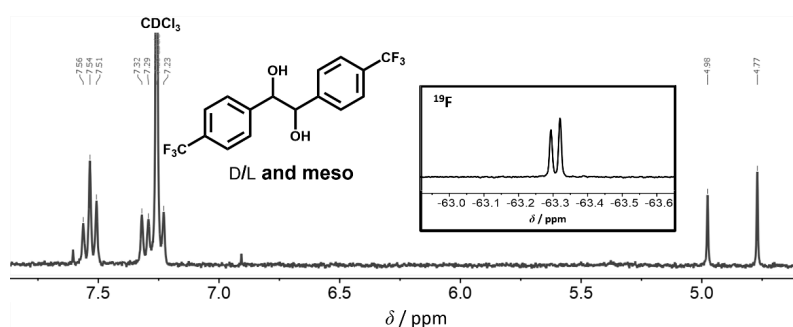


Figure S33 Main plot: ¹H NMR spectrum in CDCl₃ of the extracted reaction mixture containing **4-TFMBA** after irradiation (from Figure S32), showing the signals of the pinacol product. Inset: Corresponding ¹⁹F NMR spectrum.

1,2-bis(4-(Trifluoromethyl)phenyl)ethane-1,2-diol: ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 7.59–7.21 (m, 16H, from meso and D/L), 4.98 (s, 2H, from meso or D/L), 4.77 (s, 2H, from meso or D/L).

¹⁹F NMR (282 MHz, CDCl₃): δ [ppm] = -63.29 (s, 6F, from meso or D/L), -63.32 (s, 6F, from meso or D/L).

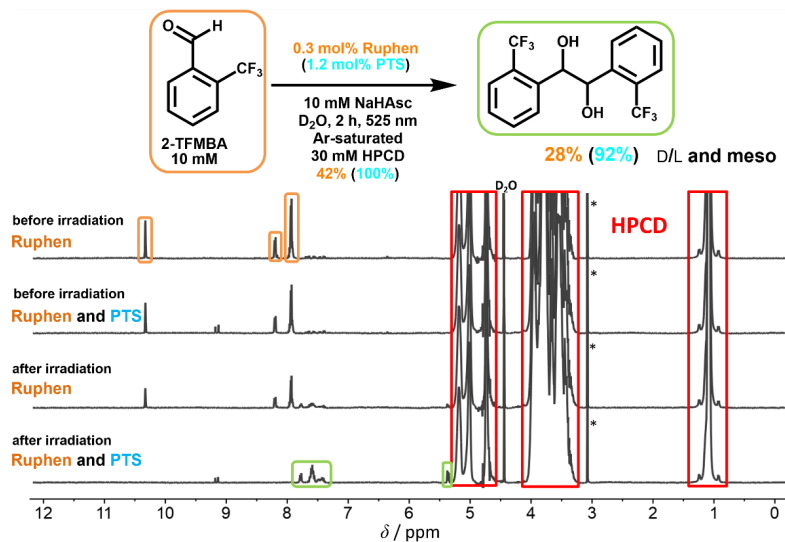


Figure S34 Reaction equation of the photocatalyzed pinacol coupling of 2-TFMBA in Ar-saturated D₂O with 30 mM HPCD at RT with the corresponding ¹H NMR spectra and assignment of reactant and product signals after 2 h of irradiation (525 nm LED). The signal marked with an asterisk (*) corresponds to the internal standard dimethyl sulfone (*c* = 2 mM).

For solubility reasons, the reaction was carried out with 30 mM of HPCD. Since no reference spectrum of the pinacol product in D₂O exists in literature, the reaction mixture containing PTS was extracted with chloroform after irradiation. The solvent of the extract was removed under reduced pressure and a ¹H and a ¹⁹F NMR spectrum in chloroform-*d*₁ was measured from the residue. The signals of the obtained product are identical to the literature known signals of 1,2-bis(2-(trifluoromethyl)phenyl)ethane-1,2-diol.^{51,52}

1,2-bis(2-(Trifluoromethyl)phenyl)ethane-1,2-diol: ¹H NMR (300 MHz, D₂O): δ [ppm] = 7.88–7.42 (m, 16H, from meso and D/L), 5.44–5.39 (m, 4H, from meso and D/L).

¹⁹F NMR (282 MHz, D₂O): δ [ppm] = -58.77 – -59.14 (m, 12F, from D/L and meso).

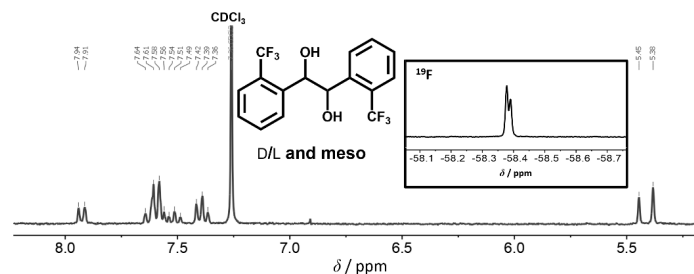


Figure S35 Main plot: ^1H NMR spectrum in CDCl_3 of the extracted reaction mixture containing **2-TFMBA** after irradiation (from Figure S34), showing the signals of the pinacol product. Inset: Corresponding ^{19}F NMR spectrum.

1,2-bis(2-(Trifluoromethyl)phenyl)ethane-1,2-diol: ^1H NMR (300 MHz, CDCl_3): δ [ppm] = 7.95–7.89 (m, 4H, from meso and D/L), 7.71–7.33 (m, 12H, from meso and D/L), 5.45 (s, 2H, (m, 2F, from meso or D/L), 5.38 (s, 2H, from meso or D/L).

^{19}F NMR (282 MHz, CDCl_3): δ [ppm] = -58.38 (s, 6F, from meso or D/L), -58.39 (s, 6F, from meso or D/L).

S6 Stern–Volmer quenching experiments

S6.1 Quenching of $^3\text{Ruphen}$ by HAsc^-

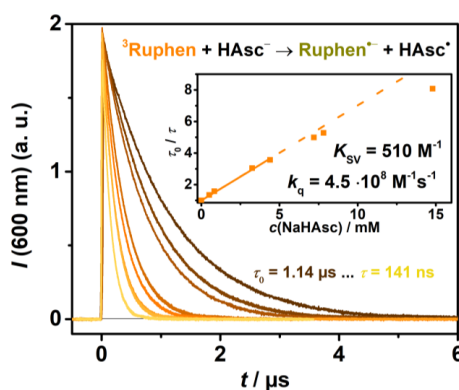


Figure S36 Main plot: Time-resolved emission traces of $^3\text{Ruphen}$ ($c(\text{Ruphen}) = 30 \mu\text{M}$) upon 532 nm laser excitation in the Stern–Volmer quenching experiment with NaHAsc in Ar-saturated water. Inset: Corresponding Stern–Volmer plot.

In the Stern–Volmer plot in Figure S36, a deviation from the linear behavior can be seen above a concentration of $c(\text{NaHAsc}) = 7.5 \text{ mM}$. This can be attributed to the kinetic salt effect, which leads to a slight decrease (for the used concentrations) in the quenching rate between the differently charged ions Ruphen and HAsc^- with increasing NaHAsc concentration (respectively increasing ionic strength).

S6.2 Quenching of ^3PTS by HAsc^-

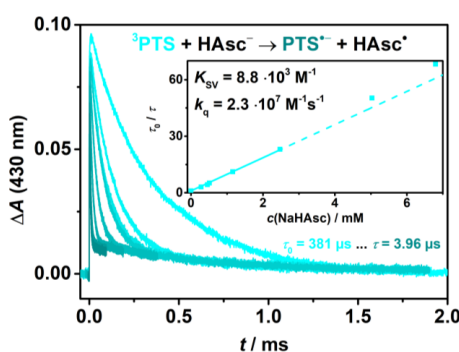


Figure S37 Main plot: Transient absorption traces of ^3PTS ($c(\text{Ruphen}) = 30 \mu\text{M}$, $c(\text{PTS}) = 120 \mu\text{M}$) in the Stern–Volmer quenching experiment with NaHAsc in Ar-saturated water upon 532 nm laser excitation. Inset: Corresponding Stern–Volmer plot. The traces of the quenched samples were fitted with a biexponential function and the faster component was used for the Stern–Volmer analysis.

In this case, the consequence of the kinetic salt effect can also be observed. With increasing **NaHAsc** concentration (increasing ionic strength), the quenching rate between the identically charged ^3PTS and **HAsc⁻** increases slightly (for the used concentrations). At the detection wavelength, the quenching product $\text{PTS}^{\bullet-}$ also absorbs. Thus, the signal is a superposition of ^3PTS decay and $\text{PTS}^{\bullet-}$ formation. The traces of the quenched samples were fitted with a biexponential function and the faster component was used for the Stern–Volmer analysis.

S6.3 Quenching of $\text{Ruphen}^{\bullet-}$ by 2-BP

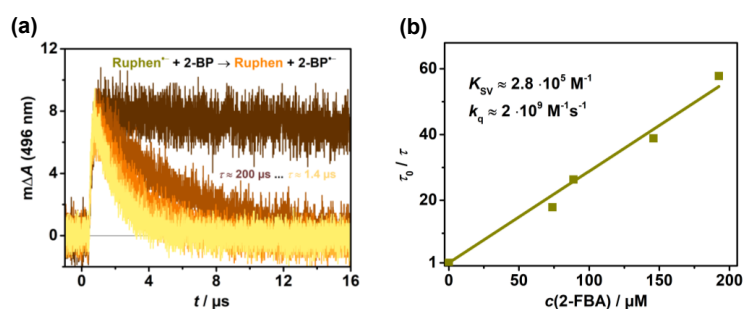


Figure S38 (a) Transient absorption traces of $\text{Ruphen}^{\bullet-}$ ($c(\text{Ruphen}) = 30 \mu\text{M}$, $c(\text{NaHAsc}) = 10 \text{ mM}$) in the Stern–Volmer quenching experiment with **2-BP** in Ar-saturated water upon 532 nm laser excitation. (b) Corresponding Stern–Volmer plot.

The decay traces of $\text{Ruphen}^{\bullet-}$ and $\text{PTS}^{\bullet-}$ in the transient absorption measurements are not perfectly monoexponential. The shown lifetimes are averaged values based on a biexponential fit. A Stern–Volmer plot was created with the averaged lifetimes to estimate K_{SV} and k_q .

S6.4 Quenching of $\text{PTS}^{\bullet-}$ by 2-BP

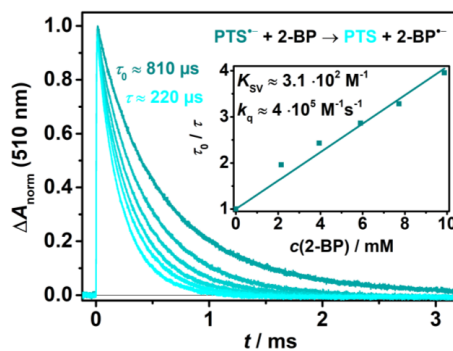


Figure S39 Main plot: Transient absorption traces of $\text{PTS}^{\bullet-}$ ($c(\text{Ruphen}) = 30 \mu\text{M}$, $c(\text{PTS}) = 120 \mu\text{M}$, $c(\text{NaHAsc}) = 10 \text{ mM}$) in the Stern–Volmer quenching experiment with **2-BP** in Ar-saturated water upon 532 nm laser excitation. Inset: Corresponding Stern–Volmer plot.

S6.5 Quenching of $\text{Ruphen}^{\bullet-}$ by 2-FBA

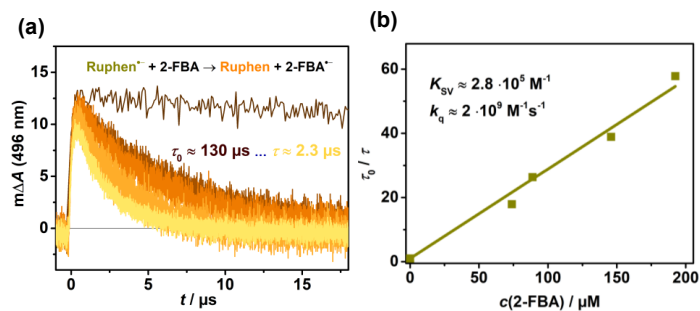


Figure S40 (a) Transient absorption traces of $\text{Ruphen}^{\bullet-}$ ($c(\text{Ruphen}) = 30 \mu\text{M}$, $c(\text{NaHAsc}) = 10 \text{ mM}$) in the Stern–Volmer quenching experiment with **2-FBA** in Ar-saturated water upon 532 nm laser excitation. (b) Corresponding Stern–Volmer plot. The underlying lifetimes are mean values based on a biexponential fit.

S6.6 Quenching of $\text{PTS}^{\bullet-}$ by 2-FBA

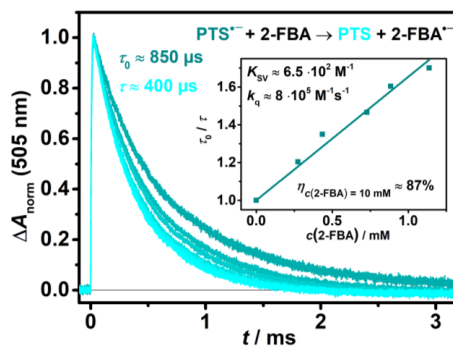


Figure S41 Main plot: Transient absorption traces of $\text{PTS}^{\bullet-}$ ($c(\text{Ruphen}) = 30 \text{ } \mu\text{M}$, $c(\text{PTS}) = 120 \text{ } \mu\text{M}$, $c(\text{NaHAsc}) = 10 \text{ mM}$) in the Stern–Volmer quenching experiment with 2-FBA in Ar-saturated water upon 532 nm laser excitation. Inset: Corresponding Stern–Volmer plot.

S7 Determination of extinction coefficients

S7.1 Extinction coefficient of PTS in water

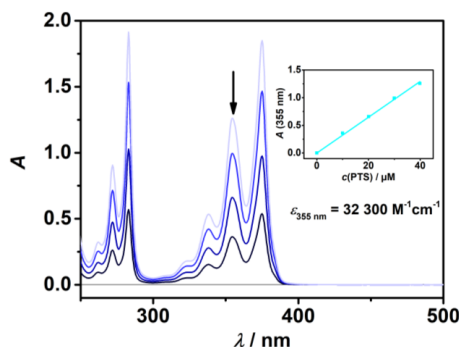


Figure S42 Beer–Lambert plot (inset) with the corresponding UV-vis spectra for the determination of the extinction coefficient of **PTS** at $\lambda = 355$ nm in pure water (cuvette path length: 1.0 cm).

The measured extinction coefficient of **PTS** in water at 355 nm of $32\,300\text{ M}^{-1}\text{cm}^{-1}$ is in good agreement with that from literature.⁵³ The extinction coefficients of **Ruphen** and **RuphenPy** in water presented in the main part (Figure 2) were taken from a recent study from our group.¹

S7.2 ³Ruphen difference extinction coefficient in water

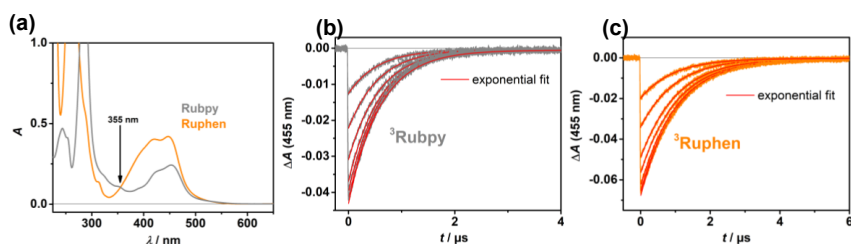


Figure S43 (a) UV-vis spectra of solutions containing **Rubpy** or **Ruphen** in Ar-saturated water. Corresponding time-resolved kinetic absorption traces ($\lambda_{\text{det}} = 455$ nm) of the ground state bleach of **Rubpy** (b) and **Ruphen** (c) after 355 nm pulses of different laser intensities.

The difference extinction coefficient of ³**Ruphen** at 455 nm was determined using the well-known difference extinction coefficient of ³**Rubpy** at the same wavelength ($\Delta\epsilon_{^3\text{Rubpy},455\text{ nm}} = -10100\text{ M}^{-1}\text{cm}^{-1}$).^{54–57}

According to the Beer–Lambert law, the observed transient absorption signal is proportional to the concentration of excited triplet states multiplied by the difference extinction coefficient and the optical path length ($\Delta A_\lambda \propto \Delta \varepsilon_\lambda \cdot c \cdot d$). The solutions of **Rubpy** and **Ruphen** in water have the same absorption at the excitation wavelength ($\lambda_{\text{exc}} = 355 \text{ nm}$) to ensure the same concentration of excited triplet states after the laser pulse (assuming quantitative triplet formation for both complexes). The maximum transient absorption value immediately after the laser pulse at one specific laser intensity $\Delta A_{0,455 \text{ nm},n}$ was determined via an exponential fit of the form

$$\Delta A_{455 \text{ nm},n}(t) = \Delta A_{0,455 \text{ nm},n} \cdot e^{-\frac{t}{\tau}}.$$

Since cuvettes of identical design were used, the layer thickness d is also identical. $\Delta \varepsilon_{455 \text{ nm},n}({}^3\text{Ruphen})$ is then given by the formula

$$\Delta \varepsilon_{455 \text{ nm},n}({}^3\text{Ruphen}) = \frac{\Delta A_{0,455 \text{ nm},n}({}^3\text{Ruphen})}{\Delta A_{0,455 \text{ nm},n}({}^3\text{Rubpy})} \cdot \Delta \varepsilon_{455 \text{ nm}}({}^3\text{Rubpy}).$$

The values obtained are displayed in **Table S4**.

Table S4 Maximum transient absorption values after laser pulses with different intensities for solutions containing **Rubpy** or **Ruphen** in water, together with the calculated difference extinction coefficient for **³Ruphen**.

Entry n (approx. laser intensity per pulse / mJ)	$\Delta A_{0,455 \text{ nm},n}({}^3\text{Rubpy})$	$\Delta A_{0,455 \text{ nm},n}({}^3\text{Ruphen})$	$\Delta \varepsilon_{455 \text{ nm},n}({}^3\text{Ruphen})$ / $\text{M}^{-1}\text{cm}^{-1}$
1 (2.2)	-0.01215	-0.01957	16268
2 (4.1)	-0.02194	-0.03403	15666
3 (5.9)	-0.03043	-0.04892	16237
4 (7.6)	-0.03624	-0.05612	15641
5 (9.2)	-0.03923	-0.06221	16016
6 (10.2)	-0.04141	-0.06534	15937
7 (10.9)	-0.04256	-0.0676	16042

The difference extinction coefficient was determined by averaging:

$$\Delta \varepsilon_{455 \text{ nm}}({}^3\text{Ruphen}) = \frac{1}{7} \cdot \sum_{i=1}^7 \Delta \varepsilon_{455 \text{ nm},n}({}^3\text{Ruphen}) = 15972 \text{ M}^{-1}\text{cm}^{-1} \approx 16000 \text{ M}^{-1}\text{cm}^{-1}.$$

S7.3 ³PTS difference extinction coefficient in water

The difference extinction coefficient of **³PTS** was determined in the same way as for **³Ruphen** using **Rubpy** as reference. Low intensities of the UV laser were used to avoid decomposition of **PTS**.³⁶ **PTS** has an ISC quantum yield of $\Phi_{\text{ISC}}(\text{PTS}) = 0.53$.³⁶ Thus, a factor of $\frac{1}{0.53}$ must also be taken into account when calculating $\Delta \varepsilon_{455 \text{ nm},n}({}^3\text{PTS})$.³⁶

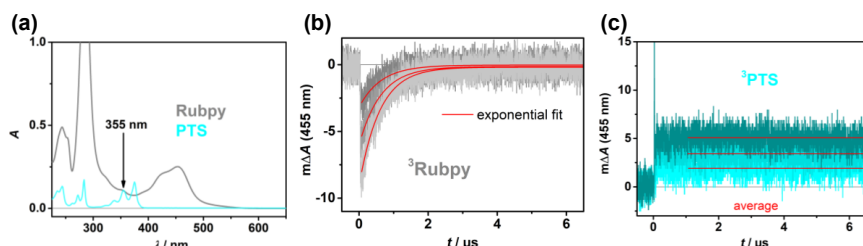


Figure S44 (a) UV-vis spectra of solutions containing **Rubpy** or **PTS** in Ar-saturated aqueous solution. (b) Time-resolved kinetic absorption traces ($\lambda_{\text{det}} = 455 \text{ nm}$) of the ground state bleach of **Rubpy** (c) and the excited-state absorption of **PTS** after different laser excitation intensities ($\lambda_{\text{exc}} = 355 \text{ nm}$).

Table S5 Maximum transient absorption values after laser pulses with different intensities for solutions containing **Rubpy** or **PTS** in water, together with the calculated difference extinction coefficient for ³**PTS**.

Entry n (approx. laser intensity per pulse / mJ)	$\Delta A_{0,455 \text{ nm},n}(\text{}^3\text{Rubpy})$	$\Delta A_{0,455 \text{ nm},n}(\text{}^3\text{PTS})$	$\Delta \varepsilon_{455 \text{ nm},n}(\text{}^3\text{PTS}) / \text{M}^{-1}\text{cm}^{-1}$
1 (0.56)	-0.00286	0.00194	12943
2 (1.10)	-0.00517	0.00341	12583
3 (1.61)	-0.00771	0.00506	12517

$$\Delta \varepsilon_{455 \text{ nm}}(\text{}^3\text{PTS}) = \frac{1}{3} \cdot \sum_{n=1}^3 \Delta \varepsilon_{455 \text{ nm},n}(\text{}^3\text{PTS}) = 12681 \text{ M}^{-1}\text{cm}^{-1} \approx 12700 \text{ M}^{-1}\text{cm}^{-1}$$

Via the TA spectrum of **PTS**, the difference extinction coefficient at an arbitrary wavelength is thus accessible. A value of $\Delta \varepsilon_{\text{}^3\text{PTS},425 \text{ nm}} = 20000 \text{ M}^{-1}\text{cm}^{-1}$ is obtained, which is in agreement with literature data ($\Delta \varepsilon_{\text{}^3\text{PTS},425 \text{ nm,Lit}} = 19400 \text{ M}^{-1}\text{cm}^{-1}$).³⁶

S7.4 Ruphen^{•−} difference extinction coefficient in water

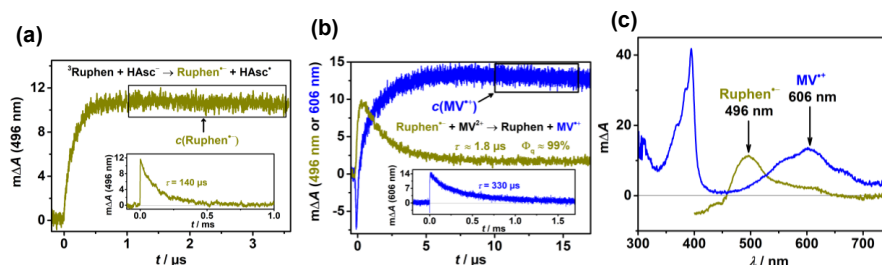


Figure S45 (a) Main plot: Transient absorption trace of a solution containing **Ruphen** (30 μM) and **NaHAsc** (10 mM) in Ar-saturated water after the laser pulse ($\lambda_{\text{exc}} = 532 \text{ nm}$). Inset: Measurement of the transient absorption on a longer time scale. (b) Main plot: Transient absorptions at 496 nm and 606 nm of a solution containing **Ruphen** (30 μM), **NaHAsc** (10 mM) and **MV²⁺** (200 μM) in Ar-saturated water after the laser pulse. Inset: Measurement of the transient absorption at 606 nm on a longer time scale. (c) Transient absorption spectra of the solutions without (ochre, delay 2 μs) and with **MV²⁺** (blue, delay 10 μs).

Methyl viologen (**MV²⁺**), which is easily reduced and whose reduced form (**MV^{•+}**) has a well-known difference extinction coefficient in water ($\Delta\epsilon_{606 \text{ nm}}(\text{MV}^{\bullet+}) = 13700 \text{ M}^{-1}\text{cm}^{-1}$),⁵⁸ was used to determine the extinction coefficient of **Ruphen^{•−}**. First, **Ruphen^{•−}** was generated by reductive quenching of **³Ruphen** by **NaHAsc**. This was then trapped by **MV²⁺**, leading to the formation of **MV^{•+}**, whose signatures are clearly seen in the TA spectrum. The concentration of **MV²⁺** was chosen sufficiently low so that no additional salt effects affect the initial quenching and that the quenching of **³Ruphen** by **MV²⁺** is assumed to be negligible.

An efficiency of 100% is assumed for the thermal electron transfer step yielding **MV^{•+}** through the reaction between **Ruphen^{•−}** and **MV²⁺**. Thus, the extinction coefficient $\Delta\epsilon_{496 \text{ nm}}(\text{Ruphen}^{\bullet-})$ can be determined as follows.

$$\begin{aligned} \Delta\epsilon_{496 \text{ nm}}(\text{Ruphen}^{\bullet-}) &= \frac{\Delta A_{496 \text{ nm}}(\text{Ruphen}^{\bullet-})}{\Delta A_{606 \text{ nm}}(\text{MV}^{\bullet+})} \cdot \frac{\Delta\epsilon_{606 \text{ nm}}(\text{MV}^{\bullet+})}{\Phi_q} = \frac{0.0107}{0.0130} \cdot \frac{13700 \text{ M}^{-1}\text{cm}^{-1}}{0.99} \\ &= 11390 \text{ M}^{-1}\text{cm}^{-1} \approx 11400 \text{ M}^{-1}\text{cm}^{-1} \end{aligned}$$

The obtained difference extinction coefficient is in good agreement with a literature value obtained in a solvent mixture of water and acetonitrile.⁵⁹

The ascorbate-derived radical has a weak absorption band at 360 nm but it is essentially transparent at wavelengths $> 400 \text{ nm}$, which is why we did not show the calibrated spectra in the UV region (main paper, Figure 7 (b)).⁶⁰

S7.5 Estimation of the difference extinction coefficient of $\text{PTS}^{\bullet-}$

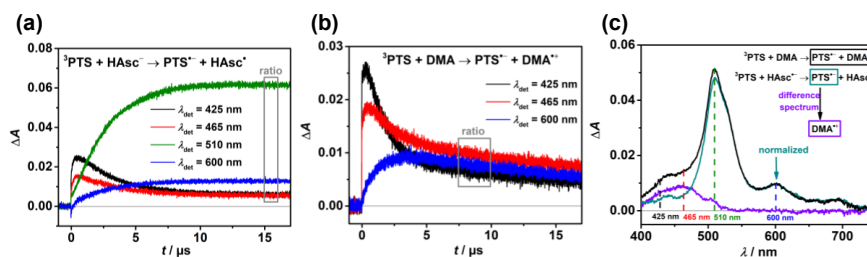


Figure S46 (a) Transient absorption traces at various wavelengths of a solution containing **Ruphen** (30 μM), **PTS** (120 μM) and **NaHAsc** (10 mM) in Ar-saturated water after laser excitation ($\lambda_{\text{exc}} = 532$ nm). (b) Transient absorption traces at various wavelengths of a solution containing **Ruphen** (30 μM), **PTS** (120 μM) and **DMA** (5 mM) in Ar-saturated water after laser excitation ($\lambda_{\text{exc}} = 532$ nm). (c) Transient absorption spectra of the solutions (with **NaHAsc**: 20 μs delay (normalized), with **DMA**: 5 μs delay) and the difference spectrum showing the signals for **DMA** $^{\bullet+}$.

In this study using the Coulombic dyad in an efficient photoredox scheme, **HAsc** $^-$ was used as a reductive quencher.⁶¹ It is well known that the quencher-derived radical **HAsc** $^\bullet$ rapidly deprotonates and then disproportionates.⁶² The deprotonated species and the products of the disproportionation do not or barely absorb in the measurement window shown.⁶⁰ Therefore, the species formed in this photoinduced electron transfer reaction, which absorbs over the whole visible range with a pronounced maximum at 510 nm and further maxima at ~ 600 nm and ~ 700 nm, can be attributed to **PTS** $^{\bullet-}$.^{63,64}

N,N-dimethylaniline (**DMA**) is a common reductive quencher primarily in acetonitrile,^{61,65} but it also has a sufficient solubility in water. Quenching of ^3PTS by **DMA** is highly efficient and yields **PTS** $^{\bullet-}$.

For **DMA** $^{\bullet+}$, the transient absorption spectrum and the extinction coefficient at 465 nm in neutral water are known.^{66,67} Since the **PTS** species formed absorbs in the entire measurement window, it is not possible to detect **DMA** $^{\bullet+}$ in isolation. According to literature data, **DMA** $^{\bullet+}$ does not absorb above 550 nm.⁶⁷ That means, that the isolated observation of **PTS** $^{\bullet-}$ is possible at 600 nm. Normalizing the spectrum of **PTS** $^{\bullet-}$ above 600 nm using **HAsc** $^-$ as reductive electron donor (petrol spectrum in Figure S46 (c)) to that of **PTS** $^{\bullet-}$ using **DMA** as reductive electron donor (black spectrum in Figure S46 (c)) reveals a difference between the two spectra for the wavelength range below 550 nm. The difference of the two normalized spectra results in a TA spectrum matching that of **DMA** $^{\bullet+}$ in water.⁶⁷ When ^3PTS is quenched by **DMA**, **PTS** $^{\bullet-}$ and **DMA** $^{\bullet+}$ are formed in a 1:1 ratio and consequently their concentrations are equal. With the knowledge of $\Delta\epsilon_{465\text{ nm}}(\text{DMA}^{\bullet+}) = 4500\text{ M}^{-1}\text{cm}^{-1}$,⁶⁶ the concentration of both radical intermediates can be determined. Using the Beer–Lambert law and the difference absorption of **PTS** $^{\bullet-}$ then allows the calculation of the difference extinction coefficient of **PTS** $^{\bullet-}$.

In the time-resolved transient absorption, the decrease in ^3PTS can be observed at 425 nm, which is almost completely quenched 5 μs after the laser pulse. Thereafter, the TA signatures of **PTS** $^{\bullet-}$ and

DMA^{•+} are present. The simultaneous decrease of the transient absorptions at all detection wavelengths indicates a relatively fast back electron transfer between the pentaanionic **PTS^{•-}** and the monocationic **DMA^{•+}**.

The absorption of **DMA^{•+}** cannot be observed in isolation at 465 nm. On the other hand, the absorption of the **PTS^{•-}** radical at 600 nm can be observed in isolation. Using the transient absorptions obtained upon quenching by **HAsc⁻**, the ratio of the absorptions of **PTS^{•-}** at 465 nm and 600 nm can be calculated (indicated with gray boxes in Figure S46 (a) and (b)). This can be used to estimate which value of the transient absorption is caused by **DMA^{•+}** at 465 nm (layer thickness: 1 cm).

$$\begin{aligned}\Delta A_{465 \text{ nm}}(\text{DMA}^{\bullet+}) &= \Delta A_{465 \text{ nm}}(\text{PTS} + \text{DMA}) - \Delta A_{600 \text{ nm}}(\text{PTS} + \text{DMA}) \cdot \frac{\Delta A_{465 \text{ nm}}(\text{PTS} + \text{HAsc}^-)}{\Delta A_{600 \text{ nm}}(\text{PTS} + \text{HAsc}^-)} \\ &= \left(0.00946 - 0.00788 \cdot \frac{0.00560}{0.0128}\right) \text{cm}^{-1} = 0.00601 \text{cm}^{-1}\end{aligned}$$

Based on the knowledge of $\Delta \epsilon_{465 \text{ nm}}(\text{DMA}^{\bullet+}) = 4500 \text{ M}^{-1}\text{cm}^{-1}$, the concentration of **DMA^{•+}** can be calculated.

$$c(\text{DMA}^{\bullet+}) = \frac{\Delta A_{465 \text{ nm}}(\text{DMA}^{\bullet+})}{\Delta \epsilon_{465 \text{ nm}}(\text{DMA}^{\bullet+})} = \frac{0.00601 \text{cm}^{-1}}{4500 \text{ M}^{-1}\text{cm}^{-1}} = 1.33 \mu\text{M}$$

Since the concentration of **PTS^{•-}** has to be identical to that of **DMA^{•+}** (as mentioned earlier in this section), the difference extinction coefficient of **PTS^{•-}** can be determined.

$$\Delta \epsilon_{600 \text{ nm}}(\text{PTS}^{\bullet-}) = \frac{\Delta A_{600 \text{ nm}}(\text{PTS} + \text{DMA})}{c(\text{PTS}^{\bullet-})} = \frac{0.00788 \text{cm}^{-1}}{1.33 \mu\text{M}} = 5925 \text{ M}^{-1}\text{cm}^{-1} \approx 6000 \text{ M}^{-1}\text{cm}^{-1}$$

For the difference extinction coefficient at 510 nm, this gives:

$$\Delta \epsilon_{510 \text{ nm}}(\text{PTS}^{\bullet-}) = \Delta \epsilon_{600 \text{ nm}}(\text{PTS}^{\bullet-}) \cdot \frac{\Delta A_{510 \text{ nm}}(\text{PTS} + \text{HAsc}^-)}{\Delta A_{600 \text{ nm}}(\text{PTS} + \text{HAsc}^-)} = 6000 \text{ M}^{-1}\text{cm}^{-1} \cdot \frac{0.0615}{0.0128} = 28828 \text{ M}^{-1}\text{cm}^{-1} \approx 29000 \text{ M}^{-1}\text{cm}^{-1}$$

S8 Determination of efficiencies

S8.1 Energy transfer efficiency of the initial step

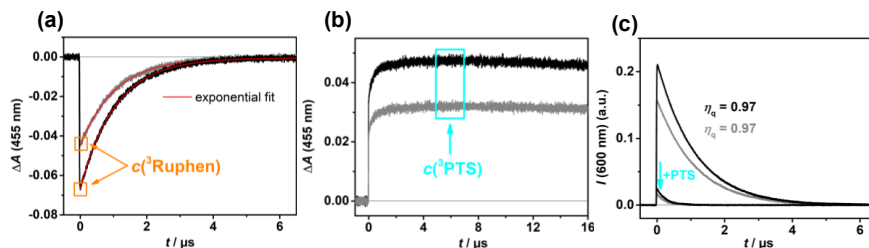


Figure S47 Transient absorption traces at 455 nm of a solution containing **Ruphen** (30 μM) (a) or **Ruphen** (30 μM) and **PTS** (120 μM) (b) in Ar-saturated water after laser excitation ($\lambda_{\text{exc}} = 532 \text{ nm}$, 28 mJ (black) and 17 mJ (gray) per laser pulse). (c) Corresponding kinetic emission traces at 600 nm.

With the known extinction coefficients $\Delta\epsilon_{^3\text{Ruphen},455 \text{ nm}}$ and $\Delta\epsilon_{^3\text{PTS},455 \text{ nm}}$ (see sections S7.2 and S7.3), the efficiency of the central energy transfer step η_{EnT} can be determined. The concentration of formed $^3\text{Ruphen}$ and ^3PTS is accessible from the transient absorption signals at 455 nm (see Figure S47). The measurement was performed with two laser intensities.

First, the initial concentration of $^3\text{Ruphen}$ was determined after laser excitation in the absence of **PTS** after laser excitation. The maximum value of transient absorption ΔA_0 of $^3\text{Ruphen}$ was determined via an exponential fit (see Figure S47 (a)). In the presence of **PTS**, after completed quenching, the transient absorption at 455 nm can be assigned to ^3PTS (ΔA averaged value in cyan box). In addition, the quenching efficiency η_q is required, which can be accessed via the kinetic emission of $^3\text{Ruphen}$ at 600 nm. Thus, the EnT efficiency for the formation of ^3PTS can be calculated with the formula

$$\eta_{\text{EnT}} = \frac{c(^3\text{PTS})}{c(^3\text{Ruphen}) \cdot \eta_q} = \frac{\frac{\Delta A_{^3\text{PTS},455 \text{ nm}}}{\Delta\epsilon_{^3\text{PTS},455 \text{ nm}}}}{\frac{\Delta A_{0,^3\text{Ruphen},455 \text{ nm}}}{\Delta\epsilon_{^3\text{Ruphen},455 \text{ nm}}} \cdot \eta_q} = 94\%$$

With both laser intensities used, an EnT efficiency of 94% was obtained. Thus, it can be concluded that **PTS** is sensitized to the triplet excited state with approximately quantitative efficiency upon quenching of $^3\text{Ruphen}$.

S8.2 Cage escape efficiency for the reduction of ³Ruphen by HAsc[−]

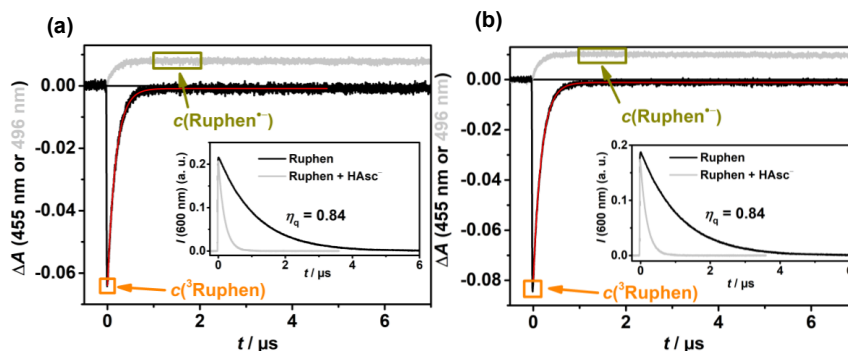


Figure S48 Main plot: Transient absorption traces for a solution containing **Ruphen** (30 μM) and **NaHAsc** (10 mM) at 455 nm or 496 nm after the laser pulse ($\lambda_{\text{exc}} = 532 \text{ nm}$, ~25 mJ (a) or ~38 mJ (b) per laser pulse). Inset: Corresponding time resolved emission traces.

To determine the cage escape efficiency for the reduction of ³**Ruphen** with **HAsc[−]**, it can be exploited that both ³**Ruphen** and the quenching product **Ruphen^{•−}** are observable in isolation at 455 nm and 496 nm at their respective isosbestic points (see Figure 7 (b) in the main part). The efficiency $\eta_{\text{CE}}(^3\text{Ruphen}, \text{HAsc}^-)$ is determined in the same way as for the determination of the EnT efficiency (section S8.1).

$$\eta_{\text{CE},n}(^3\text{Ruphen}, \text{HAsc}^-) = \frac{c(\text{Ruphen}^{\bullet-})}{c(^3\text{Ruphen}) \cdot \eta_{q,n}} = \frac{\frac{\Delta A_{\text{Ruphen}^{\bullet-}, 496 \text{ nm}, n}}{\Delta \varepsilon_{\text{Ruphen}^{\bullet-}, 496 \text{ nm}, n}}}{\frac{\Delta A_{0, ^3\text{Ruphen}, 455 \text{ nm}, n}}{\Delta \varepsilon_{^3\text{Ruphen}, 455 \text{ nm}, n}} \cdot \eta_{q,n}}$$

Table S6 Maximum transient absorption values after laser pulses with different intensities for solutions containing **Ruphen** and **NaHAsc** in water, together with the calculated cage escape efficiency.

Entry <i>n</i> (approx. laser intensity per pulse / mJ)	$\Delta A_{\text{Ruphen}^{\bullet-}, 496 \text{ nm}, n}$	$\Delta A_{0, ^3\text{Ruphen}, 455 \text{ nm}, n}$	$\eta_{\text{CE}, n}(^3\text{Ruphen}, \text{HAsc}^-)$
1 (25)	0.00800	-0.0640	0.209
2 (38)	0.0102	-0.0840	0.203

On average, a cage escape efficiency of $\frac{(0.209+0.203)}{2} = 0.206 \approx 0.21$ was determined.

S8.3 Cage escape efficiency for the reduction of ³PTS by HAsc⁻

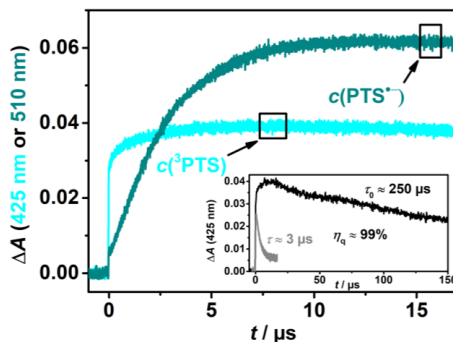


Figure S49 Main plot: Transient absorption traces of a solution containing **Ruphen** (30 μM) and **PTS** (120 μM) (cyan) or **Ruphen** (30 μM), **PTS** (120 μM) and **NaHAsc** (10 mM) (petrol) in Ar-saturated water after the laser pulse ($\lambda_{\text{exc}} = 532 \text{ nm}$). Inset: Transient absorption traces of the same solutions (black: without **NaHAsc**, gray: with **NaHAsc**) at 425 nm.

The cage escape efficiency for the reductive quenching of ³PTS by HAsc⁻ was determined in a manner similar to that between ³Ruphen and HAsc⁻ (section S8.2). The concentration of ³PTS can be determined with the solution excluding **NaHAsc** based on the kinetic absorbance at 455 nm. After the addition of HAsc⁻, the determination of the concentration of PTS^{•-} at 510 nm is possible.

$$\eta_{\text{CE}}(^3\text{PTS}, \text{HAsc}^-) = \frac{c(\text{PTS}^{\bullet-})}{c(^3\text{PTS}) \cdot \eta_q} = \frac{\frac{\Delta A_{\text{PTS}^{\bullet-}, 510 \text{ nm}}}{\Delta \epsilon_{\text{PTS}^{\bullet-}, 510 \text{ nm}}}}{\frac{\Delta A_{0, ^3\text{PTS}, 425 \text{ nm}}}{\Delta \epsilon_{^3\text{PTS}, 425 \text{ nm}}} \cdot \eta_q} = \frac{\frac{0.0615 \text{ cm}^{-1}}{29000 \text{ M}^{-1}\text{cm}^{-1}}}{\frac{0.0391 \text{ cm}^{-1}}{20000 \text{ M}^{-1}\text{cm}^{-1}}} = 1.08 \approx 1$$

The extinction coefficients determined in this study are expected to have an estimated relative error of 10%. With the pure numbers a quantum yield of 1.08 is obtained, which is not plausible. However, it can be concluded that quenching ³PTS by HAsc⁻ leads approximately quantitatively to the formation of PTS^{•-}, which is more efficient by a factor of 5 compared to the quenching of ³Ruphen by HAsc⁻. This is in agreement with the observations made in the lab-scale irradiation experiment for pinacol coupling of **2-FBA** and the **2-BP** dehalogenation.

S8.3 Additional investigations

S8.3.1 Static and dynamic quenching observed by time-resolved emission and absorption

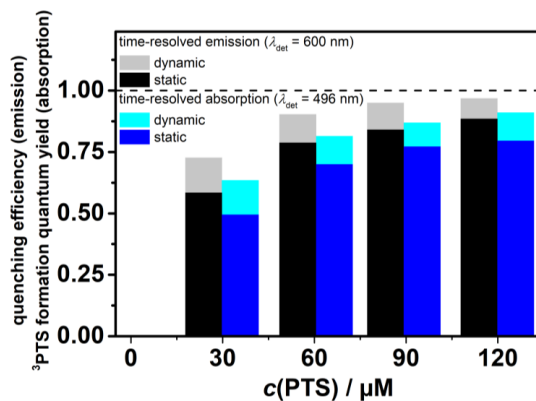


Figure S50 Comparison between the contribution of static and dynamic quenching for the total quenching efficiency based on time-resolved emission (black and gray, raw data sets are displayed in Figure 3 (a) in the main part) and for the quantum yield of ^3PTS formation based on transient absorption measurements (blue and cyan, based on the raw data sets from Figure 3 (c) in the main part, the quenching efficiency and the efficiency for ^3PTS formation determined in section S8.1 for $c(\text{PTS}) = 120 \mu\text{M}$).

The contributions of static and dynamic quenching to the quantum yield of ^3PTS formation from $^3\text{Ruphen}$ quenching observed by transient absorption closely mirrors the contributions of static and dynamic quenching in the overall quenching efficiency determined by time-resolved emission (see Figure S50). Regardless of the **PTS** concentration, the desired EnT is the main quenching pathway contributing to about 90 % of the observed quenching. This minor discrepancy is within the experimental error, taking the challenges in the calibration of excited-state absorption spectra into account.

S8.3.2 Estimation of the back energy transfer rate between ^3PTS and **Ruphen**

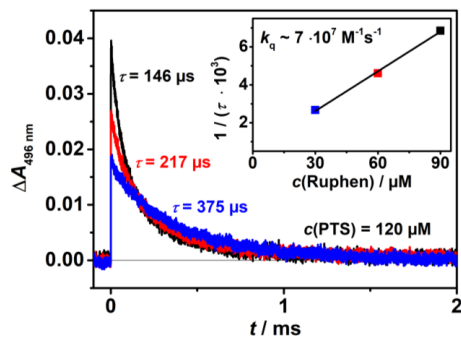


Figure S51 Main plot: Time-resolved absorption traces of ^3PTS at different concentrations of **Ruphen** in Ar-saturated water after laser excitation ($\lambda_{\text{exc}} = 532 \text{ nm}$). Inset: Estimated quenching rate of ^3PTS by **Ruphen** using a linear fit according to the rearranged Stern–Volmer equation.

S8.3.3 Ionic strength dependent formation of the key species ^3PTS and PTS^-

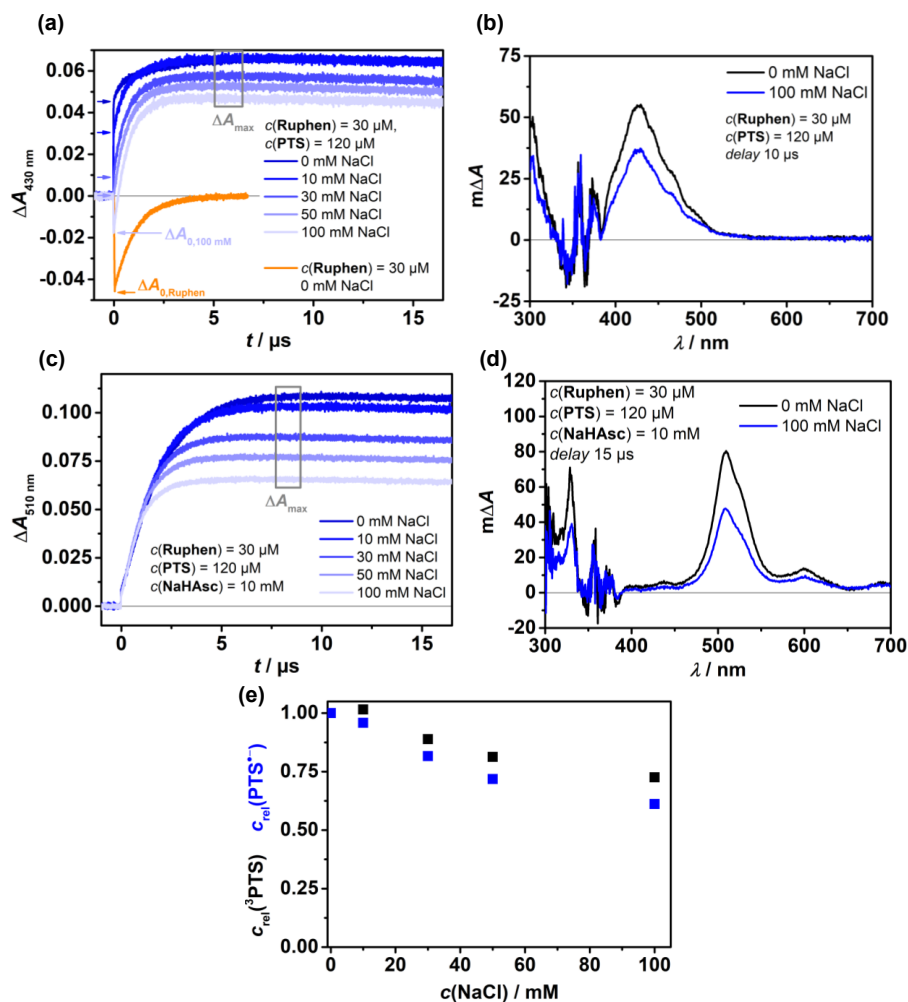


Figure S52 (a) Time-resolved absorption traces of a solution containing **Ruphen** in air-saturated water (orange) or **Ruphen** and **PTS** at different NaCl concentrations in Ar-saturated water (blue) after laser excitation ($\lambda_{\text{exc}} = 532 \text{ nm}$). The initial value ΔA_0 after the laser pulse is indicated by arrows. (b) Transient absorption spectra of the solutions used in (a) with **Ruphen** and **PTS** at a NaCl concentration of 0 mM and 100 mM after laser excitation ($\lambda_{\text{exc}} = 532 \text{ nm}$). (c) Time-resolved absorption traces of a solution containing **Ruphen**, **PTS** and **NaHAsc** at different NaCl concentrations in Ar-saturated water after laser excitation ($\lambda_{\text{exc}} = 532 \text{ nm}$). (d) Transient absorption spectra of the solutions used in (c) at a NaCl concentration of 0 mM and 100 mM after laser excitation ($\lambda_{\text{exc}} = 532 \text{ nm}$). (e) Relative concentrations of the key species ^3PTS and PTS^- after laser excitation at different NaCl concentrations based on the measured ΔA_{max} (mean value within the gray boxes in (a) and (c)).

The following analysis is based on the assumption that the molar absorption coefficients of ^3PTS and PTS^- do not depend on the NaCl concentration. The spectral shapes and peak positions of the absorption

bands of these species are hardly affected. These observations might indicate that the molar absorption coefficients remain identical, too. For the quenching of ³Ruphen by PTS, the total quenching efficiency (η_q), the static quenching efficiency ($\eta_{q,stat}$) and the dynamic quenching efficiency ($\eta_{q,dyn}$) for the selected NaCl concentrations can be calculated using the quenching efficiency at $c(\text{NaCl}) = 0 \text{ mM}$ as a reference ($\eta_{q,0 \text{ mM NaCl}} = 0.97$, from the Stern–Vomer analysis shown in Figure 3 (a) in the main part) and the values $\Delta A_{\max}$ and ΔA_0 shown in Figure S52 (a) ($c(\text{Ruphen}) = 30 \text{ }\mu\text{M}$, $c(\text{PTS}) = 120 \text{ }\mu\text{M}$):

$$\eta_{q,X \text{ mM NaCl}} = \eta_{q,0 \text{ mM NaCl}} \cdot \frac{\Delta A_{\max,X \text{ mM NaCl}}}{\Delta A_{\max,0 \text{ mM NaCl}}}$$

$$\eta_{q,stat,X \text{ mM NaCl}} = \eta_{q,0 \text{ mM NaCl}} \cdot \frac{\Delta A_{0,X \text{ mM NaCl}} - \Delta A_{0,\text{Ruphen}}}{\Delta A_{\max,X \text{ mM NaCl}} - \Delta A_{0,\text{Ruphen}}}$$

$$\eta_{q,dyn,X \text{ mM NaCl}} = \frac{\eta_{q,X \text{ mM NaCl}} - \eta_{q,stat,X \text{ mM NaCl}}}{1 - \eta_{q,stat,X \text{ mM NaCl}}}$$

These formulas fulfill the general expression for the overall quenching efficiency in the case of mixed dynamic and static quenching.⁶⁸

$$\eta_{q,X \text{ mM NaCl}} = \eta_{q,stat,X \text{ mM NaCl}} + (1 - \eta_{q,stat,X \text{ mM NaCl}}) \cdot \eta_{q,dyn,X \text{ mM NaCl}}$$

The resulting quenching efficiencies for the used NaCl concentrations are shown in Figure S53.

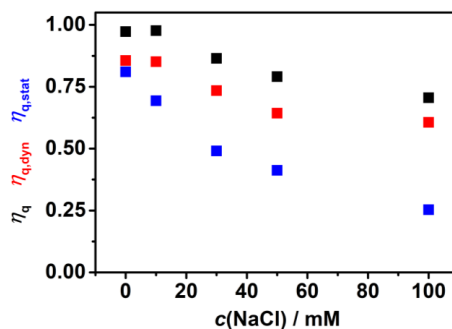


Figure S53 The overall (black), dynamic (red) and static (blue) quenching efficiency of ³Ruphen by PTS at different NaCl concentrations in water determined by the maximum (gray box in Figure S52 (a)) and initial value ΔA_0 (after the laser pulse, see Figure S52 (a)). See text for details.

The overall quenching efficiency of ³Ruphen by PTS for $c(\text{Ruphen}) = 30 \text{ }\mu\text{M}$ and $c(\text{PTS}) = 120 \text{ }\mu\text{M}$ in water is reduced from 97% at $c(\text{NaCl}) = 0 \text{ mM}$ to 71% at $c(\text{NaCl}) = 100 \text{ mM}$ (see Figure S53). The efficiency of static quenching is reduced to 25%. In contrast, there is only a slight decrease in the dynamic quenching efficiency to 61%.

9 Identification of other Coulombic dyads

9.1 Osmium-based Coulombic dyad

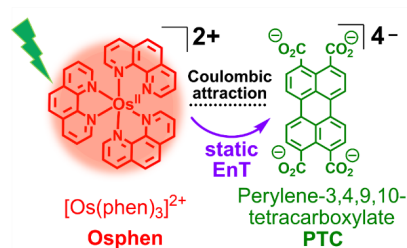


Figure S54 Structures and abbreviations of a further Coulombic dyad in water, which is based on the highly efficient and static Dexter energy transfer, forming a long-lived organic triplet.

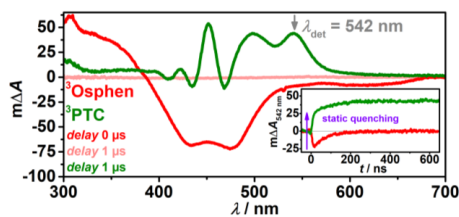


Figure S55 Transient absorption spectra of a solution containing $c(\text{Osphen}) = 16 \mu\text{M}$ without (red: delay $0 \mu\text{s}$, pale red: delay $1 \mu\text{s}$) or with $c(\text{PTC}) = 30 \mu\text{M}$ (green, $1 \mu\text{s}$ delay) after selective **Osphen** laser excitation ($\lambda_{\text{exc}} = 532 \text{ nm}$). Inset: Time-resolved absorption at 542 nm of the same solutions shown in the main graph.

The observed transient absorption spectrum in the presence of **PTC** as energy acceptor is similar to the spectrum obtained for the triplet state of perylene,⁶⁹ indicating an efficient energy transfer yielding ^3PTC . Due to the short unquenched lifetime of $^3\text{Osphen}$, the quenching process by **PTC** mainly takes place in a static manner, which is indicated by the kinetic traces in the inset of Figure S55.

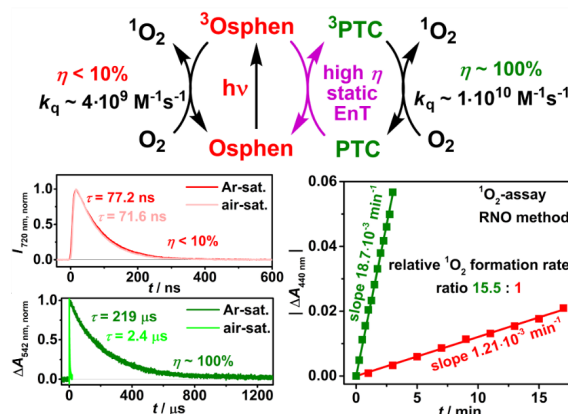
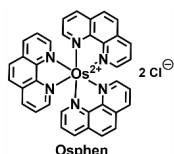


Figure S56 Reaction scheme of the less efficient formation of $^1\text{O}_2$ without and the much more efficient formation of $^1\text{O}_2$ with the energy acceptor **PTC**. (bottom, left) Time-resolved emission of an Ar- or air-saturated aqueous solution containing $c(\text{Osphen}) = 16 \mu\text{M}$ (red) and time-resolved absorption of a solution containing additionally $c(\text{PTC}) = 150 \mu\text{M}$ (green) under similar conditions. (bottom, right) Results of an $^1\text{O}_2$ assay displaying different $^1\text{O}_2$ formation rates for an aqueous solution containing $c(\text{Osphen}) = 15 \mu\text{M}$ without (red) or with $c(\text{PTC}) = 45 \mu\text{M}$ (green).

The low unquenched lifetime of $^3\text{Osphen}$ in pure water of about 77 ns leads to a very low quenching efficiency by molecular oxygen of only 0.073 in air-saturated water, as shown in Figure S56. In contrast, almost all of the sensitized ^3PTC is effectively quenched by molecular oxygen, since its lifetime is more than three orders of magnitude higher. A specific comparative assay for $^1\text{O}_2$ formation rates²⁰ performed in the presence of $c(\text{PTC})$ at $45 \mu\text{M}$ revealed a remarkable 15.5-fold increase compared to the presence of only **Osphen** as photosensitizer. A quenching efficiency of 0.40 is achieved for $^3\text{Osphen}$ with the **PTC** concentration used, whereby static quenching dominates. In the present case, the overall quenching efficiency for the reaction with molecular oxygen increases from 0.073 to 0.40, which in principle results in a 5.5-fold increase. The significantly greater difference observed in the $^1\text{O}_2$ assay is due to differences in the inherent quantum yield f_Δ , which displays the proportion of $^1\text{O}_2$ that is formed by the quenching process with molecular oxygen.⁷⁰ It is assumed that in the case of the purely organic ^3PTC mainly an energy transfer takes place with the formation of $^1\text{O}_2$ and in the case of the metal complex $^3\text{Osphen}$ mainly an electron transfer takes place,⁸ forming $\text{O}_2^{\bullet-}$. This mechanistic change would explain the significant improvement in the formation of $^1\text{O}_2$ when using **PTC**.

Synthesis of Tris(1,10-phenanthroline)osmium(II) dichloride (Osphen)



Osphen was prepared by a modified procedure of Constable *et al.*⁷¹ 1,10-Phenanthroline monohydrate (0.20 g, 1.00 mmol, 3.0 eq), potassium-hexachloroosmat(IV) (0.16 g, 0.33 mmol, 1.0 eq.) and ethylene glycol (100 ml) were added to a three-necked 250 ml round-bottom flask equipped with a dimroth condenser. Argon was bubbled through the solution for 30 minutes to remove any dissolved oxygen. The solution was then heated at reflux for 2 h. After cooling to room temperature, the reaction mixture was poured into 100 ml of an aqueous solution containing ammoniumhexafluorophosphate (1.00 g, 6.10 mmol, 18.0 eq.) and stirred for 15 minutes. A black precipitate formed, which was filtered off, washed several times with MilliQ water and dried under vacuum to yield a black solid (0.29 g, 0.28 mmol, 85%).

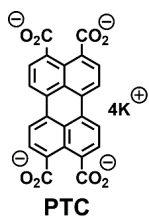
Anion exchange was carried out with the ion exchange resin Amberlite IRA-410. 50 g of this resin was first washed several times with 40 ml ethanol until the wash solution remained clear. The resin then swelled in ethanol in a glass column for 24 hours. To condition the resin for chloride, it was rinsed four times with 40 ml of an aqueous 10 mM NaCl solution, with the aqueous solution remaining on the column for one hour for each run. The column was then washed three times with 40 ml methanol. The PF₆ salt (65 mg, 0.064 mmol) was dissolved in 15 ml methanol and filled into the column. After 2 h, the solution was drained and rinsed five times with 30 ml methanol each, resulting in a clear and colorless solution in the last washing step. The combined organic phases were evaporated to dryness under reduced pressure. This yielded a black solid (51 mg, 0.064 mmol, 100%).

¹H NMR (300 MHz, D₂O): δ [ppm] = 8.35 (dd, J = 8.3, 1.2 Hz, 6H), 8.21 (s, 6H), 8.00 (dd, J = 5.4, 1.2 Hz, 6H), 7.51 (dd, J = 8.3, 5.4 Hz, 6H).

UV-vis spectrum in H₂O (rel. absorbance): λ [nm] = 560 (0.049), 478 (0.17), 432 (0.18), 316 (0.058), 264 (1.0).

The NMR and UV-vis data sets are in agreement with the literature.⁷²

Synthesis of 3,4,9,10-Prylenetetra-carboxylic acid tetrapotassium salt (PTC)



PTC was prepared by a modified procedure of Wang *et al.*⁷³ In a 250 ml round-bottom flask equipped with a dimroth condenser, 3,4,9,10-perylenetetra-carboxylic acid dianhydride (1.98 g, 5.1 mmol, 1.0 eq) was added to 75 ml water followed by the addition of potassium hydroxide (1.12 g, 20.4 mmol, 4.0 eq). The reaction solution was heated for 18 h under reflux. After heating, the initially red suspension yielded a yellow-red, clear solution. The solvent was removed under reduced pressure and the orange solid was washed three times with 60 ml abs. ethanol each time. The solid was dried under reduced pressure. This yielded 2.70 g of an orange solid (2.70 g, 4.7 mmol, 93%).

¹H NMR (300 MHz, D₂O): δ [ppm] = 8.40 (d, J = 7.9 Hz, 4H), 7.79 (d, J = 7.8 Hz, 4H).

UV-vis spectrum in H₂O (rel. absorbance): λ [nm] = 439 (0.81), 466 (1.0).

The NMR and UV-vis data sets are in agreement with the literature.⁷³

9.2 Ruthenium-based Coulombic dyad in an organic solvent

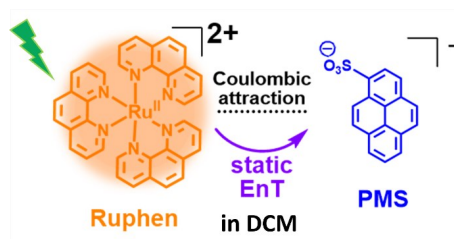


Figure S57 Structures and abbreviations of another Coulombic dyad in dichloromethane, which is based on the highly efficient and static Dexter energy transfer, forming a long-lived organic triplet.

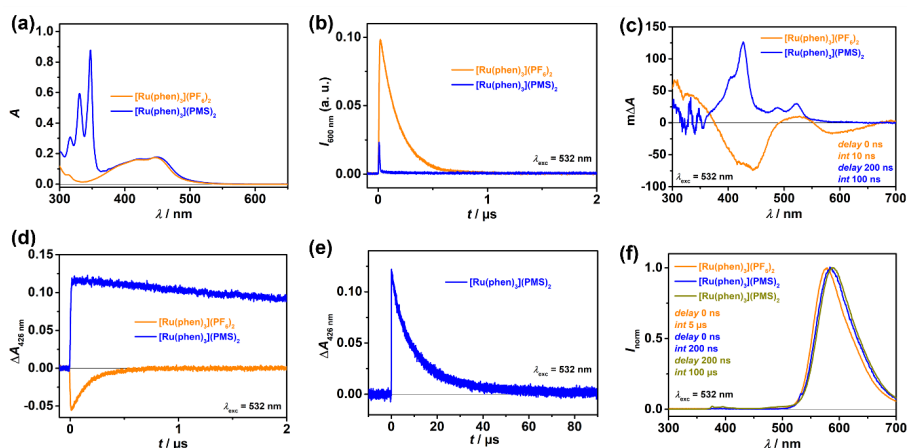


Figure S58 Spectroscopic features of the $[\text{Ru}(\text{phen})_3](\text{PMS})_2$ salt (blue) compared to the parent complex **Ruphen** (orange) in Ar-purged dichloromethane. Unless otherwise specified, the parameters and settings of the measurements shown in one graph are identical. (a) UV-vis spectra, recorded in 2 mm cuvettes. (b) Time-resolved emission. (c) Transient absorption spectra. (d) Transient absorption traces. (e) Transient absorption traces. (f) Spectral emission. See text for further details.

The spectroscopic features of the Coulombic dyad salt $[\text{Ru}(\text{phen})_3](\text{PMS})_2$ (still available from a former project²) in dichloromethane are strikingly similar to those reported for the well-known molecular dyad consisting of a **Ruphen** covalently linked to pyrene.¹ Both chromophores **Ruphen** and **PMS** are only in close contact due to Coulombic interactions. Those are much weaker compared to **Ruphen** and **PTS**

(charges: +2 and -1), but in the apolar solvent dichloromethane sufficiently strong to lead to a high binding constant. For a concentration of 50 μM **Ruphen** and 100 μM **PMS**, resulting from the stoichiometry of the respective salt, the following observations can be made:

The MLCT band in the ground state absorption spectrum (a) of the Coulombic dyad is red-shifted compared to the parent complex, indicating a ground state association of **Ruphen** and **PMS** in solution. In the time-resolved emission (b), a nearly quantitative quenching of the prompt $^3\text{Ruphen}$ emission can be observed, indicating a static and ultrafast energy transfer to **PMS**. The resulting transient absorption spectrum (c) clearly shows the formation of ^3PMS as a result of the quenching process. The time-resolved absorption (d) underlines the sub-ns formation of ^3PMS . ^3PMS has a lifetime of 10.6 μs under the shown conditions (e). The organic triplet state is in thermal equilibrium with the $^3\text{Ruphen}$ state, which is demonstrated by the spectral emission impressively (f). Only the emission of **Ruphen** can be seen there and essentially no emission of $^1\text{PMS}^*$ or excimers like $^1(\text{PMS})_2^*$, which is typically seen in the presence of ^3PMS in sTTA studies.² This indicates that the depopulation of ^3PMS is mainly driven by the thermal equilibrium with the $^3\text{Ruphen}$ state, as is also observed in molecular dyads, and highlights the importance of the lower triplet energy of **PTS** to achieve maximum triplet lifetimes.^{1,74}

S10 Miscellaneous

S10.1 77 K phosphorescence spectrum of PTS

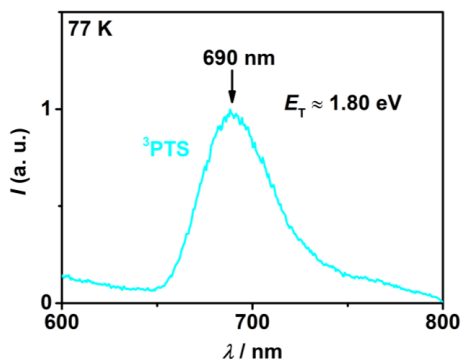


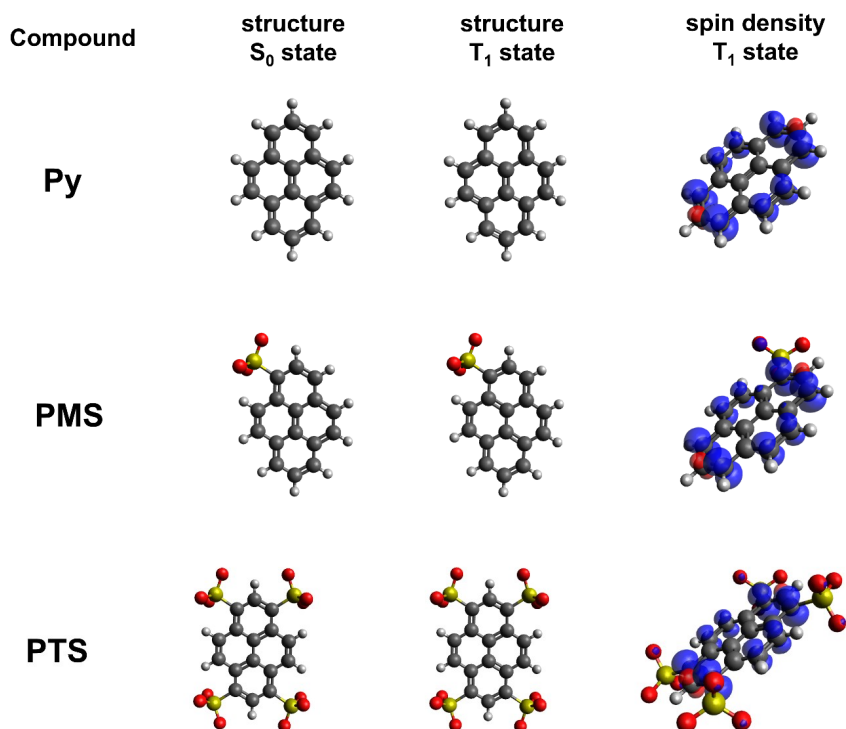
Figure S59 77 K phosphorescence spectrum of ³PTS ($c(\text{PTS}) = 20 \mu\text{M}$) in an ethanol-methanol (4:1) solvent mixture after laser excitation ($\lambda_{\text{exc}} = 355 \text{ nm}$, delay: 500 ns, integration time: 1 ms). The triplet state energy was estimated from the emission maximum at 690 nm.

S10.2 DFT calculations

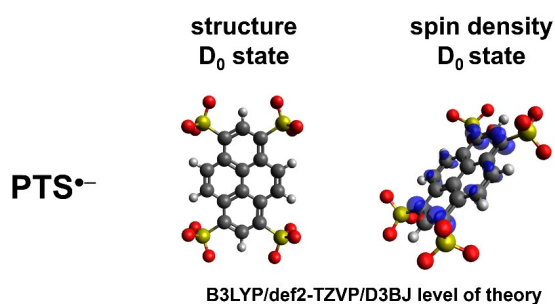
Table S7 Predicted triplet-state energies based on DFT calculations (B3LYP/def2-SVP level of theory).

compound	E_T / eV
Py (charge: 0)	2.08
PMS (charge: -1)	1.99
PTS (charge: -4)	1.85

The literature value for pyrene of 2.09 eV^{21} is approximately reproduced, which implies a sufficient reliability of the employed method.



For **PMS** and **PTS**, spin density is also located on the substituents, which is in line with the decreased triplet state energy compared to **Py**. Total number of spin populations for each triplet state: 2.000.



In the reduced species **PTS^{•-}**, the unpaired electron is located on the pyrene moiety, near the binding sites of the electron-withdrawing sulfonate groups. Total number of spin populations for the doublet state: 1.000.

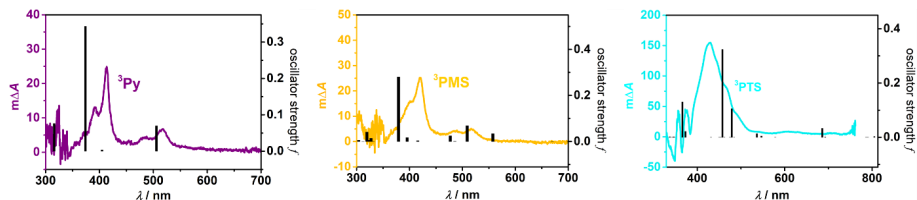


Figure S60 Experimental transient absorption spectra of the triplet states of the pyrene species reported herein in acetonitrile (**Py**) or water (**PMC**, **PTS**) after laser excitation ($\lambda_{\text{exc}} = 532$ nm, delay 2 μs (**PTS** and **PMS**), delay 3 μs (**Py**)) in the presence of **Ruphen** as the sensitizer ($c(\text{Ruphen}) = 30$ μM , concentration of pyrene derivatives: 120 μM (**Py** and **PMS**) or 30 μM (**PTS**)) in combination with the calculated oscillator strengths from TD-DFT calculations (B3LYP/def2-SVP level of theory).

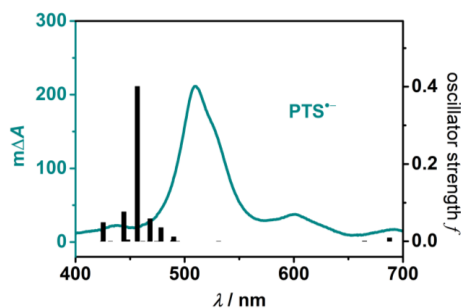


Figure S61 Experimental transient absorption spectrum of the reduced species $\text{PTS}^{\bullet-}$ in water after laser excitation ($\lambda_{\text{exc}} = 532$ nm, delay 16 μs) in the presence of $c(\text{Ruphen}) = 30$ μM $c(\text{PTS}) = 120$ μM and $c(\text{NaHAsc}) = 10$ mM, in combination with the calculated oscillator strengths from TD-DFT calculations (B3LYP/def2-TZVP/D3BJ level of theory, lowest 50 transitions calculated).

S10.3 Supplementary data

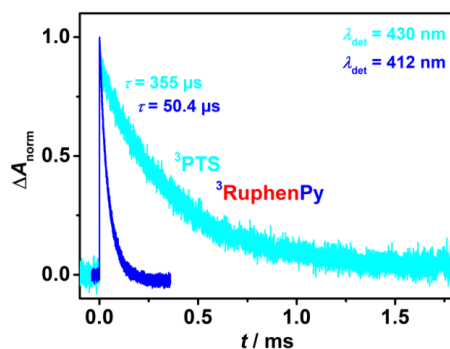


Figure S62 Entire normalized transient absorption traces which are shown incompletely in Figure 4 of the main part of the manuscript.

S10.4 NMR spectrum of methyl phenyl sulfoxide

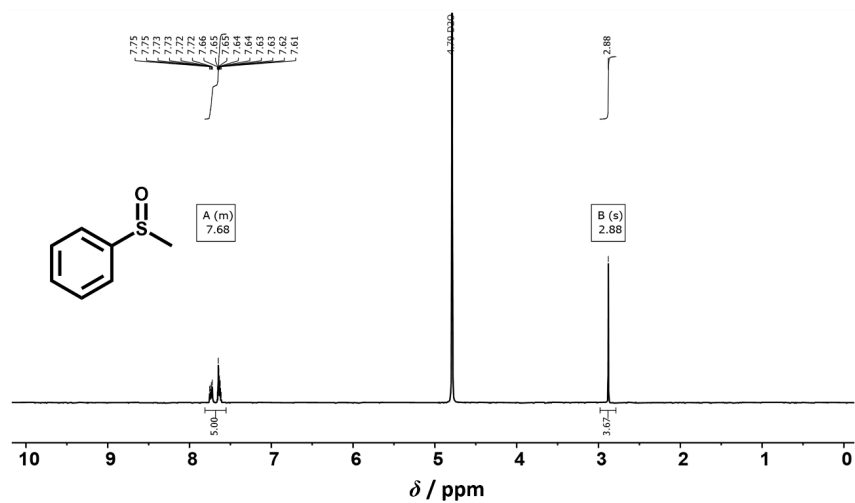


Figure S63 ^1H NMR spectrum of methyl phenyl sulfoxide in D_2O .

References

- (1) Sell, A. C.; Wetzel, J. C.; Schmitz, M.; Maijenburg, A. W.; Woltersdorf, G.; Naumann, R.; Kerzig, C. Water-Soluble Ruthenium Complex-Pyrene Dyads with Extended Triplet Lifetimes for Efficient Energy Transfer Applications. *Dalton Trans.* **2022**, 51 (28), 10799–10808. <https://doi.org/10.1039/D2DT01157C>.
- (2) Glaser, F.; Schmitz, M.; Kerzig, C. Coulomb Interactions for Mediator-Enhanced Sensitized Triplet–Triplet Annihilation Upconversion in Solution. *Nanoscale* **2024**, 16 (1), 123–137. <https://doi.org/10.1039/D3NR05265F>.
- (3) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, 29 (9), 2176–2179. <https://doi.org/10.1021/om100106e>.
- (4) Zhang, F.-F.; Jiang, M.-H.; Sun, L.-L.; Zheng, F.; Dong, L.; Shah, V.; Shen, W.-B.; Ding, Y. Quantitative Analysis of Sitagliptin Using the ¹⁹F-NMR Method: A Universal Technique for Fluorinated Compound Detection. *The Analyst* **2015**, 140 (1), 280–286. <https://doi.org/10.1039/C4AN01681E>.
- (5) Kerzig, C.; Wenger, O. S. Reactivity Control of a Photocatalytic System by Changing the Light Intensity. *Chem. Sci.* **2019**, 10 (48), 11023–11029. <https://doi.org/10.1039/C9SC04584H>.
- (6) Neese, F. The ORCA Program System. *WIREs Comput. Mol. Sci.* **2012**, 2 (1), 73–78. <https://doi.org/10.1002/wcms.81>.
- (7) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, 32 (7), 1456–1465. <https://doi.org/10.1002/jcc.21759>.
- (8) Bertrams, M.-S.; Kerzig, C. Converting *p*-Terphenyl into a Novel Organo-Catalyst for LED-Driven Energy and Electron Transfer Photoreactions in Water. *Chem. Commun.* **2021**, 57 (55), 6752–6755. <https://doi.org/10.1039/D1CC01947C>.
- (9) Blum, T. R.; Miller, Z. D.; Bates, D. M.; Guzei, I. A.; Yoon, T. P. Enantioselective Photochemistry through Lewis Acid–Catalyzed Triplet Energy Transfer. *Science* **2016**, 354 (6318), 1391–1395. <https://doi.org/10.1126/science.aai8228>.
- (10) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: An Advanced Semantic Chemical Editor, Visualization, and Analysis Platform. *J. Cheminform.* **2012**, 4 (1), 17. <https://doi.org/10.1186/1758-2946-4-17>.
- (11) Thordarson, P. Determining Association Constants from Titration Experiments in Supramolecular Chemistry. *Chem. Soc. Rev.* **2011**, 40 (3), 1305–1323. <https://doi.org/10.1039/C0CS00062K>.
- (12) Brynn Hibbert, D.; Thordarson, P. The Death of the Job Plot, Transparency, Open Science and Online Tools, Uncertainty Estimation Methods and Other Developments in Supramolecular Chemistry Data Analysis. *Chem. Commun.* **2016**, 52 (87), 12792–12805. <https://doi.org/10.1039/C6CC03888C>.
- (13) Barendt, T. A.; Myers, W. K.; Cornes, S. P.; Lebedeva, M. A.; Porfyrakis, K.; Marques, I.; Félix, V.; Beer, P. D. The Green Box: An Electronically Versatile Perylene Diimide Macrocyclic Host for Fullerenes. *J. Am. Chem. Soc.* **2020**, 142 (1), 349–364. <https://doi.org/10.1021/jacs.9b10929>.
- (14) Docker, A.; Johnson, T. G.; Kuhn, H.; Zhang, Z.; Langton, M. J. Multistate Redox-Switchable Ion Transport Using Chalcogen-Bonding Anionophores. *J. Am. Chem. Soc.* **2023**, 145 (4), 2661–2668. <https://doi.org/10.1021/jacs.2c12892>.
- (15) Li, Y.-H.; Zheng, S.-P.; Wang, D.; Barboiu, M. Selective Proton-Mediated Transport by Electrogenic K⁺-Binding Macrocycles. *Chem* **2020**, 2 (1), 11–21. <https://doi.org/10.3390/chemistry2010003>.
- (16) Wezenberg, S. J.; Feringa, B. L. Supramolecularly Directed Rotary Motion in a Photoresponsive Receptor. *Nat. Commun.* **2018**, 9 (1), 1984. <https://doi.org/10.1038/s41467-018-04249-x>.
- (17) Wagay, S. A.; Ali, R. Facile Synthesis and Anion Binding Studies of Fluorescein/Benzo-12-Crown-4 Ether Based Bis-Dipyrrromethane (DPM) Receptors. *RSC Adv.* **2023**, 13 (43), 30420–30428. <https://doi.org/10.1039/D3RA05171D>.

- (18) Benesi, H. A.; Hildebrand, J. H. A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons. *J. Am. Chem. Soc.* **1949**, *71* (8), 2703–2707. <https://doi.org/10.1021/ja01176a030>.
- (19) Genovese, D.; Cingolani, M.; Rampazzo, E.; Prodi, L.; Zaccheroni, N. Static Quenching upon Adduct Formation: A Treatment without Shortcuts and Approximations. *Chem. Soc. Rev.* **2021**, *50* (15), 8414–8427. <https://doi.org/10.1039/D1CS00422K>.
- (20) Kraljić, I.; Mohsni, S. E. A New Method for the Detection of Singlet Oxygen in Aqueous Solutions. *Photochem. Photobiol.* **1978**, *28* (4–5), 577–581. <https://doi.org/10.1111/j.1751-1097.1978.tb06972.x>.
- (21) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; CRC Press, 2006. <https://doi.org/10.1201/9781420015195>.
- (22) Glaser, F.; Kerzig, C.; Wenger, O. S. Multi-Photon Excitation in Photoredox Catalysis: Concepts, Applications, Methods. *Angew. Chem. Int. Ed.* **2020**, *59* (26), 10266–10284. <https://doi.org/10.1002/anie.201915762>.
- (23) Soupard, A.; Alary, F.; Heully, J.-L.; Elliott, P. I. P.; Dixon, I. M. Theoretical Study of the Full Photosolvolytic Mechanism of $[\text{Ru}(\text{Bpy})_3]^{2+}$: Providing a General Mechanistic Roadmap for the Photochemistry of $[\text{Ru}(\text{N}^{\wedge}\text{N})_3]^{2+}$ -Type Complexes toward Both Cis and Trans Photoproducts. *Inorg. Chem.* **2020**, *59* (20), 14679–14695. <https://doi.org/10.1021/acs.inorgchem.0c01843>.
- (24) Varchola, J.; Huntosova, V.; Jancura, D.; Wagnières, G.; Miskovsky, P.; Bánó, G. Temperature and Oxygen-Concentration Dependence of Singlet Oxygen Production by RuPhen as Induced by Quasi-Continuous Excitation. *Photochem. Photobiol. Sci.* **2014**, *13* (12), 1781–1787. <https://doi.org/10.1039/c4pp00202d>.
- (25) Seret, A.; Gandin, E.; Van De Vorst, A. Flash Photolysis of Eosin in Aqueous Micellar Dispersions. *Chem. Phys. Lett.* **1987**, *135* (4–5), 427–431. [https://doi.org/10.1016/0009-2614\(87\)85183-7](https://doi.org/10.1016/0009-2614(87)85183-7).
- (26) Usui, Y. Determination of Quantum Yield of Singlet Oxygen Formation by Photosensitization. *Chem. Lett.* **1973**, *2* (7), 743–744. <https://doi.org/10.1246/cl.1973.743>.
- (27) Nilsson, R.; Merkel, P. B.; Kearns, D. R. Kinetic Properties of the Triplet States of Methylene Blue and Other Photosensitizing Dyes. *Photochem. Photobiol.* **1972**, *16* (2), 109–116. <https://doi.org/10.1111/j.1751-1097.1972.tb07342.x>.
- (28) Nemoto, M.; Kokubun, H.; Koizumi, M. Determination of S*–T Transition Probabilities of Some Xanthene and Thiazine Dyes on the Basis of T-Energy Transfer. II. Results in the Aqueous Solution. *Bull. Chem. Soc. Jpn.* **1969**, *42* (9), 2464–2470. <https://doi.org/10.1246/bcsj.42.2464>.
- (29) Usui, Y.; Kamogawa, K. A Standard System to Determine the Quantum Yield of Singlet Oxygen Formation in Aqueous Solution. *Photochem. Photobiol.* **1974**, *19* (3), 245–247. <https://doi.org/10.1111/j.1751-1097.1974.tb06506.x>.
- (30) Mills, A.; Lawrence, C.; Douglas, P. Photoreduction of Water Sensitized by Rose Bengal. *J. Chem. Soc. Faraday Trans. 2* **1986**, *82* (12), 2291–2303. <https://doi.org/10.1039/t29868202291>.
- (31) Gandin, E.; Lion, Y.; Van De Vorst, A. Quantum Yield of Singlet Oxygen Production by Xanthene Derivatives. *Photochem. Photobiol.* **1983**, *37* (3), 271–278. <https://doi.org/10.1111/j.1751-1097.1983.tb04472.x>.
- (32) Nardello, V.; Brault, D.; Chavalle, P.; Aubry, J.-M. Measurement of Photogenerated Singlet Oxygen ($^1\text{O}_2(^1\Delta_g)$) in Aqueous Solution by Specific Chemical Trapping with Sodium 1,3-Cyclohexadiene-1,4-Diethanoate. *J. Photochem. Photobiol. B* **1997**, *39* (2), 146–155. [https://doi.org/10.1016/S1011-1344\(97\)00005-5](https://doi.org/10.1016/S1011-1344(97)00005-5).
- (33) Galkin, K. I.; Ananikov, V. P. When Will 5-Hydroxymethylfurfural, the “Sleeping Giant” of Sustainable Chemistry, Awaken? *ChemSusChem* **2019**, *12* (13), 2976–2982. <https://doi.org/10.1002/cssc.201900592>.
- (34) Heugebaert, T. S. A.; Stevens, C. V.; Kappe, C. O. Singlet-Oxygen Oxidation of 5-Hydroxymethylfurfural in Continuous Flow. *ChemSusChem* **2015**, *8* (10), 1648–1651. <https://doi.org/10.1002/cssc.201403182>.
- (35) Wilkinson, F.; Helman, W. P.; Ross, A. B. Rate Constants for the Decay and Reactions of the Lowest Electronically Excited Singlet State of Molecular Oxygen in Solution. An Expanded and Revised Compilation. *J. Phys. Chem. Ref. Data* **1995**, *24* (2), 663–677. <https://doi.org/10.1063/1.555965>.

- (36) Bohne, C.; Abuin, E. B.; Scaiano, J. C. Characterization of the Triplet-Triplet Annihilation Process of Pyrene and Several Derivatives under Laser Excitation. *J. Am. Chem. Soc.* **1990**, *112* (11), 4226–4231. <https://doi.org/10.1021/ja00167a018>.
- (37) Bonesi, S. M.; Fagnoni, M.; Albini, A. Hammett Correlations in the Photosensitized Oxidation of 4-Substituted Thioanisoles. *J. Org. Chem.* **2004**, *69* (3), 928–935. <https://doi.org/10.1021/jo035679e>.
- (38) Foote, C. S.; Peters, J. W. Chemistry of Singlet Oxygen. XIV. Reactive Intermediate in Sulfide Photooxidation. *J. Am. Chem. Soc.* **1971**, *93* (15), 3795–3796. <https://doi.org/10.1021/ja00744a055>.
- (39) Akasaka, T.; Yabe, A.; Ando, W. Charge-Transfer Photooxygenation of Sulfides in a Cryogenic Oxygen Matrix. IR Spectroscopic Observation of Persulfoxides. *J. Am. Chem. Soc.* **1987**, *109* (26), 8085–8087. <https://doi.org/10.1021/ja00260a024>.
- (40) Baciocchi, E.; Crescenzi, C.; Lanzalunga, O. Photoinduced Electron Transfer Reactions of Benzyl Phenyl Sulfides Promoted by 9,10-Dicyanoanthracene. *Tetrahedron* **1997**, *53* (12), 4469–4478. [https://doi.org/10.1016/S0040-4020\(97\)00119-1](https://doi.org/10.1016/S0040-4020(97)00119-1).
- (41) Ye, C.; Zhang, Y.; Ding, A.; Hu, Y.; Guo, H. Visible Light Sensitizer-Catalyzed Highly Selective Photo Oxidation from Thioethers into Sulfoxides under Aerobic Condition. *Sci. Rep.* **2018**, *8* (1), 2205. <https://doi.org/10.1038/s41598-018-20631-7>.
- (42) Yao, H.; Ke, H.; Zhang, X.; Pan, S.-J.; Li, M.-S.; Yang, L.-P.; Schreckenbach, G.; Jiang, W. Molecular Recognition of Hydrophilic Molecules in Water by Combining the Hydrophobic Effect with Hydrogen Bonding. *J. Am. Chem. Soc.* **2018**, *140* (41), 13466–13477. <https://doi.org/10.1021/jacs.8b09157>.
- (43) Borunda, T.; Myers, A.; Mary Fisher, J.; Crans, D.; Johnson, M. Confinement Effects on Chemical Equilibria: Pentacyano(Pyrazine)Ferrate(II) Stability Changes within Nanosized Droplets of Water. *Molecules* **2018**, *23* (4), 858. <https://doi.org/10.3390/molecules23040858>.
- (44) Kerzig, C.; Henkel, S.; Goetz, M. A New Approach to Elucidating Repair Reactions of Resveratrol. *Phys. Chem. Chem. Phys.* **2015**, *17* (21), 13915–13920. <https://doi.org/10.1039/C5CP01779C>.
- (45) Pavlik, J. W.; Vongnakorn, T. Vapor Phase Phototransposition of Pyrazine Deuterium Labeling Studies. *Tetrahedron Lett.* **2007**, *48* (39), 7015–7018. <https://doi.org/10.1016/j.tetlet.2007.07.144>.
- (46) López-Martínez, J. L.; Torres-García, I.; Rodríguez-García, I.; Muñoz-Dorado, M.; Álvarez-Corral, M. Stereoselective Barbier-Type Allylations and Propargylations Mediated by CpTiCl₃. *J. Org. Chem.* **2019**, *84* (2), 806–816. <https://doi.org/10.1021/acs.joc.8b02643>.
- (47) Davies, M. B.; Austin, J.; Partridge, D. A. *Vitamin C: Its Chemistry and Biochemistry*; Royal society of chemistry paperbacks; The Royal society of chemistry: Cambridge, 1991.
- (48) Li, F.; Lin, S.; Chen, Y.; Shi, C.; Yan, H.; Li, C.; Wu, C.; Lin, L.; Duan, C.; Shi, L. Photocatalytic Generation of π -Allyltitanium Complexes via Radical Intermediates. *Angew. Chem. Int. Ed.* **2021**, *60* (3), 1561–1566. <https://doi.org/10.1002/anie.202010780>.
- (49) Zhang, S.; Li, L.; Li, J.; Shi, J.; Xu, K.; Gao, W.; Zong, L.; Li, G.; Findlater, M. Electrochemical Arylation of Aldehydes, Ketones, and Alcohols: From Cathodic Reduction to Convergent Paired Electrolysis. *Angew. Chem. Int. Ed.* **2021**, *60* (13), 7275–7282. <https://doi.org/10.1002/anie.202015230>.
- (50) Cao, K.; Tan, S. M.; Lee, R.; Yang, S.; Jia, H.; Zhao, X.; Qiao, B.; Jiang, Z. Catalytic Enantioselective Addition of Prochiral Radicals to Vinylpyridines. *J. Am. Chem. Soc.* **2019**, *141* (13), 5437–5443. <https://doi.org/10.1021/jacs.9b00286>.
- (51) Broeker, J.; Knollmueller, M.; Gaertner, P. Chiral Linker. Part 3: Synthesis and Evaluation of Aryl Substituted m-Hydrobenzoins as Solid Supported Open Chain Chiral Auxiliaries for the Diastereoselective Reduction of α -Keto Esters. *Tetrahedron Asymmetry* **2006**, *17* (16), 2413–2429. <https://doi.org/10.1016/j.tetasy.2006.08.017>.
- (52) Rauniyar, V.; Zhai, H.; Hall, D. G. Catalytic Enantioselective Allyl- and Crotylboration of Aldehydes Using Chiral Diol•SnCl₄ Complexes. Optimization, Substrate Scope and Mechanistic Investigations. *J. Am. Chem. Soc.* **2008**, *130* (26), 8481–8490. <https://doi.org/10.1021/ja8016076>.
- (53) Hasegawa, M.; Yamasaki, Y.; Sonta, N.; Shindo, Y.; Sugimura, T.; Kitahara, A. Clustering of Aerosol OT Reversed Micelles As Studied by Nonradiative Energy Transfer of Solubilized Probes. *J. Phys. Chem.* **1996**, *100* (38), 15575–15580. <https://doi.org/10.1021/jp961528m>.

- (54) Müller, P.; Brettel, K. [Ru(Bpy)₃]²⁺ as a Reference in Transient Absorption Spectroscopy: Differential Absorption Coefficients for Formation of the Long-Lived ³MLCT Excited State. *Photochem. Photobiol. Sci.* **2012**, *11* (4), 632–636. <https://doi.org/10.1039/c2pp05333k>.
- (55) Goez, M.; Kerzig, C.; Naumann, R. An “All-Green” Catalytic Cycle of Aqueous Photoionization. *Angew. Chem.* **2014**, *126* (37), 10072–10074. <https://doi.org/10.1002/ange.201405693>.
- (56) Neumann, S.; Kerzig, C.; Wenger, O. S. Quantitative Insights into Charge-Separated States from One- and Two-Pulse Laser Experiments Relevant for Artificial Photosynthesis. *Chem. Sci.* **2019**, *10* (21), 5624–5633. <https://doi.org/10.1039/C9SC01381D>.
- (57) Bürgin, T. H.; Glaser, F.; Wenger, O. S. Shedding Light on the Oxidizing Properties of Spin-Flip Excited States in a Cr^{III} Polypyridine Complex and Their Use in Photoredox Catalysis. *J. Am. Chem. Soc.* **2022**, *144* (31), 14181–14194. <https://doi.org/10.1021/jacs.2c04465>.
- (58) Watanabe, T.; Honda, K. Measurement of the Extinction Coefficient of the Methyl Viologen Cation Radical and the Efficiency of Its Formation by Semiconductor Photocatalysis. *J. Phys. Chem.* **1982**, *86* (14), 2617–2619. <https://doi.org/10.1021/j100211a014>.
- (59) Ohno, Takeshi.; Yoshimura, Akio.; Mataga, Noboru. Bell-Shaped Energy-Gap Dependence of Backward Electron Transfer Occurring within Geminate Radical Pairs Produced by Quenching of Ruthenium(II) Polypyridine Complexes by Aromatic Amines. *J. Phys. Chem.* **1990**, *94* (12), 4871–4876. <https://doi.org/10.1021/j100375a023>.
- (60) Brautzsch, M.; Kerzig, C.; Goez, M. Sustainable, Inexpensive and Easy-to-Use Access to the Super-Reductant e⁻_{aq} through 355 nm Photoionization of the Ascorbate Dianion—an Alternative to Radiolysis or UV-C Photochemistry. *Green Chem.* **2016**, *18* (17), 4761–4771. <https://doi.org/10.1039/C6GC01113F>.
- (61) Pellegrin, Y.; Odobel, F. Sacrificial Electron Donor Reagents for Solar Fuel Production. *C. R. Chim.* **2017**, *20* (3), 283–295. <https://doi.org/10.1016/j.crci.2015.11.026>.
- (62) Guttentag, M.; Rodenberg, A.; Kopelent, R.; Probst, B.; Buchwalder, C.; Brandstätter, M.; Hamm, P.; Alberto, R. Photocatalytic H₂ Production with a Rhenium/Cobalt System in Water under Acidic Conditions. *Eur. J. Inorg. Chem.* **2012**, *2012* (1), 59–64. <https://doi.org/10.1002/ejic.201100883>.
- (63) Mori, Y.; Shinoda, H.; Nakano, T.; Kitagawa, T. Formation and Decay Behaviors of Laser-Induced Transient Species from Pyrene Derivatives 1. Spectral Discrimination and Decay Mechanisms in Aqueous Solution. *J. Phys. Chem. A* **2002**, *106* (48), 11743–11749. <https://doi.org/10.1021/jp020332l>.
- (64) Hai-Xia, Y.; Hu-Xiang, P.; Yan-Lin, W.; Jian-Feng, Z.; Wen-Bo, D.; 复旦大学环境科学与工程系, 上海 200433; Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, P. R. China; 海军医学研究所, 上海 200433, Institute of Naval Medicine, Shanghai 200433, P. R. China. Laser Flash Photolysis Mechanism of Pyrenetetrasulfonate in Aqueous Solution. *Acta Phys.-Chim. Sin.* **2012**, *28* (04), 957–962. <https://doi.org/10.3866/PKU.WHXB201202203>.
- (65) Haga, M.; Dodsworth, E. S.; Eryavec, G.; Seymour, P.; Lever, A. B. P. Luminescence Quenching of the Tris(2,2'-Bipyrazine)Ruthenium(II) Cation and Its Monoprotonated Complex. *Inorg. Chem.* **1985**, *24* (12), 1901–1906. <https://doi.org/10.1021/ic00206a041>.
- (66) Holcman, J.; Sehested, K. Dissociation of the Hydroxyl Adduct of *N,N*-Dimethylaniline in Aqueous Solution. *J. Phys. Chem.* **1977**, *81* (20), 1963–1966. <https://doi.org/10.1021/j100535a017>.
- (67) Sundararajan, C.; Falvey, D. E. Photorelease of Carboxylic and Amino Acids from *N*-Methyl-4-Picolinium Esters by Mediated Electron Transfer. *Photochem. Photobiol. Sci.* **2006**, *5* (1), 116–121. <https://doi.org/10.1039/b511269a>.
- (68) *Principles of Fluorescence Spectroscopy*; Lakowicz, J. R., Ed.; Springer US: Boston, MA, 2006. <https://doi.org/10.1007/978-0-387-46312-4>.
- (69) Alqahtani, N. Z.; Blevins, T. G.; McCusker, C. E. Quantifying Triplet State Formation in Zinc Dipyrin Complexes. *J. Phys. Chem. A* **2019**, *123* (46), 10011–10018. <https://doi.org/10.1021/acs.jpca.9b08682>.
- (70) DeRosa, M. Photosensitized Singlet Oxygen and Its Applications. *Coord. Chem. Rev.* **2002**, *233–234*, 351–371. [https://doi.org/10.1016/S0010-8545\(02\)00034-6](https://doi.org/10.1016/S0010-8545(02)00034-6).

- (71) Constable, E. C.; Raithby, P. R.; Smit, D. N. The X-Ray Crystal Structure of Tris (2,2'-Bipyridine)Osmium(II) Hexafluorophosphate. *Polyhedron* **1989**, *8* (3), 367–369. [https://doi.org/10.1016/S0277-5387\(00\)80428-3](https://doi.org/10.1016/S0277-5387(00)80428-3).
- (72) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. Lifetimes, Spectra, and Quenching of the Excited States of Polypyridine Complexes of Iron(II), Ruthenium(II), and Osmium(II). *J. Am. Chem. Soc.* **1980**, *102* (4), 1309–1319. <https://doi.org/10.1021/ja00524a014>.
- (73) Wang, Y.; Gao, X.; Xiao, Y.; Zhao, Q.; Yang, J.; Yan, Y.; Huang, J. Temperature Dependent Coordinating Self-Assembly. *Soft Matter* **2015**, *11* (14), 2806–2811. <https://doi.org/10.1039/C4SM02717E>.
- (74) Tyson, D. S.; Henbest, K. B.; Bialecki, J.; Castellano, F. N. Excited State Processes in Ruthenium(II)/Pyrenyl Complexes Displaying Extended Lifetimes. *J. Phys. Chem. A* **2001**, *105* (35), 8154–8161. <https://doi.org/10.1021/jp011770f>.

6.8 Supporting Information for Organic photo(redox) catalyst with triplet-mediated energy and electron transfer reactivity (Section 2.2)

Electronic Supplementary Information for
**Converting *p*-terphenyl into a novel organo-catalyst for LED-driven
energy and electron transfer photoreactions in water**
M.-S. Bertrams and C. Kerzig

Contents

1	Experimental section	S2
1.1	General experimental details	S2
1.2	Synthetic procedures and characterization data	S4
2	Singlet and triplet excited states of SO₂TDS	S5
2.1	Singlet quenching of SO₂TDS	S5
2.2	Triplet lifetime	S6
2.3	LFP quenching studies with NDS	S7
2.4	LFP quenching studies with F-Cin	S7
2.5	ISC quantum yield of SO₂TDS	S8
3	SO₂TDS radical anion	S10
3.1	Radical anion formation	S10
3.2	Radical anion quenching by ACP	S11
4	Quantum-mechanical computations	S12
5	Energetic considerations	S14
6	Irradiation experiments	S15
6.1	Experimental setup	S15
6.2	Additional UV-Vis spectra	S17
6.3	Interactions with DTAC and SDS micelles	S19
6.4	Additional data and details for pinacol coupling reactions	S20
6.5	Additional data and details for isomerization reactions	S23
6.6	Benchmark reactions for comparison of water-soluble photocatalysts	S25
7	NMR spectra of TDS and SO₂TDS	S27
7.1	¹ H and ¹³ C NMR spectra of TDS	S27
7.2	¹ H, ¹³ C and 2D (¹ H, ¹³ C) NMR spectra of SO₂TDS	S29
8	Supplementary references	S31

Department of Chemistry
Johannes Gutenberg University Mainz
Duesbergweg 10–14, 55128 Mainz
Germany
E-mail: ckerzig@uni-mainz.de

1 Experimental section

1.1 General experimental details

All chemicals for optical for optical spectroscopy, preparative experiments and photocatalysis were obtained commercially in high purity and used without further purification (Table S 1).

Table S 1 List of substances used throughout the project, together with their purities and manufacturers.

Compound	Purity / %	Manufacturer
acetophenone (ACP)	>99	Aldrich
anisaldehyde	>99	TCI
4-benzoylbenzoic acid	99	Aldrich
4-(chloromethyl)benzoic acid	>98	TCI
<i>trans</i> -cinnamylalcohol	98	Aldrich
dodecyltrimethylammonium chloride (DTAC)	99	Aldrich
eosinY	100 weight %	Alfa Aesar
<i>trans</i> -3-fluorocinnamic acid (F-Cin)	98	Aldrich
fuming sulfuric acid	95-99	Fisher Scientific
<i>trans</i> -N-methylcinnamylamine	95	ChemBridge
4-methoxybenzyl alcohol	98	Aldrich
potassium acetate	97	Acros Organics
1-pyrenecarboxylic acid	97	Sigma Aldrich
<i>trans</i> -3-(4-pyridyl)acrylic acid	97	Alfa Aesar
sodium ascorbate (NaHAsc)	>99	Aldrich
sodium chloroacetate	98	Aldrich
sodium dodecyl sulfate (SDS)	99	Abcr
sodium hydroxide	>98	Aldrich
sodium 1,5-naphthalenedisulfonate (NDS)	98	TCI
sodium phosphate dibasic	>99	Aldrich
sodium phosphate monobasic monohydrate	>99	Aldrich
sulfuric acid	>95	Acros Organics
riboflavin (vitamin B2)	>98	Sigma Aldrich
<i>p</i> -terphenyl	>99	Acros Organics
trifluoro acetic acid (TFA)	99	Fluorochem
4-(trifluoromethyl)-acetophenone (CF ₃ -ACP)	98	Abcr
(<i>R/S</i>)(1-[4-(trifluoromethyl)phenyl]ethanol	96	Alfa Aesar
tris(2,2'-bipyridyl)dichlororuthenium(II) · 6 H ₂ O (Rubpy)	99.9	Sigma Aldrich

The solvent used for all synthetic reaction steps, optical spectroscopy and irradiation experiments was ultrapure Millipor MilliQ water (specific resistance 18.2 MΩ cm). Acetonitrile (99.9 %, VWR) and MeOH (>99.8%, HPLC grade from Fisher Chemicals) were used for purification purposes. The solutions for optical spectroscopy, except indicated otherwise, were purged with argon (4.8, PanGas or 5.0, Nippon Gases) or high-quality nitrogen from the general nitrogen supply of the university for 5 minutes before the measurements and sealed under inert gas (1 atm) in septum cap cuvettes.

NMR spectra of **SO₂TDS** and TDS were recorded on a *Bruker Avance III* 500 MHz or a *Bruker Avance II* 400 MHz at 298 K and for the irradiation experiments *Bruker Avance III* HD 300 MHz and *Bruker Avance II* 400 MHz instruments were used. The deuterated solvents for NMR experiments were used as follows: D₂O from Cambridge Isotope Laboratories, Inc. (99.5 %) or from DEUTERO (99.9 %), DMSO-*d*₆ from Cambridge Isotope Laboratories, Inc. (99.5 %, ¹³C NMR) and NaOD solution (40 wt% in D₂O 99.5 %) from Aldrich. ¹H NMR spectra in D₂O were referenced using the solvent peak (δ = 4.79 ppm). ¹³C NMR spectra measured

in DMSO-*d*₆ or D₂O were referenced using the solvent peak of DMSO-*d*₆ (δ = 39.39 ppm).¹ TFA was used as reference compound for ¹⁹F NMR spectroscopy (δ = -76.2 ppm).² ESI mass spectra were recorded on a Di-ESI-MS 8030 Plus instrument (Shimadzu).

Steady-state measurements

Absorption spectra were recorded using a Cary 5000 spectrophotometer from Varian or a LAMBDA 365 from Perkin Elmer. Emission measurements were carried out with a Fluorolog-3-22 from Horiba Jobin-Yvon or a FL-6500 from Perkin Elmer. All steady-state absorption and emission measurements were performed at room temperature (295 ± 2 K) and the emission spectra were corrected for the wavelength-dependent sensitivity of the respective emission spectrometer. Very low concentrations of the emissive compounds were employed to avoid filter effects.³

E_{0,0} energies were determined from the intersections of the respective absorption and emission spectra. The **fluorescence quantum yields** were measured against known standard compounds (*p*-terphenyl in cyclohexane³ for TDS and anthracene in EtOH³ for **SO₂TDS**). To avoid filter effects,³ the absorption was adjusted below 0.1 at the excitation wavelengths and in the overlap region of absorption and luminescence spectra. Emission spectra were measured at three different excitation wavelengths, out of which the average value was calculated. Finally, two correction factors were included: i) different refractive indices of the solvents and ii) different optical densities at the excitation wavelengths such that the following well-known formula (**Eqn. 1**)³ was used to determine the fluorescence quantum yields (ϕ ... quantum yield, I ... integrated luminescence intensity, A ... optical density at the excitation wavelength and n ... refractive index of the solvent; subscript "r" refers to the parameters of the reference compound):

$$\phi = \phi_r \frac{I}{I_r} \frac{A_r}{A} \frac{n^2}{n_r^2}$$

(Eqn. 1)

The fluorescence quantum yields so obtained are 0.98 ± 0.01 (TDS) and 0.48 ± 0.01 (**SO₂TDS**), both in argon-saturated aqueous solution.

Time-resolved measurements

The fluorescence lifetimes of TDS and **SO₂TDS** were recorded on a LifeSpec II spectrometer from Edinburgh Instruments (time-correlated single photon counting TCSPC technique) with a pulsed LED peaking at 313 nm as a light source.

For the laser flash photolysis (LFP) measurements an LP920-KS apparatus from Edinburgh Instruments was used. The energy of the 355 nm laser pulse (frequency-tripled Nd:YAG laser from Quantel with ~10 ns pulses) was modified by the Q-switch delay (5 mJ to 12 mJ). Kinetic traces were recorded at a single wavelength with a photomultiplier tube and for measuring transient absorption (TA) spectra an iCCD camera from Andor was employed. Depending on the signal-to-noise ratio, TA spectra were time-integrated between 10 and 100 ns. The **SO₂TDS** concentrations for LFP measurements were adjusted such that the absorptions of the aqueous solutions were between 0.03 and 0.1 at the laser wavelength 355 nm, corresponding to **SO₂TDS** concentrations between 6 μM and 18 μM. Control laser experiments on all suitable quenchers/substrates upon 355 nm excitation in the absence of **SO₂TDS** did not yield any quencher-/substrate-derived signals in the transient absorption traces.

The rate constants k_x for the pertinent decay processes of the singlet excited states of TDS and **SO₂TDS** (fluorescence and intersystem crossing) were calculated with the following formula (τ_{S1} ... lifetime of the excited singlet state and ϕ_x ...quantum yield of the decay process under study):³

$$k_x = \frac{\phi_x}{\tau_{S1}}$$

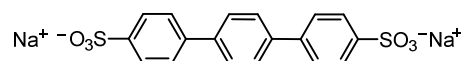
(Eqn. 2)

To determine quenching rate constants, **Stern-Volmer** analyses of the quenching experiments were performed. The τ_0/τ values from LFP or TCSPC studies were plotted against the concentration of the quencher. A linear fit with the intersection fixed at 1 yielded the Stern-Volmer constant (K_{SV}) and division by the known τ_0 lifetime of the respective excited state under given conditions resulted in the bimolecular quenching rate constant.³ All lifetimes used for kinetic analyses of bimolecular reactions were measured under pseudo first-order conditions and these lifetimes were derived by monoexponential fits. Examples are given in Figs. S 4 c) and S 6 b) (inset).

1.2 Synthetic procedures and characterization data

Disodium *p*-terphenyldisulfonate (TDS)

The synthesis of TDS has been reported recently by us,⁴ because we investigated its properties for photon upconversion in water. However, we largely reproduce the synthetic procedure in the following paragraph for clarity.



H₂SO₄ (95 %, 8.0 mL, 143 mmol, 7.1 eq.) was heated to 110 °C and *p*-terphenyl (4.60 g, 20.0 mmol, 1.0 eq.) was added portion-wise. After stirring for 4.5 h at 160 °C, the reaction mixture was allowed to cool to rt. H₂O (100 mL) was poured into the reaction mixture and the solution was filtered over Celite. The filtrate was adjusted to pH 6-7 (aq. NaOH, 1.75 M) and a precipitate formed. This mixture was then heated to 95 °C and upon addition of H₂O (1.0 L) a dim solution was obtained which was stirred overnight at 95 °C. Cooling to rt initiated precipitation of the product, which was filtered off and dried *in vacuo* yielding TDS as an off-white powder (6.86 g, 15.8 mmol, 79%). ¹H NMR data obtained in D₂O are in agreement with those presented in ref.⁵.

Further purification for optical spectroscopy was performed by dissolving a small amount of the crude product (100 mg, 230 μmol) in MilliQ water (10 mL) and heating to 95 °C until a clear solution was obtained. After cooling to rt a precipitate formed, which was filtered, washed with MilliQ water, and dried *in vacuo* to give TDS as a white solid (65 mg, 150 μmol, 65%).

For the NMR spectra of TDS, see Figs. S 23 – S 25.

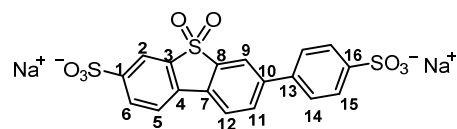
¹H NMR (500 MHz, 298 K, D₂O): δ = 7.93 – 7.88 (m, 12H) ppm.

¹H NMR (500 MHz, 298 K, DMSO-*d*₆): δ = 7.78 (s, 4H), 7.69 (s, 8H) ppm.

¹³C{¹H} NMR (126 MHz, 298 K, DMSO-*d*₆): δ = 147.5, 139.5, 138.8, 127.2, 126.2, 125.9 ppm.

ESI-MS (*m/z*): calcd. for C₁₈H₁₂O₆S₂ ([M-2Na⁺]): 194.0; found: 194.0.

Sulfone-bridged TDS (SO₂TDS)



A round bottom flask equipped with a magnetic stirring bar was evacuated and dried, sealed with a septum cap, and kept under inert atmosphere. Fuming sulfuric acid (1.0 mL, 18.8 mmol, 28.8 eq.) was added into the flask. *p*-Terphenyl (150 mg, 0.7 mmol, 1.0 eq.) was

added portion-wise under N₂ flow and the mixture was stirred for 3 h at 50 °C. After the reaction mixture was cooled to rt, MilliQ water (4.0 mL, cooled to ~10°C) was poured into the reaction mixture, the solution was filtered over Celite and washed with 1.0 mL of MilliQ water. The filtrate was adjusted to a pH of 6-7 (aq. NaOH, 3.0 M) and precipitation of a colourless solid was initiated. After 4 days of precipitation the solid was filtered off and washed with ice-cooled (0 °C) MilliQ water (2.0 mL) yielding an off-white solid (213 mg, 57 %). The reaction was carried out several times with similar yields. Further purification was performed by suspending 200 mg of the solid raw product in a 15 mL mixture of H₂O and MeOH (1:2) and after vigorous stirring for 30 min the solid was filtered off. The mother liquor was evaporated, and the white solid so obtained was dried at 35 °C under reduced pressure yielding a white solid (120 mg, 60 %; overall yield 34 %). NMR signals have been assigned using 2D NMR spectra (see Figs. S 26 – S 29).

¹H NMR (500 MHz, 298 K, D₂O): δ = 8.18 (d, 1H, J_{HH} = 1.8 Hz, **H2**), 8.05 (dd, 1H, J_{HH} = 8.1 Hz, J_{HH} = 1.8 Hz, **H6**), 7.98 (pseudo-s, 1H, **H9**), 7.88 (d, 1H, J_{HH} = 8.1 Hz, **H5**), 7.83 (m, 2H, **H14**), 7.81 (m, 1H, **H11**), 7.75 (d, 1H, **H12**), 7.64 (m, 2H, **H15**) ppm.

¹³C {¹H}NMR (126 MHz, 298 K, D₂O): δ = 145.4 (**C3**), 142.8 (**C16**), 142.3 (**C13**), 140.4 (**C10**), 136.9 (**C7**), 136.4 (**C4**), 133.3 (**C11**), 133.2 (**C1**), 132.2 (**C6**), 129.5 (**C8**), 127.1 (**C15**), 126.3 (**C14**), 123.1 (**C12**), 122.9 (**C5**), 120.4 (**C9**), 119.4 (**C2**) ppm.

¹³C {¹H}NMR (100 MHz, 298 K, DMSO-*d*₆): δ = 150.6, 148.3, 142.4, 138.5, 137.8, 136.9, 132.9, 131.6, 130.7, 129.5, 126.5, 126.4, 123.6, 122.8, 120.0, 118.8 ppm.

ESI-MS (*m/z*): calcd. for C₁₈H₁₀O₈S₃ ([M-2Na⁺]): 225.0; found: 225.0.

Elemental analysis of TDS and **SO₂TDS** could not be carried out owing to incomplete combustion of the salts. However, quantitative NMR experiments indicate that the water content of both terphenyl-derived compounds is below 10%.

2 Singlet and triplet excited states of **SO₂TDS**

2.1 Singlet quenching of **SO₂TDS**

To ensure that the triplet state is the key species for the photocatalytic activity of **SO₂TDS**, additional singlet quenching experiments were performed (Fig. S 1). The radical anion **SO₂TDS**^{•−} for the mechanistic studies on pinacol coupling reactions was generated through triplet state quenching by HAsc[−] (see main paper and Section 3), but the driving force for the corresponding ¹**SO₂TDS**^{*} reduction is much higher. Hence, we also investigated the quenching behaviour of ¹**SO₂TDS**^{*} in the presence of HAsc[−] (Fig. S 1). Our measurements of the singlet lifetime with increasing HAsc[−] concentrations yielded a linear Stern-Volmer plot and a diffusion-controlled quenching rate constant taking Coulombic repulsion into account ($2.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). Owing to the short lifetime of ¹**SO₂TDS**^{*} (as opposed to ³**SO₂TDS**), the actual efficiency of reductive singlet state quenching is below 20 % under the conditions employed for photocatalysis experiments (HAsc[−] concentrations between 10 mM and 20 mM). On the other hand, triplet quenching by HAsc[−] already occurs with an efficiency close to unity (> 99 %) at quencher concentrations as low as 0.3 mM. In addition to the kinetics that predict a predominant triplet photoreduction under our conditions, the small fraction of reductive singlet state quenching does not necessarily contribute to the overall formation of **SO₂TDS**^{•−}, given that the inherent yield of photoinduced electron transfer reactions with singlet states is usually low as a result of unproductive in-cage recombination.^{6–8} Quantitative LFP experiments monitoring the **SO₂TDS**^{•−} formation with different HAsc[−] concentrations (up to 20 mM) did not show a signal increase at higher quencher concentrations (i.e., under conditions with quantitative triplet quenching and additional singlet quenching). We, therefore, exclude productive quenching of ¹**SO₂TDS**^{*} by HAsc[−] in our system and the

catalyst triplet is indeed the key species (see main paper and Section 3.1 for its productive quenching by HAsc^-). Similar kinetic estimations and control experiments with the model substrate F-Cin revealed that $^3\text{SO}_2\text{TDS}$ is the key species for the lab-scale isomerization reactions as well.

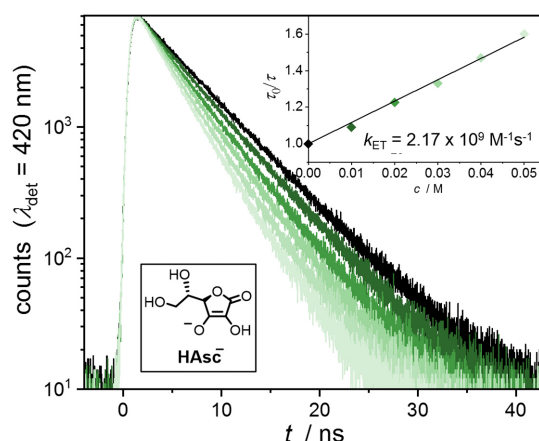


Fig. S 1 Lifetime changes of $^1\text{SO}_2\text{TDS}^*$ ($\lambda_{\text{exc}} = 313 \text{ nm}$ and $\lambda_{\text{det}} = 420 \text{ nm}$) in aqueous phosphate buffer (20 mM at pH 7.2) with increasing (lighter green) HAsc^- (sodium salt) concentrations. Inset: corresponding Stern-Volmer plot (same color code) and resulting quenching rate constant.

2.2 Triplet lifetime

In bimolecular quenching reactions with charged species, the concentration of ions in solution can modify the rate constant significantly. This so-called kinetic salt effect can be approximated by the Brønsted-Bjerrum equation and several studies address this effect in literature,^{9–15} but it is only valid at rather low ionic strengths of the solutions. For the LFP quenching experiments (see following sections), the solutions were usually prepared in phosphate buffer, such that the addition of the (ionic) quencher would not modify the ionic strength drastically, and the electron or energy transfer rate constant is not influenced by this effect. As expected, the lifetimes of $^3\text{SO}_2\text{TDS}$ also varied depending on the ionic strength (concentration of phosphate buffer and SO_2TDS itself) of the solution. Furthermore, with a long integration time and suppressing the detection of prompt fluorescence by a sufficiently long delay time, we detected delayed $^1\text{SO}_2\text{TDS}^*$ fluorescence in the time-gated emission spectra. This finding is indicative for triplet-triplet annihilation (TTA) of two $^3\text{SO}_2\text{TDS}$ species thereby adding a second order decay pathway, which is, however, rather inefficient under our conditions.

Both effects complicate the exact determination of the triplet lifetime. Keeping this in mind, the respective τ_0 values were determined individually before starting the LFP quenching experiments. Moreover, for all LFP experiments that required more than one sample, stock solutions containing the buffer and SO_2TDS (and HAsc^- for Section 3.2) were used such that the ionic strength within one series of measurements remained as equal as possible.

All unquenched triplet lifetimes that were measured throughout the LFP experiments exceeded 100 μs , which is why this value is given as lower limit for the lifetime of $^3\text{SO}_2\text{TDS}$ (Table 1 of the main paper).

2.3 LFP quenching studies with NDS

NDS is a known water-soluble triplet energy acceptor and has been investigated thoroughly concerning its triplet-triplet absorption spectrum, triplet energy and extinction coefficients.^{4,16–18} For a detailed analysis of the formed species observed in the TA spectrum upon 355 nm excitation of **SO₂TDS**, we performed LFP quenching experiments with NDS (Figs. S 2 and S 4). DFT calculations predict that the triplet energies are close (Sections 4 and 5) and therefore a triplet-triplet energy transfer (TTET) is thermodynamically possible. Initially we observed the decrease of the **³SO₂TDS** lifetime with increasing NDS concentrations and from the obtained data we performed a Stern-Volmer analysis and calculated a k_{TTET} of $7.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (Fig. S 2 b), c)). This TTET rate constant is three orders of magnitude below the diffusion limit ($\sim 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; for uncharged species)³ and a brief discussion of the TTET kinetics is given in Section 5. For the TA spectrum of **³NDS** measured after TTET from **³SO₂TDS**, see main paper and Fig. S 4.

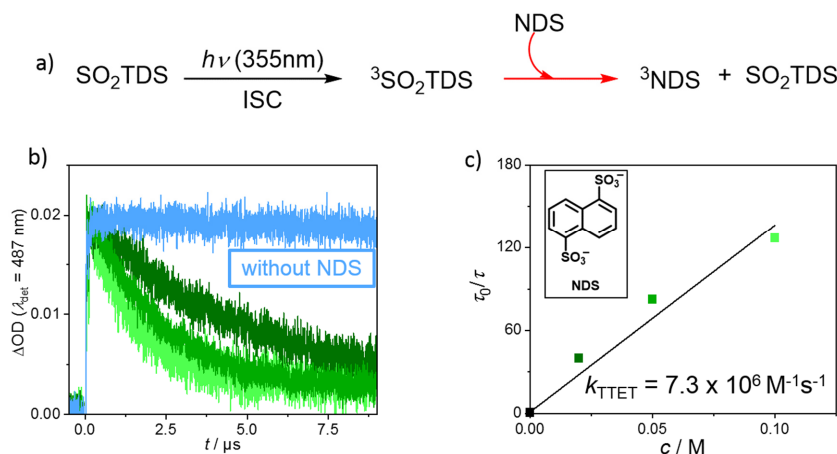


Fig. S 2 LFP quenching of **³SO₂TDS** with NDS: a) Reaction scheme with excitation wavelength (355 nm, 8 mJ) and the observed quenching reaction indicated by the red arrows. b) Kinetic traces monitoring **³SO₂TDS** at 487 nm without NDS (blue) and with increasing NDS concentrations (high concentrations correspond to lighter green). c) Stern-Volmer plot, together with the resulting quenching constant k_{TTET} . For a TA spectrum of the quenching product **³NDS**, see main paper or Fig. S 4. All solutions (10 mM phosphate buffer at pH 7.2) were degassed with Ar for 5 min.

2.4 LFP quenching studies with F-Cin

Having established the optical properties of the **³SO₂TDS** species with LFP studies, we further investigated the quenching of this triplet excited state by F-Cin. In the irradiation experiments we observed a *cis/trans* isomerization leading to a photostationary state (see main paper and Section 6.5). Previously (Section 2.1), we established that **¹SO₂TDS*** is not quenched by F-Cin employed at concentrations of a few mM, which is why the triplet excited state was suggested to initiate the isomerization with a TTET as the underlying mechanism. LFP quenching studies confirmed this hypothesis and efficient triplet quenching was indeed observed: The lifetime of **³SO₂TDS** (after direct excitation of **SO₂TDS** at 355 nm and ISC, see Fig. S 3) was monitored at the absorption maximum ($\lambda_{\text{det}} = 485 \text{ nm}$) in the absence of a quencher (blue trace) and with increasing quencher concentration (F-Cin, red traces, Fig. S 3 c). The lifetimes were analysed using a Stern-Volmer plot and a rate constant for the TTET ($k_{\text{TTET}} = 1.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) close to the diffusion limit was extracted. Additional TA spectra after a time delay of 6 μs did not show any absorbing species, which is in line with complete

$^3\text{SO}_2\text{TDS}$ quenching (see black trace in the inset of Fig. S 3 c)). The expected quencher-derived product, $^3\text{F-Cin}$, could not be detected, indicating that the triplet of this olefinic substrate is a short-lived species. Similar observations have been made for (perpendicular) triplets of other compounds containing isomerizable double bonds.¹⁹

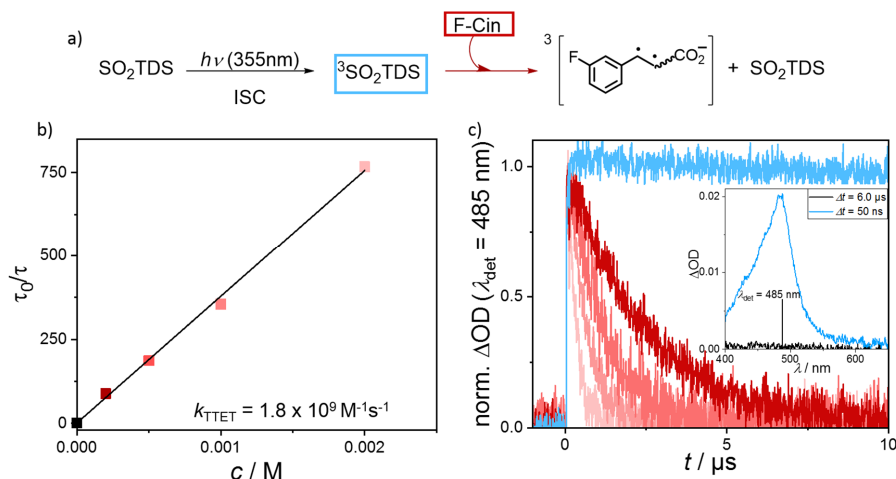
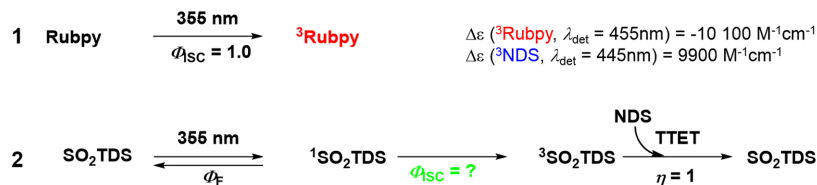


Fig. S 3 LFP quenching of $^3\text{SO}_2\text{TDS}$ with F-Cin: a) Scheme of the reaction sequence under investigation with the observed quenching reaction highlighted with red arrows. b) Stern-Volmer plot of the quenching experiments with increasing F-Cin concentrations (lighter color). c) Main plot: Kinetic traces (excitation at $\lambda_{\text{exc}} = 355\text{ nm}$, 9 mJ) detected at $\lambda_{\text{det}} = 485\text{ nm}$ of the unquenched (blue) $^3\text{SO}_2\text{TDS}$ with increasing F-Cin concentrations (high concentrations correspond to lighter color). Inset: TA spectra of $^3\text{SO}_2\text{TDS}$ with 0.5 mM F-Cin measured after a time delay of 50 ns (blue) and 6.0 μs (black). All aqueous solutions (50 mM phosphate buffer at pH 7.2) were degassed with Ar for 5 min prior to the experiments.

2.5 ISC quantum yield of SO_2TDS

The unknown ISC quantum yield (ϕ_{ISC}) of SO_2TDS was estimated with a Rubpy (ruthenium-tris(2,2'-bipyridin)) reference sample ($\phi_{\text{ISC}} = 1$)²⁰ employing relative actinometry.^{16,21} Both solutions were adjusted to an absorption of about 0.1 at the excitation wavelength ($\lambda_{\text{exc}} = 355\text{ nm}$, slight differences will be considered later in this section) ensuring practically identical concentrations of (singlet) excited states right after the laser pulse. The exact triplet state concentrations can be calculated with the *Beer-Lambert* law using the TA absorption signal(s), but this is only possible for compounds with known extinction coefficients of the triplet-excited species. For Rubpy the $\Delta\epsilon$ (i.e. the difference extinction coefficient between ground and triplet state) at $\lambda_{\text{det}} = 455\text{ nm}$ is literature known ($\sim 10\,000\text{ M}^{-1}\text{cm}^{-1}$),^{22,23} whereas such data set for $^3\text{SO}_2\text{TDS}$ is unavailable as this species has not been observed so far. For converting $^3\text{SO}_2\text{TDS}$ into an intermediate that can be quantified, we used NDS present at high concentrations as triplet energy acceptor with a known $\Delta\epsilon = 9900\text{ M}^{-1}\text{cm}^{-1}$ at $\lambda_{\text{det}} = 445\text{ nm}$.¹⁶ We established that NDS does not absorb at the excitation wavelength¹⁶ ($\lambda_{\text{exc}} = 355\text{ nm}$; compare, absorption spectra shown in Section 6.2) but quenches $^3\text{SO}_2\text{TDS}$ such that the detected ^3NDS in solution can only originate from a TTET (Scheme S1).



Scheme S1 Reaction scheme for relative actinometry with the Rubpy (1) reference system and the solution with SO₂TDS and NDS (2) as triplet energy acceptor with known extinction coefficient of the triplet excited state. The unknown ϕ_{ISC} is highlighted in green.

With that methodology, we can assume that the initial concentration of ³SO₂TDS right after ISC equals the ³NDS concentration (after quenching) under the given conditions ensuring quantitative TTET (> 99 %). This not only allows the indirect calculation of the quantum yield of ³SO₂TDS but also the determination of the extinction coefficient of that species:

The ratio of the triplet quantum yields equals the ratio of the concentrations of the triplet excited species, which again can be determined using the *Beer-Lambert* law. Thus, the following equation (**Eqn. 3**) can be used for estimating ϕ_{ISC} of SO₂TDS:

$$\frac{\phi_{ISC}^{SO_2TDS}}{\phi_{ISC}^{Rubpy}} = \frac{[{}^3SO_2TDS]}{[{}^3Rubpy]} = \frac{[{}^3NDS]}{[{}^3Rubpy]} \Rightarrow \phi_{ISC}^{SO_2TDS} = \phi_{ISC}^{Rubpy} \frac{[{}^3NDS]}{[{}^3Rubpy]}$$

(Eqn. 3)

The values for the optical densities ΔOD were obtained directly from the kinetic transient absorption traces (Fig. S 4 arrows in b) and c)). As already seen in **Eqn. 1** for a related method, a correction for the known, but slightly different (ground-state) absorptions at the excitation wavelength was considered. The final value for ϕ_{ISC} of SO₂TDS including the correction factor ($\times 1.11$) amounts to 34.4 %.

Assuming that [³SO₂TDS]=[³NDS] we were able to estimate an extinction coefficient of triplet-excited SO₂TDS at the detection wavelength 487 nm: $\Delta\epsilon = 20\,900\text{ M}^{-1}\text{cm}^{-1}$.

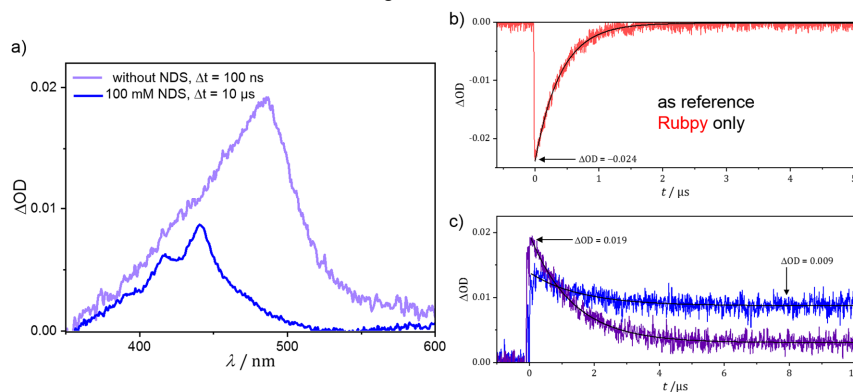


Fig. S 4 Quantitative LFP measurements for calculating ϕ_{ISC} and $\Delta\epsilon$ of ³SO₂TDS. The excitation wavelength for all spectra and kinetic traces was $\lambda_{exc} = 355\text{ nm}$ with a constant laser energy of 8 mJ. The solutions were prepared in aqueous NaOH (10 mM) and purged for 5 min with Ar: a) TA spectrum of ³SO₂TDS (purple, 100 ns time delay) without NDS and in the presence of 100 mM NDS (blue, 10 μs time delay). b) Kinetic trace monitoring the Rubpy bleach recovery at 455 nm. c) Kinetic traces upon excitation of SO₂TDS in the presence of NDS (100 mM, same solution as in part a) of the Fig.) detected at 487 nm (purple trace, ³SO₂TDS decay) and at 445 nm (blue trace, ³NDS formation). The ΔOD values used for the quantum yield calculations were taken from the kinetic traces. Arrows in b) and c) point to the positions that were selected to determine those values. For further explanations, see text.

3 SO₂TDS radical anion

3.1 Radical anion formation

Besides the observed TTET donor reactivity, our catalyst shows electron transfer reactivity in the presence of the reductive quencher ascorbate HAsc[−] (see main paper). The corresponding LFP studies confirming reductive triplet state quenching and the formation of **SO₂TDS^{•−}** are presented in this section. Upon excitation (355 nm) **³SO₂TDS** is formed, which is subsequently reduced by HAsc[−] as sacrificial donor forming the radical anion as indicated by the characteristic spectrum displayed in part a) of Fig. S 5 (purple spectrum). This spectrum shows two absorption maxima ($\lambda_{\text{max}} = 485 \text{ nm}$ and 700 nm) of similar intensities and the additional absorption band in the red/NIR region (compared to **³SO₂TDS**) is indicative of radical anion formation.²⁴ The formation rate constant for this species was determined by monitoring the **³SO₂TDS** lifetime decrease upon HAsc[−] addition followed by a Stern-Volmer analysis. Both species, the triplet and the radical anion show an absorption band with a maximum around 485 nm but with different extinction coefficients, which is why the kinetic traces of the triplet do not entirely decrease back to the baseline after the quenching process. A rate constant slightly below the diffusion limit ($9.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) was determined at the detection wavelength 485 nm (triplet decay). As a further control experiment, we monitored the formation kinetics of the radical anion at 700 nm (Fig. S 5 c), top), which gave practically the same rate constant for reductive quenching as observed at 485 nm. However, owing to the higher sensitivity of the employed TA instrument at the latter detection wavelength and the resulting much better data quality, we used the kinetic traces recorded at 485 nm for the Stern-Volmer analysis presented in part b) of Fig. S 5.

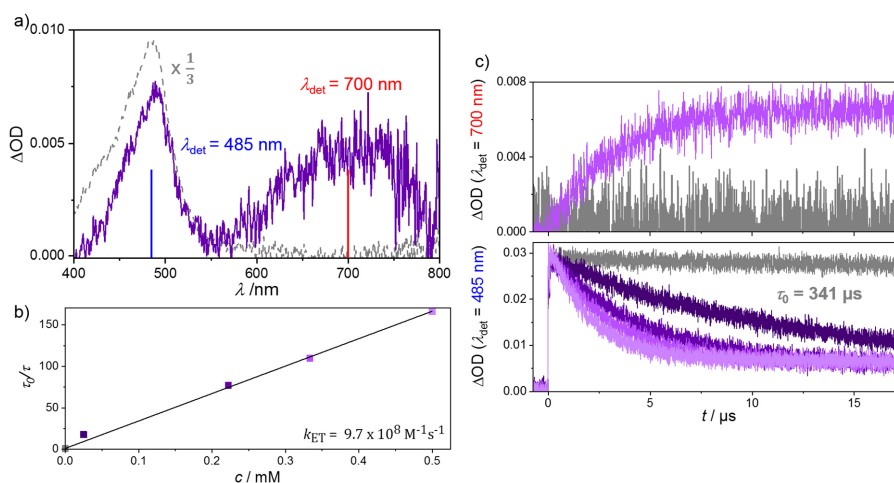


Fig. S 5 LFP experiments on the formation of **SO₂TDS^{•−}** ($\lambda_{\text{exc}} = 355 \text{ nm}$, 6 mJ): a) TA spectrum of the radical anion (aq. solution with **SO₂TDS**, 5 mM HAsc[−] and 10 mM phosphate buffer at pH 7.2, 5 μs time delay) in purple with **³SO₂TDS** (grey dashed line) for comparison as well as the detection wavelengths of the kinetic traces displayed in part c) of the Fig. b) Stern-Volmer plot and resulting rate constant of the electron transfer (ET) reaction. c) Bottom: Kinetic traces of triplet quenching at $\lambda_{\text{det}} = 485 \text{ nm}$ with increasing concentrations of HAsc[−] (color code as in b)) as well as the unquenched triplet lifetime (grey trace). Top: Sample kinetic trace showing radical anion formation at $\lambda_{\text{det}} = 700 \text{ nm}$, same color code as in b). Only one trace in the presence of HAsc[−] is shown for clarity. For further explanations, see text.

3.2 Radical anion quenching by ACP

For the final confirmation of the reaction mechanism and $\text{SO}_2\text{TDS}^{\bullet-}$ as catalytically active species, we aimed to find spectroscopic evidence of the intermediate produced by the reaction between ACP and the SO_2TDS radical anion. The TA spectrum of the expected intermediate, the $\text{ACP}^{\bullet-}$ species,^{25,26} is well known at basic pH. However, under our usual reaction conditions (neutral solution) $\text{ACP}^{\bullet-}$ is in a fast equilibrium with the protonated ketyl radical $\text{ACPH}^{\bullet}$ ($pK_a = 9.6$ ^{25,26}, part a) of Fig. S 6). The latter is thus the predominant species at pH ~ 7 . This neutral ACP-derived radical absorbs in the UV region (< 350 nm) overlapping with HAsc^- and corresponding quenching or related decomposition products,¹⁶ as well as with SO_2TDS . Thus, detection of the $\text{ACP}^{\bullet-}$ or $\text{ACPH}^{\bullet}$ is not possible under the standard reaction conditions of the irradiation experiments. Initially, we analyzed the bimolecular quenching of the SO_2TDS radical anion by ACP at pH 7 yielding the expected linear Stern-Volmer plot and a rate constant of $4.9 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (Fig. S 7). The TA spectra completely return to the baseline in the visible region (Fig. S 6 b) and Fig. S 7 b)), as expected for the formation of $\text{ACPH}^{\bullet}$ as final quenching product (compare, Fig. S 6 a)). This situation changes completely at pH 12; under these conditions, the delayed TA spectra show a new absorption band at 445 nm (Fig. S 6 c)), which corresponds to the ACP radical anion as the product of the reaction with $\text{SO}_2\text{TDS}^{\bullet-}$. Because of a noticeable extinction coefficient of Asc^{2-} , which is the predominant ascorbate species at pH 12,¹⁵ at our laser wavelength (355 nm), we reduced the overall ascorbate concentration for these measurements on alkaline solutions, and we were indeed able to observe the reaction sequence presented in Fig. S 6 a).

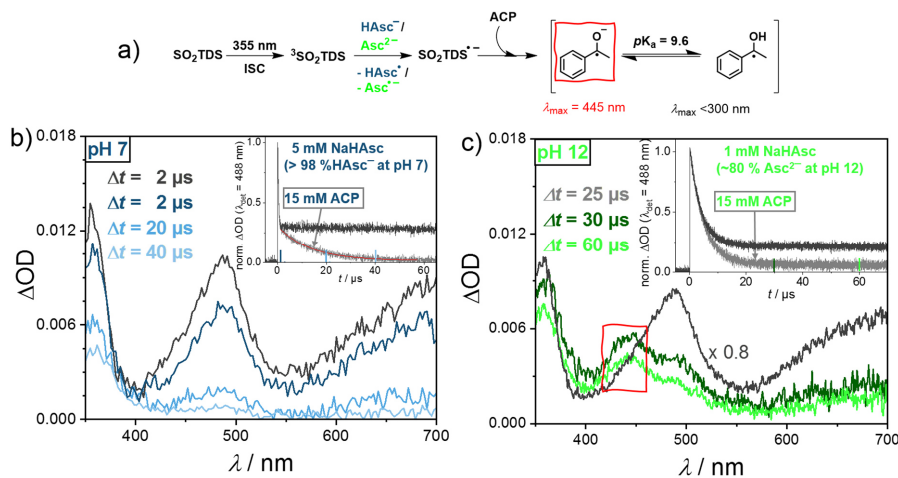


Fig. S 6 Detection of the ACP radical anion^{25,26} with pH-dependent LFP experiments: a) Reaction sequence at pH 7 (HAsc^-) and pH 12 (Asc^{2-}), molecular structure of the ACP radical anion intermediate (red frame), and the pK_a for the equilibrium with the protonated ketyl radical. b) Main plot: TA spectrum of $\text{SO}_2\text{TDS}^{\bullet-}$ at pH 7 (grey) and TA spectra under the same conditions but with ACP (15 mM) added and measured at different delay times (dark blue to light blue). Inset: Kinetic traces monitoring $\text{SO}_2\text{TDS}^{\bullet-}$ with (light grey, red line indicates a monoexponential fit) and without ACP (dark grey) with the detection delay times (vertical lines) of the TA spectra in the same color code as in the main plot. c) TA spectrum of $\text{SO}_2\text{TDS}^{\bullet-}$ at pH 12 in grey and TA spectra under the same conditions with ACP added, but at different delay times (dark green, 30 μs and light green, 60 μs). In addition to the $\text{SO}_2\text{TDS}^{\bullet-}$ absorption bands at 488 nm and 700 nm, we observed a new species in the green spectra with a maximum at 445 nm (red frame), which corresponds to the ACP radical anion. Inset: Kinetic traces monitoring $\text{SO}_2\text{TDS}^{\bullet-}$ (dark grey) and its quenching by ACP (light grey). Ascorbate-derived species do not absorb above 400 nm. The initial fast signal decay at 485 nm is due to SO_2TDS triplet quenching. Triplet quenching is well-separated from $\text{SO}_2\text{TDS}^{\bullet-}$ quenching in neutral solution (i.e., under the conditions of Fig. S 7 as well), whereas both quenching processes cannot be separated in alkaline solution. See text for details.

The fact that the $\text{SO}_2\text{TDS}^{\bullet-}$ absorption bands persist to some extent in the green spectra of part c) in Fig. S 6 (i.e., in the presence of ACP) implies a reversibility of the electron transfer between $\text{SO}_2\text{TDS}^{\bullet-}$ and ACP.

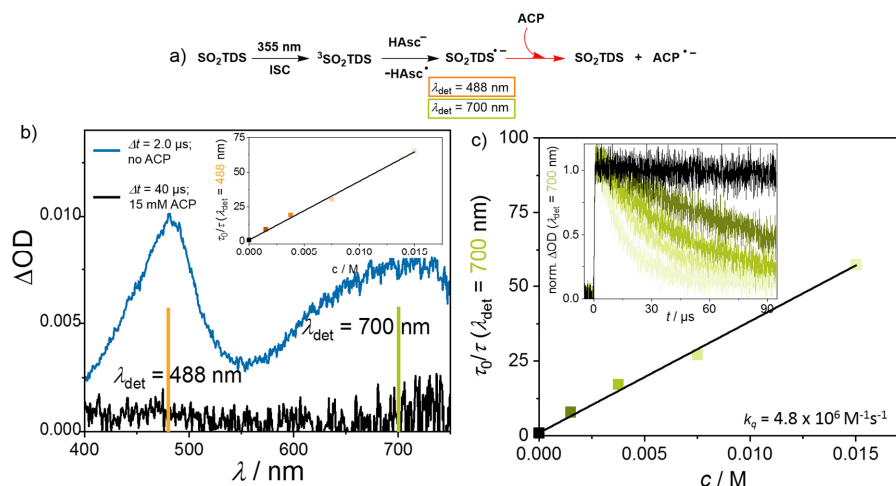


Fig. S 7 Kinetic studies on the reaction between $\text{SO}_2\text{TDS}^{\bullet-}$ and ACP: a) Reaction scheme with the observed quenching step highlighted by red arrows. b) Main plot: TA spectrum of the radical anion (blue trace, time delay 2 μs , without ACP) and after the addition of 15 mM ACP (black trace, time delay 40 μs ; ACP-derived quenching products cannot be observed at neutral pH, which is in perfect agreement with ACP radical anion protonation as displayed in Fig. S 6 a) with the detection wavelengths as vertical lines. Inset: Stern-Volmer analysis of the $\text{SO}_2\text{TDS}^{\bullet-}$ quenching detected at $\lambda_{\text{det}} = 488 \text{ nm}$ ($k_q = 4.9 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$). c) Main plot: Stern-Volmer plot and corresponding kinetic traces (inset) detected at $\lambda_{\text{det}} = 700 \text{ nm}$ ($k_q = 4.8 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$). All solutions were prepared in aq. phosphate buffer (200 mM, pH 7.2) and a standardized $\text{HAsc}^{\bullet-}$ concentration (5.0 mM) was employed.

4 Quantum-mechanical computations

All DFT calculations were carried out with the Gaussian 09 software package²⁷ using the B3LYP functional in combination with the 6-31+G(d,p) basis set. The solvation model was IEFPCM with water as solvent. The geometry optimizations of *p*-terphenyl and the derivatives under study were accompanied by frequency analyses. The optimized structures used for further computations did not show negative vibrational frequencies, indicating convergence on minimum structures. The frontier orbitals of the singlet ground states were obtained by additional single-point calculations with population analyses, and time-dependent DFT computations with identical functional and basis were used to calculate vertical excitation energies as well as oscillator strengths.

Starting from the energy-minimized singlet ground state geometries, the corresponding lowest triplet states and radical anions were calculated. The triplet state energies were determined simply by comparing the energies of both optimized structures (i.e., singlet ground state and triplet state) for a given compound.^{14,28–30} Optimized structures, frontier orbitals and spin densities for the relevant intermediates derived from *p*-terphenyl, TDS and SO_2TDS are displayed in Fig. S 8 and Fig. S 9. Pertinent energies are summarized in Table S 2. All results clearly indicate that the computed and experimental (see main paper) properties for *p*-terphenyl and TDS are almost identical. Computationally, SO_2TDS shows substantial differences in terms of spin density and orbital coefficient distributions, orbital energies as well as vertical excitation energies. The smaller HOMO-LUMO gap for SO_2TDS (and the lower $E_{0,0}$ accordingly) can be explained by a significant LUMO stabilization owing to the sulfone group, as our comparative orbital energy analysis revealed.

Table S 2 Pertinent computed energies (in eV) and oscillator strengths for TDS and **SO₂TDS** relative to those of the parent compound *p*-terphenyl.

	<i>p</i> -terphenyl	TDS	ΔE (TDS) ^[e]	SO₂TDS	ΔE (SO₂TDS) ^[e]
$E_{0,0}$ (DFT) ^[a]	4.17	4.02	-0.15	3.56	-0.61
$E_{0,0}$ (exp.) ^[b]	3.99	3.75	-0.24	3.37	-0.62
ΔE (HOMO-LUMO) ^[c]	4.61	4.49	-0.12	4.10	-0.51
f (HOMO-LUMO) ^[d]	1.06	1.38	+0.32	0.66	-0.40
E_T	2.62 ^[f]	2.60	-0.02	2.47	-0.15

[a] Vertical excitation energies. [b] Experimental results, see Fig. 1 and Table 1 of the main paper for details. [c] HOMO-LUMO gap. [d] Oscillator strength of the HOMO-LUMO transition. [e] Comparison with *p*-terphenyl. [f] Experimental triplet energy, 2.53 eV.³

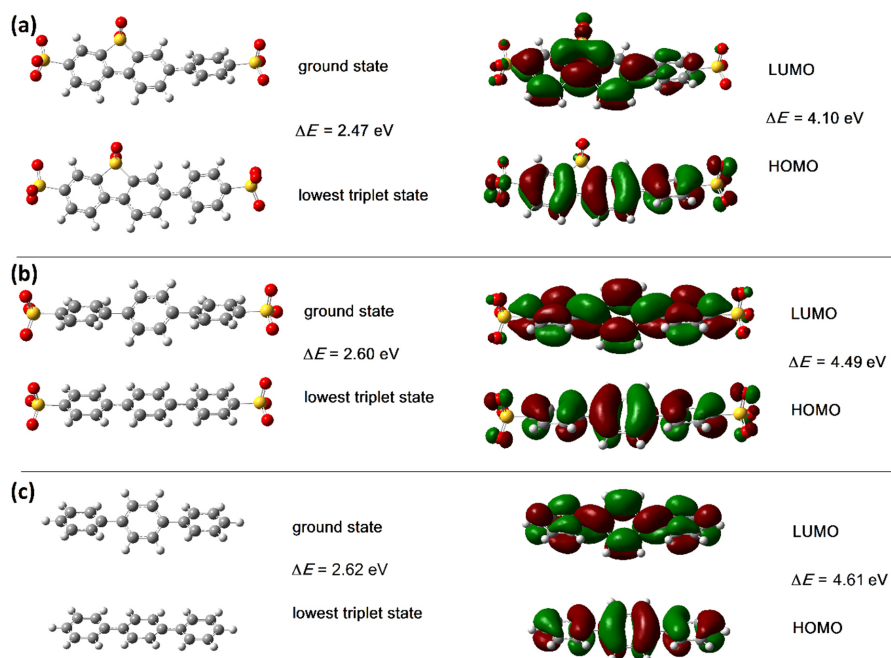


Fig. S 8 Left: Optimized structures of the ground states as well as the lowest triplet states of **SO₂TDS** (a), TDS (b) and *p*-terphenyl (c) at the B3LYP/6-31+G(d,p) level of theory and the solvation model IEFPCM for water, together with their corresponding energy differences. Right: Frontier orbitals of the ground states using the same computational method. See text for details.

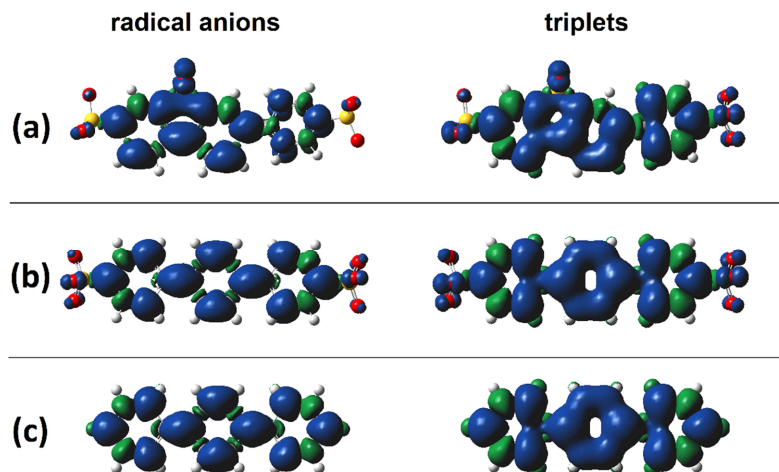


Fig. S 9 Computed spin densities (B3LYP/6-31+G(d,p), solvation model IEFPCM for water) for the optimized radical anion (left) and triplet (right) structures of **SO₂TDS** (a), **TDS** (b) and *p*-terphenyl (c). Blue color represents positive spin densities, whereas green represents negative spin densities. See text for details.

5 Energetic considerations

The energies of the **excited singlet states** were determined experimentally from the intersections of the absorption and fluorescence spectra of the respective terphenyl derivatives (Table 1 of the main paper). The predicted energies from DFT calculations (compare, Table S 2 in Section 4) are too high by about 0.2 eV, but they clearly support the experimentally observed trends. In principle, the triplet energies can be extracted from low-temperature emission spectra, but the low ISC quantum yield of TDS and the poor glass formation ability of water hamper such triplet energy determinations.

To obtain the **triplet energy** (E_T) of our catalyst **SO₂TDS**, we took the DFT calculated E_T (2.47 eV) and considered the results of our quenching experiments with well-characterized energy acceptors. Dexter energy transfer (TTET) reactions can proceed with diffusion-controlled kinetics for $E_T(\text{donor}) > E_T(\text{acceptor})$, or they can proceed in an activation-controlled fashion with rate constants significantly below the diffusion limit.³¹ From the quenching with NDS ($E_T(\text{NDS}) = 2.58 \text{ eV}$)³² as acceptor we determined a rate constant for the energy transfer three orders of magnitude below the diffusion limit (see Section 2.3) indicating an “uphill” energy transfer, which is endergonic by 0.11 eV based on our DTF calculations. The relation between the triplet energy difference and the (uphill) Dexter energy transfer kinetics is well established.^{19,33} Assuming $1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ as the diffusion rate constant for the reaction between two dianionic species in our reaction medium and the above-mentioned ΔE_T (0.11 eV), an energy transfer rate of $1.1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ can be calculated, which is very close to the experimental value ($7.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$).

Moreover, the LFP quenching studies with F-Cin also confirm the $E_T(\text{SO}_2\text{TDS})$ obtained from DFT calculations. The triplet energy of F-Cin is on the order of 2.4 eV.^{3,34} Hence, the energy transfer from **³SO₂TDS** to F-Cin is exergonic by about 0.1 eV, and we indeed observed diffusion-controlled energy transfer kinetics (see Section 2.4). All these experimental results strongly support the calculated $E_T(\text{SO}_2\text{TDS}) = 2.47 \text{ eV}$, and this value was used for an estimation of the **SO₂TDS** reduction potential, as described in the next paragraphs.

The **redox potential** for the reduction of **SO₂TDS** was not measured directly due to the difficulties associated with (reductive) cyclic voltammetry in water. However, we estimated that quantity using a comparative method. We rely on studies concerning the Rehm-Weller equation, which describes the relation between the energetics of a photoinduced electron transfer reaction and the corresponding rate constant.^{35,36} Our LFP investigations gave a k_{ET} for the reduction of **³SO₂TDS** with HAsc[−] of about $1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (see Section 3.1). The reductive quenching of singlet-excited **SO₂TDS** by HAsc[−] (Fig. S 1), which has to be strongly exergonic owing to the high singlet-state energy of **SO₂TDS**, is more than twice as fast and we regard that value ($2.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) as the diffusion limit for a reaction between a dianionic compound and a monoanionic quencher.^{12,37} Electron transfer reactions with rate constants slightly below the diffusion limit, as measured for the reduction of **³SO₂TDS**, usually have a driving force approaching zero, i.e. $\Delta G \sim 0 \text{ eV}$.^{35,38,39} This Gibbs energy for photoinduced electron transfer reactions (with triplet-excited states) is composed of four energies/potentials of the reactants and described by the following formula:^{6,35}

$$\Delta G = E_{1/2}(D) - E_{1/2}(A) - E_T(A) + E_{Coul}$$

(Eqn. 4)

With ΔG as the Gibbs energy, $E_{1/2}$ as the redox potential of the electron donor (D, HAsc[−]) or acceptor (A, **SO₂TDS**), the triplet energy of the acceptor $E_T(A)$ as well as a coulomb term E_{Coul} (which is very close to zero due to the involvement of the uncharged HAsc[•] and the highly polar solvent water).^{3,16} With the previous assumption of $\Delta G = 0 \text{ eV}$, $E_T(\text{SO}_2\text{TDS}) = 2.47 \text{ eV}$, $E_{1/2}(\text{HAsc}^-/\text{HAsc}^\bullet) = 0.72 \text{ V vs. NHE}$ ⁴⁰ and after rearranging (Eqn. 4), the reduction potential of **SO₂TDS** can be estimated: it amounts to -1.75 V vs NHE . This estimation does only depend on a redox potential of a well-investigated reference system (ascorbate in water), excited-state energies and rate constants that have been directly measured in water. We, therefore, regard our comparative procedure as more reliable than measuring the presumably highly solvent dependent reduction potential of **SO₂TDS** in an organic solvent. Interestingly, the SOMO of the *p*-terphenyl radical anion (redox potential, -2.39 V vs. NHE)⁴¹ is higher in energy than that of **SO₂TDS^{•−}** by about 0.7 V . The relative SOMO energies of radical anions should reflect their electron donating abilities. Given that, these DFT-calculated properties of the radical anions support the redox potential estimations. The latter predict **SO₂TDS^{•−}** to be less reactive by 0.64 V compared to the *p*-terphenyl radical anion, as presented above. This reactivity difference seems reasonable considering the electron-withdrawing effects of the sulfur-containing groups in **SO₂TDS**.

6 Irradiation experiments

6.1 Experimental setup

All irradiation experiments were performed under inert atmosphere, either in sealed NMR tubes (solvent D₂O) or in substance vials under Ar atmosphere (solvent H₂O). The quantitative analyses of the NMR spectra for the irradiation experiments were carried out by adding well-defined amounts of reference compounds (sodium chloroacetate, trifluoroacetic acid or potassium acetate). Some of the products formed throughout the irradiation experiments are more hydrophobic than the starting compounds and precipitated in our system, thereby hampering a reliable analysis. To avoid solubility-related errors in the NMR analysis originating from such precipitations, several reactions were performed using micelle-forming surfactants (SDS or DTAC). The characteristic NMR signals of the *cis* isomers formed during the isomerization reactions (Section 6.5) allowed straightforward product identification and quantification. The identification of the desired pinacol products (Section

-S15-

6.4) as well as the differentiation between pinacol and monomeric alcohol was carried out with reference spectra from the literature^{4,38,42} or with authentic reference substances. Details concerning our photoirradiation setup and product analyses are given below.

Preparation of sealed substance vials (Fig. S 10 a): The reaction mixtures (substrate, 50 mM phosphate buffer, reference compound, DTAC if necessary, **SO₂TDS**) were dissolved in H₂O (3.0 - 4.0 mL), purged with Ar for 3 min within a substance vial, which was sealed using a septum cap. Throughout the irradiation, the vials were connected to the Schlenk line and kept under a constant Ar pressure. The vials were kept in a water bath to ensure ambient temperature, stirred with a magnetic stirrer, and placed closely to the LED. For the NMR measurements, small samples of the reaction mixture were removed and 10 vol. % D₂O (with TFA as reference for ¹⁹F NMR measurements) were added.

Preparation of sealed NMR tubes (Fig. S 10 b): The reaction mixtures (substrate, 50 mM phosphate buffer, reference compound, additives such as DTAC or SDS) were dissolved in D₂O (2.5 mL). The resulting solution was used to prepare two septum-sealed Schlenk flasks (1.0 mL), and **SO₂TDS** was added to one of them. The reaction mixtures were degassed by two freeze-pump-thaw cycles using Ar as inert gas, liquid N₂ for cooling and Schlenk line vacuum (down to 0.5 mbar). Under a flow of Ar gas, NaHAsc was added and after a final freeze-pump-thaw cycle, the Schlenk flask was set under an Ar atmosphere. The NMR tubes were evacuated and flushed with Ar three times. An aliquot of the reaction mixture (0.5 mL) was transferred into the prepared NMR tubes, which then were sealed either with a septum cap or melted off after oxygen removal. To maintain the Ar atmosphere throughout the reaction time, the septum-sealed NMR tubes were connected to the Schlenk line and kept under a constant Ar pressure. During the NMR measurements, the tubes had to be disconnected from the Schlenk line for a short time (max. 20 min). Overnight irradiation experiments were carried out with an Ar gas reservoir to maintain the inert atmosphere. Two NMR tubes were placed in a water bath closely to the LED during photoirradiation, as displayed in Fig. S 10 b).

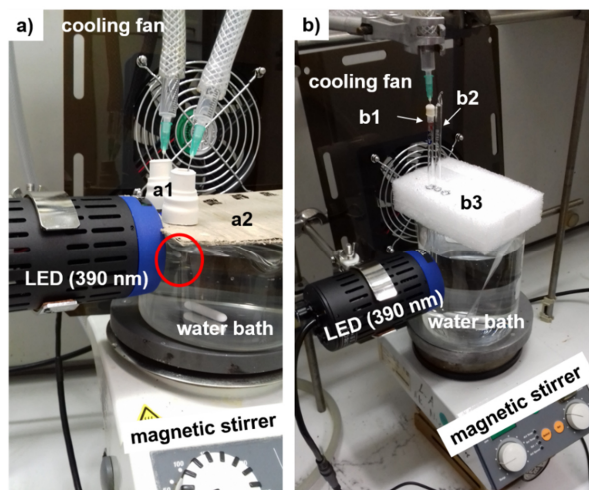


Fig. S 10 Experimental setup for the photoreactions performed in substance vials a) or in NMR tubes b). The samples were placed in custom-made holders (**a2** or **b3**) in front of the 390 nm (or 370 nm) LED. The water bath provided ambient temperature and for longer reaction times (> 2h) the cooling fan was used in addition. a) Substance vials sealed with a septum cap (**a1**) and equipped with a stirring bar (red circle). The vials have been connected to a Schlenk line (Ar). b) NMR tubes sealed with a septum cap and connected to a Schlenk line (**b1**) or flame-sealed under vacuum (**b2**).

6.2 Additional UV-Vis spectra

The following three figures display the absorption spectra of the compounds used for the NMR-scale reactions, pinacol coupling or dechlorination (Fig. S 11) and isomerization reactions (Fig. S 12), as well as the compounds relevant for optical spectroscopy (Fig. S 13). The buffer systems/concentrations were chosen to resemble the respective conditions of the sample reactions or LFP measurements. All compounds are fully transparent in the emission range of the 390 nm LED used for photocatalysis and at 355 nm, the excitation wavelength for LFP experiments. The only exception is the ascorbate dianion (Fig. S 13) with a very low molar absorption coefficient at 355 nm,¹⁵ which was therefore used in low concentrations (for further explanations, see Section 3 and Fig. S 6).

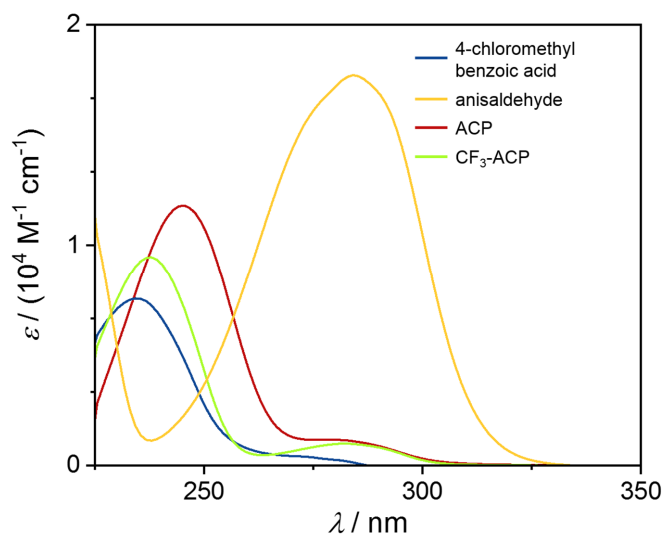


Fig. S 11 Absorption spectra of the carbonyl compounds for the pinacol coupling reactions, measured in 50 mM phosphate buffer (pH 7.2) and the substrate used for the dechlorination, measured in 10 mM Na_2HPO_4 .

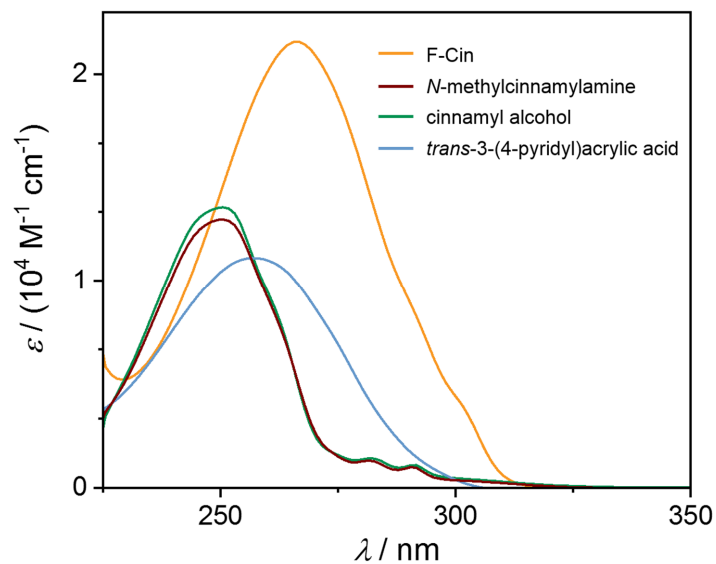


Fig. S 12 Absorption spectra of the substrates used for the isomerization reactions (F-Cin and cinnamyl alcohol in 50 mM phosphate buffer at pH 7.2; *N*-methylcinnamylamine in 10 mM NaH_2PO_4 ; *trans*-3-(pyridyl)acrylic acid in 10 mM Na_2HPO_4).

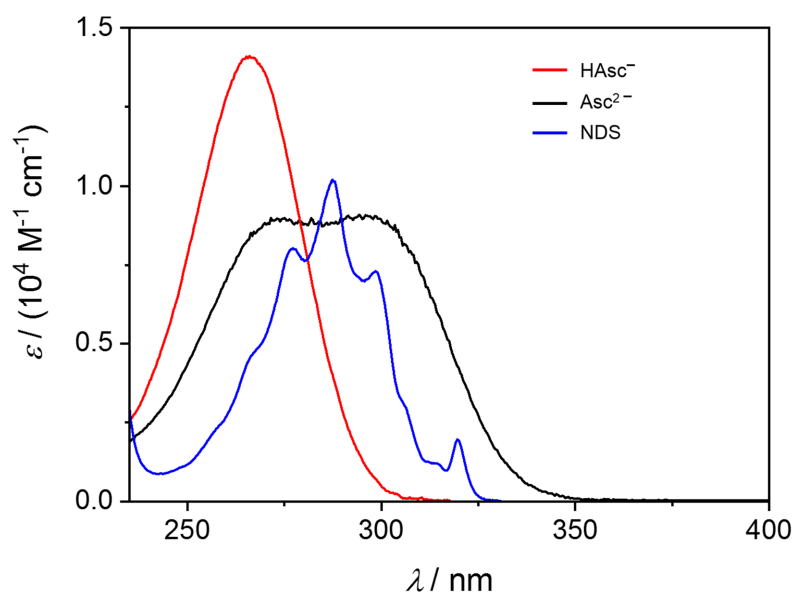


Fig. S 13 Absorption spectra of NDS, ascorbate monoanion (pH 7.6) and dianion (pH 12.7).

6.3 Interactions with DTAC and SDS micelles

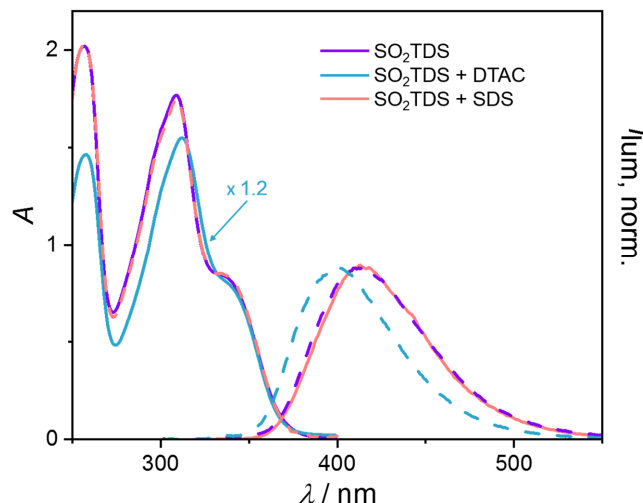


Fig. S 14 Comparison of absorption and emission spectra of aqueous solutions containing **SO₂TDS** (80 μ M) in neat water (purple), with DTAC (48 mM, turquoise) and with SDS (25 mM, pink). The absorption and emission spectra have been scaled such that the long wavelength absorption bands and the emission bands are at the same intensity.

Both absorption and emission spectra of **SO₂TDS** in the presence of DTAC employed at concentrations well above its critical micelle concentration⁴³ show pronounced changes as compared to the spectra in neat water (Fig. S 14). Specifically, the emission spectrum is blue-shifted in the presence of cationic DTAC micelles and the main UV absorption bands are less intense. Moreover, the fluorescence lifetime of singlet-excited **SO₂TDS** decreases significantly from 5.2 ns to 3.3 ns upon DTAC addition.

These effects clearly indicate an interaction between the catalyst molecules and DTAC micelles. We speculate that the **SO₂TDS** molecules are located in close proximity to the cationic head groups as a result of Coulombic attraction. In the case of anionic SDS micelles, absorption and emission spectra remained unmodified, and interactions with **SO₂TDS** as observed for DTAC micelles are less likely. This can be explained by the Coulombic repulsion between the negatively charged head groups of the SDS molecules/micelles and the doubly negatively charged **SO₂TDS**. Micelles in solution are not a static construct but are in a dynamic equilibrium with their environment. Consequently, all molecules in a micellar solution take part in this equilibrium and micelles can act as a dynamic reservoir for catalyst molecules, substrates or products. For the electron transfer reactions (pinacol coupling with CF₃-ACP) with a microheterogeneous environment of SDS micelles, this effect has proven useful.

The concentration of micelles in solution was estimated using the following equation ([mic]...concentration of micelles, [surfactant]...weight-in concentration of either SDS or DTAC, cmc...critical micelle concentration, N_{agg} ...aggregation number):⁴³

$$[\text{mic}] = \frac{[\text{surfactant}] - \text{cmc}}{N_{agg}} \quad (\text{Eqn. 5})$$

The values for cmc (cmc(DTAC) = 22 mM, cmc(SDS) = 8 mM) and N_{agg} (N_{agg} (DTAC) = 60, N_{agg} (SDS) = 60) were taken from ref.⁴³.

6.4 Additional data and details for pinacol coupling reactions

Acetophenone (ACP)

Most results of the pinacol coupling with ACP as starting material are discussed in the main paper. Control experiments confirm that the entire catalytic system is required for the reaction to occur successfully. Besides the reaction scheme and selected ^1H NMR spectra (for all control experiments, see Fig. 3 of the main paper), Fig. S 15 shows a plot with the temporal evolution of the ^1H NMR signals of the product (blue) and consumption of the starting material (red) during photoirradiation, together with a fit curve to guide the eye. For this analysis, we used the integrated methyl ^1H NMR peaks corresponding to ACP and the *dl*/*meso* forms of the product (same color code for all parts of Fig. S 15). The plot does not show a lag phase, which can be seen in the region below 5 h. This observation indicates a direct reaction of $\text{SO}_2\text{TDS}^{\bullet-}$ with ACP (and not with catalyst-derived decomposition products) and thus provides additional evidence for the proposed reaction mechanism (see main paper and Section 3.2).

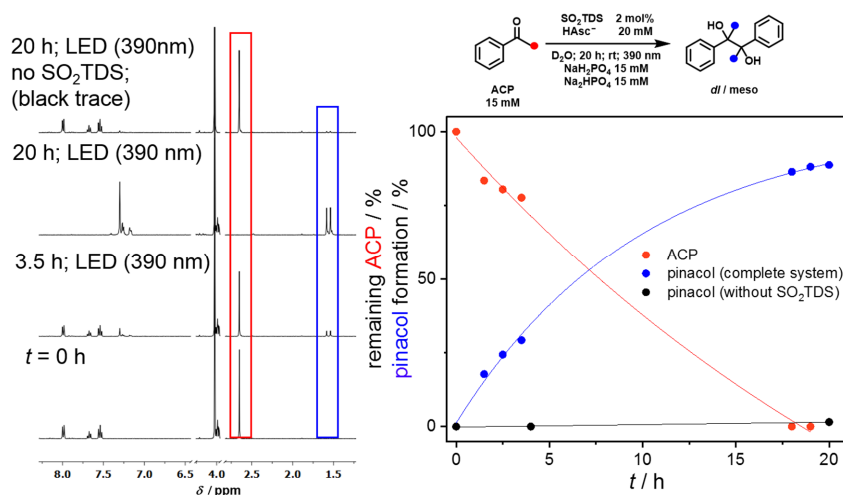


Fig. S 15 Additional experiments on the pinacol coupling reaction of ACP. The reaction scheme includes the pertinent conditions. The time-dependent conversion of the ACP (red trace) and the formation of the pinacol product (blue trace) was obtained from quantitative NMR experiments by analyzing the color-coded methyl signals. The black data set corresponds to the control experiment, which was irradiated under the same reaction conditions, but lacking SO_2TDS and yields practically no pinacol product. For further information, see main paper and text.

Anisaldehyde

This substrate was chosen because of the electron-donating effect of the methoxy substituent, which makes the one-electron reduction of the carbonyl group more difficult. Without the supramolecular environment, only traces of the desired pinacol were observed after 12 h of irradiation, as well as partial precipitation of the product. The consumption of anisaldehyde in this irradiation experiment (without DTAC micelles) is almost 50 % after 12 h, but side product formation and only about 2% of the pinacol were observed (NMR spectrum 1, signals in the blue frame in Fig. S 16). Also, the signals of the pinacol product and the reduced alcohol overlap. Related experiments (higher catalyst loading) with DTAC micelles resulted in a high yield of the pinacol after 18 h of irradiation.

The table in Fig. S 16 lists our reaction conditions. The ascorbate concentrations were increased at higher catalyst loadings. It is worth mentioning that all end-point NMR spectra

still showed signals corresponding to the ascorbate (not shown here). We conclude that for all reactions this compound was added in excess and therefore it is unlikely that different ascorbate concentrations are responsible for the observed results.

The ^1H NMR spectra of the irradiation experiment without DTAC showed several overlapping peaks of different intensities (Fig. S 16, spectrum 1, product mixture [a]). The comparison to spectra from literature allowed us to identify the two main products. The two most intense doublets of similar intensity in the aromatic region correspond to the reduced alcohol (4-methoxybenzylalcohol),⁴² which is an undesired side product in our case. The second compound is the desired pinacol product,³⁸ which is formed as *dl*/meso mixture. As expected, four doublets can be seen in the corresponding ^1H NMR spectrum, out of which three are overlapping with the starting material or the reduced (monomeric) alcohol. This irradiation experiment resulted in a conversion of 44 % (Fig. S 16, table, entry 1), which slightly differs from the yield of detected (side) products. An explanation for this effect is provided by the decreased water solubility of the pinacol product, which resulted in precipitation in the NMR tube.

To confirm the pinacol formation for the reactions with DTAC micelles (and to exclude alcohol formation), a ^1H NMR spectrum (not shown) of the reduced alcohol was recorded under the corresponding reaction conditions. The additional signals so obtained did not overlap with those of the successful pinacol reactions (Fig. S 16, spectra 2 and 3) but they did show the expected signals (two doublets with identical intensities) of the reduced (monomeric) alcohol. We, therefore, conclude that the micellar approach is indeed useful for increasing the selectivity for pinacol formation.

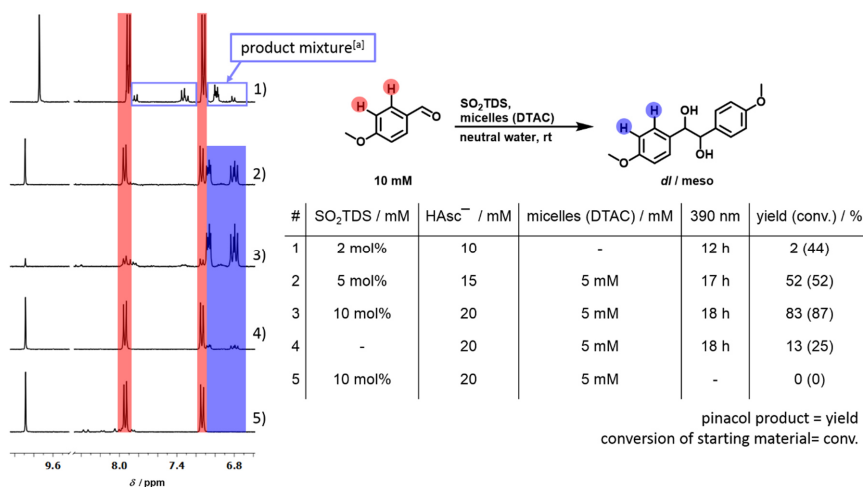


Fig. S 16 Pinacol coupling of anisaldehyde. The reaction scheme contains general experimental conditions and the structure of the (diastereomeric) pinacol product. The table below lists all (control) experiments performed and the corresponding ^1H NMR spectra show conversion / product formation under the respective reaction conditions. For the quantitative NMR analysis, the aromatic protons were used (same color code as in the reaction scheme). Entry 1 corresponds to the irradiation without the micellar environment, which also explains the shifted signals in the ^1H NMR spectrum. [a] For further information, see text.

4-(Trifluoromethyl)acetophenone (CF₃-ACP)

Exact conditions of the pinacol coupling of CF₃-ACP and corresponding control experiments are given in the reaction scheme and in the table presented in Fig. S 17. The irradiation experiments without microheterogeneous environment were performed in non-deuterated water using ¹⁹F NMR spectroscopy for the quantitative analysis (see Section 6.1 for details). Owing to the broad water signal, the corresponding ¹H NMR spectra were not used for the evaluation of the reaction outcome. Full conversion was observed (¹⁹F NMR) after 5 h of irradiation, but merely half of the expected integrals were found in the product peaks (spectra 3) and 4)). We ascribe this effect, combined with the turbidity of the solution, to the low solubility of the pinacol product. To improve the solubility of the reaction product for a reliable quantification, we performed additional experiments with SDS micelles in the reaction mixture (see main paper). The irradiation experiments with SDS micelles were performed in D₂O and quantified using the ¹H NMR spectra (spectra 1) and 2)). To verify the success of the coupling reaction, we added the reduced alcohol (1-(4-(trifluoromethyl)phenyl)ethanol) into the NMR tube containing solution 1. The corresponding ¹⁹F NMR spectrum (Fig. S 17 bottom, right) shows an additional, distinct, and non-overlapping signal (a similar observation was made for ¹H NMR, spectra are not shown) confirming the formation of the desired pinacol product as the result of our photoreaction.

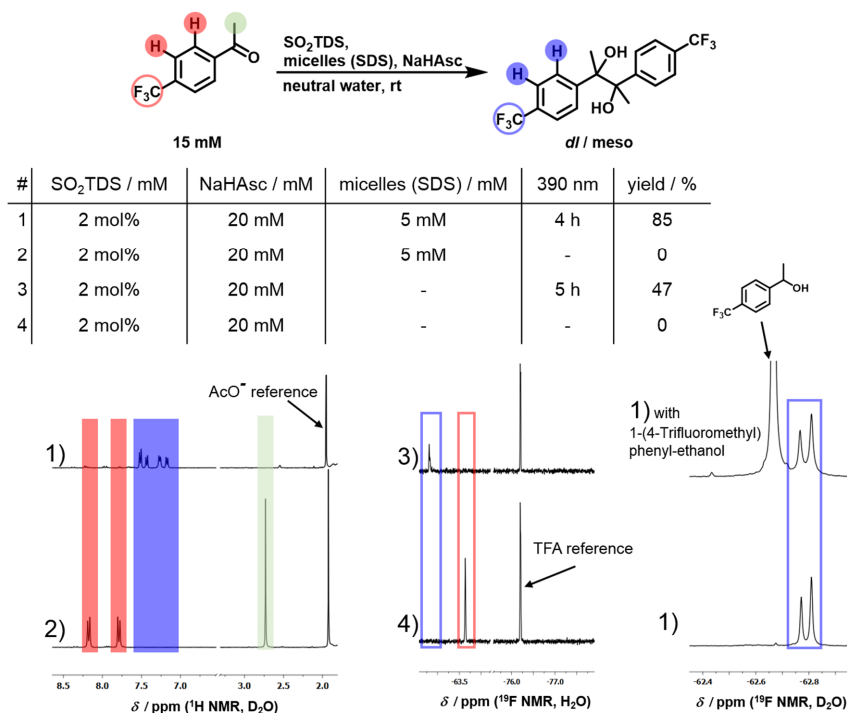


Fig. S 17 Pinacol coupling of CF₃-ACP. Reaction scheme and table with conditions of the (control) experiments as well as the desired coupling product. The corresponding NMR spectra show the signals used for the quantitative analysis with the same color code as in the scheme. NMR spectra: Left, ¹H NMR spectra of reactions 1) and 2) in D₂O with acetate as reference compound for quantifications. Middle, ¹⁹F NMR spectra of 3) and 4) in H₂O with TFA as reference. Right, comparison of the ¹⁹F NMR spectra of the pinacol product with that of the reduced monomeric alcohol (*R/S*)-1-(4-(trifluoromethyl)phenyl)ethanol. For further explanations, see text.

6.5 Additional data and details for isomerization reactions

Unless indicated otherwise, we did not observe substrate-derived side products or turbid solutions after irradiation. Hence, the NMR quantifications of the *cis-trans* ratios directly reflect the yields of the desired *cis* isomers.

370 nm driven isomerization of F-Cin

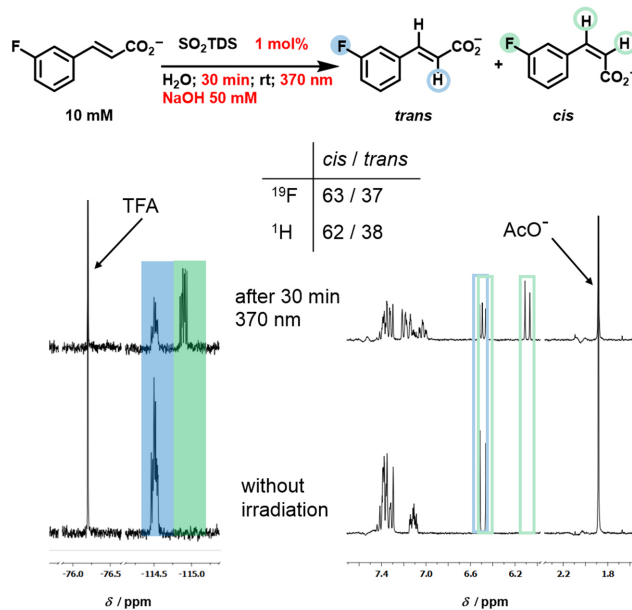


Fig. S 18 Reaction scheme for the F-Cin isomerization reaction under 370 nm LED irradiation employing a lower catalyst loading, together with the corresponding ¹⁹F and ¹H NMR spectra and the quantitative evaluation. The signals used for the quantitative analysis are color-coded. This reaction was performed in NaOH to improve the solubility of both substrate and product.

N-Methylcinnamylamine (protonated)

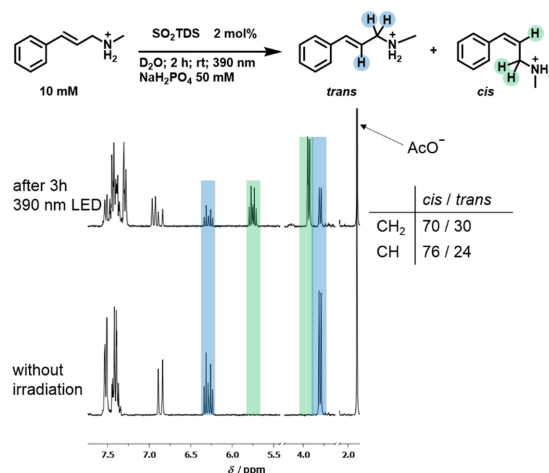


Fig. S 19 Reaction scheme of the *N*-methylcinnamylamine isomerization, ¹H NMR spectra and the corresponding quantitative analysis. The proton signals used for the evaluation of the NMR spectra are color-coded with the corresponding product protons in the reaction scheme. The pH of the solution was adjusted to ~4 using NaH₂PO₄ in order to convert the substrate into its protonated water-soluble form.

Cinnamyl alcohol without DTAC

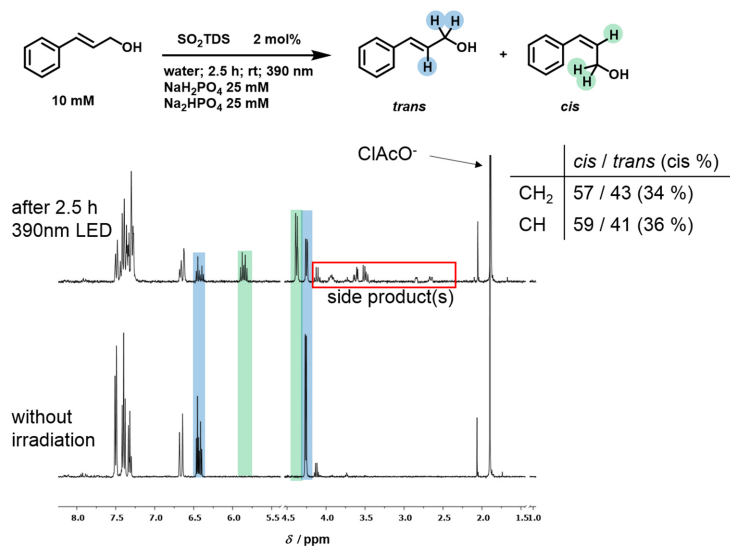


Fig. S 20 Reaction scheme and conditions for the isomerization reaction of cinnamyl alcohol, as well as ¹H NMR spectra and the corresponding quantitative analysis with the absolute *cis* yield given in brackets. The signals used for the quantitative evaluation are color-coded with the product protons in the reaction scheme. Highlighted with the red frame are the signals of the undesired side product(s) that formed during the reaction. The singlet next to the reference peak is an impurity in the starting material and not involved in the reaction (integral remains identical).

Cinnamyl alcohol with DTAC micelles

The addition of DTAC leads to an increase of the absolute *cis* yield of the isomerization reaction by suppressing side reactions, as the quantitative analyses of our comparative photoreactions shown in Figs. S 20 and S 21 unambiguously demonstrate.

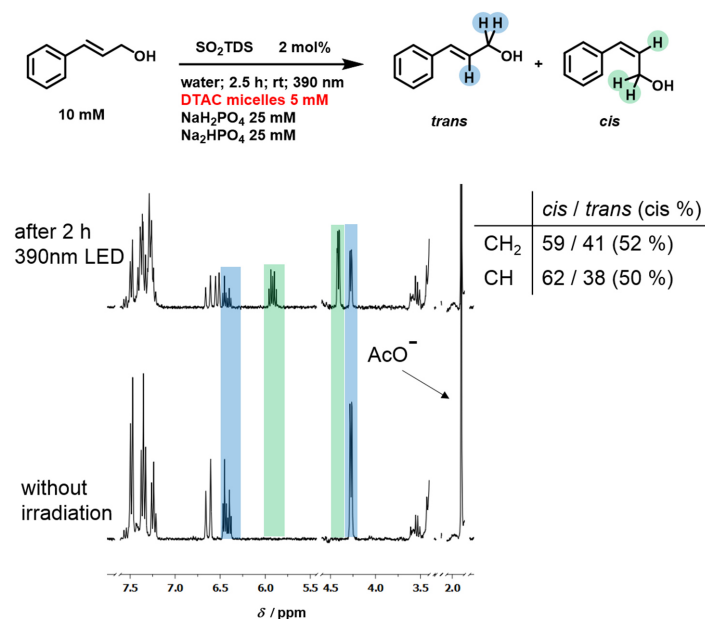


Fig. S 21 Reaction scheme and conditions for the cinnamyl alcohol isomerization with DTAC addition, as well as ¹H NMR spectra and the corresponding quantitative analysis with the absolute *cis* yield given in brackets. The signals used for the quantitative evaluation are color-coded with the product protons in the reaction scheme. The reference signal overlaps slightly with the DTAC signals, which should not affect the quantitative analysis as both species are not involved in the reaction.

6.6 Benchmark reactions for comparison of water-soluble photocatalysts

For both reaction types, electron and energy transfer, we have chosen one reference reaction to compare **SO₂TDS** with other water-soluble photocatalysts (compare, Table S 3) that are known for triplet reactivity.

For the electron transfer, a dechlorination reaction of 4-(chloromethyl)benzoic acid was investigated, yielding either the deuterated monomer or a dimeric dibenzyl-like product (left part of Fig. S 22). The NMR-based analysis of the reaction outcome and the differentiation between both products is straightforward, as described recently.³⁴ The sample ¹H NMR spectrum before the irradiation (0 h) also shows peaks corresponding to the photocatalyst Rubpy, which are marked with asterisks.

Both isomers *cis*- and *trans*-3-(4-pyridyl)acrylate show isolated signals in the ¹H NMR spectra and therefore all signal integrals were considered for the quantification of the *cis* isomer as reaction product (right part of Fig. S 22).

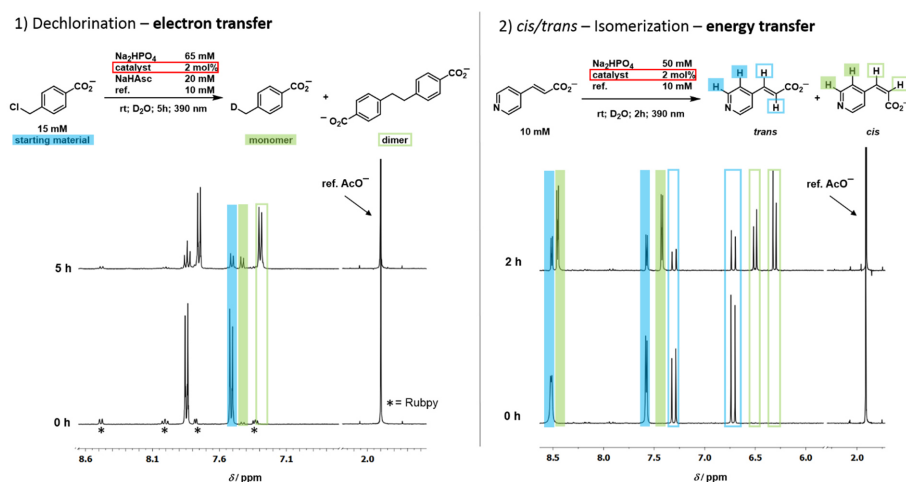


Fig. S 22 Reaction schemes including the pertinent conditions for dechlorination **1)** and isomerization **2)** reaction. Several water-soluble photocatalysts have been tested with a 2 mol% catalyst loading (red frame, for details see Table S 3). The lower part shows representative sample ¹H NMR spectra before (0 h) and after (electron transfer, 5h, Rubpy as catalyst; energy transfer, 2h, SO₂TDS as catalyst) irradiation. For both reaction types 1) and 2), the substrate signals used for quantification are highlighted in blue, whereas product signals are highlighted in green.

The results obtained for the two reactions and different catalysts are summarized in Table S 3. Under the selected sustainable reaction conditions with neutral water as solvent, and a 390 nm LED as energy source, only SO₂TDS is a suitable and efficient photocatalyst for both reaction types.

Table S 3 Results of the dechlorination **1)** and isomerization **2)** reactions (for conditions see Fig. S 22 using different water-soluble photocatalysts. Color code: >70% green; 30–70% orange; <20% red.

photocatalyst	1) electron transfer^[b] % dichlorination (% dimer)	2) energy transfer^[b] % cis isomer
Rubpy	84 (72)	16
eosinY	17 (4)	11
4-benzoylbenzoic acid	11 (3)	37
riboflavin (vit. B2)	10 (2)	81
1-pyrenecarboxylic acid ^[a]	47 (22)	53
-	8 (1)	5
SO₂TDS	93 (68)	71

^[a] Poor solubility under the given reaction conditions, which was improved by addition of NaOD ^[b] Carried out with the setup shown in Fig. S 10 b).

7 NMR spectra of TDS and **SO₂TDS**

7.1 ¹H and ¹³C NMR spectra of TDS

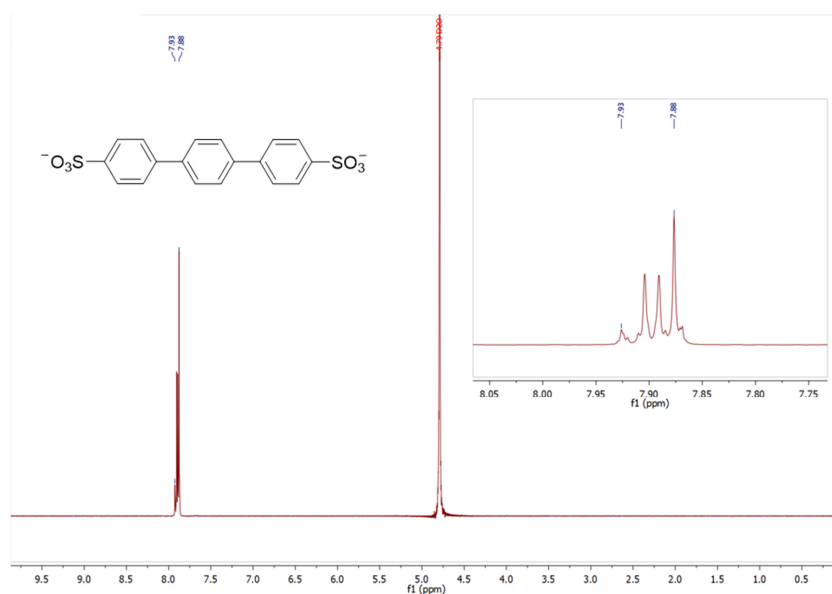


Fig. S 23 ¹H NMR spectrum of TDS in D₂O.

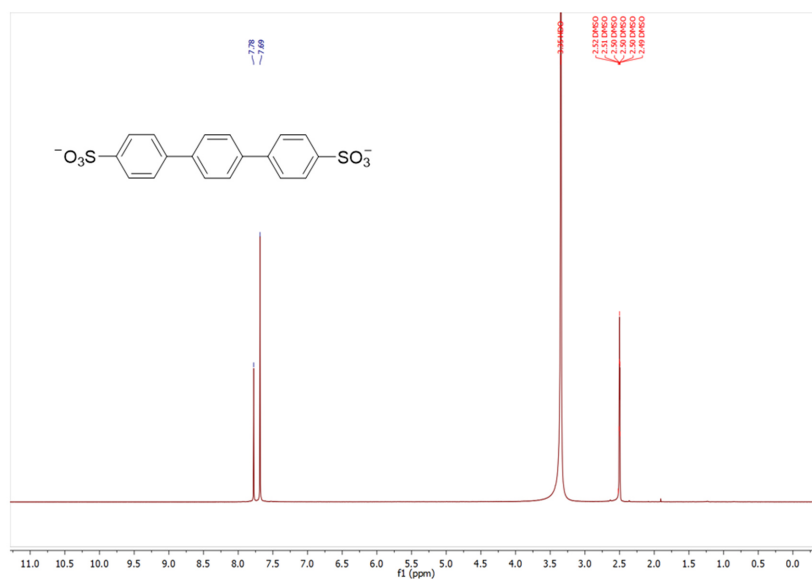


Fig. S 24 ¹H NMR spectrum of TDS in DMSO-*d*₆.



[illegible]

Chemical shifts (ppm): 150.58, 148.28, 145.40, 138.46, 137.93, 135.94, 127.85, 127.60, 126.71, 126.46, 125.53, 125.35, 123.64, 122.79, 120.91, 119.82, 77.03 (CDCl₃ solvent).

Fig. S 27 ^{13}C NMR spectrum of **SO₂TDS** in neat DMSO-*d*₆.

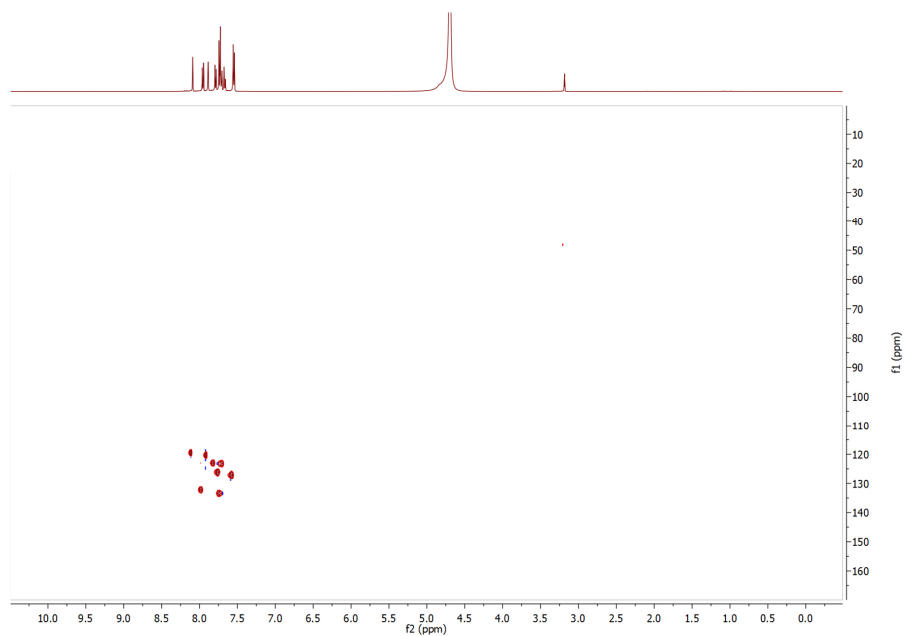


Fig. S 28 HMBC spectrum of **SO₂TDS** in D₂O with DMSO-*d*₆ added as reference.

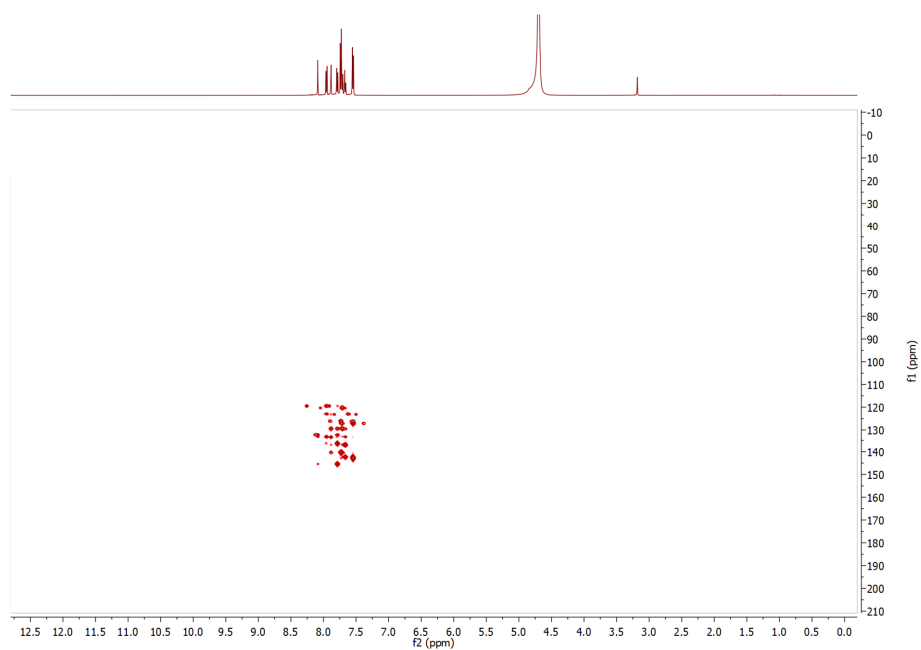


Fig. S 29 HMBC spectrum of **SO₂TDS** in D₂O with DMSO-*d*₆ added as reference.

8 Supplementary references

- 1 H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512–7515.
- 2 F. Zhang, M. Jiang, L.-L. Sun, F. Zheng, L. Dong, V. Shah, W.-B. Shen and Y. Ding, *Analyst*, 2015, **140**, 280–286.
- 3 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook Of Photochemistry*, 2006.
- 4 B. Pfund, D. M. Steffen, M. R. Schreier, M. S. Bertrams, C. Ye, K. Börjesson, O. S. Wenger and C. Kerzig, *J. Am. Chem. Soc.*, 2020, **142**, 10468–10476.
- 5 T. W. T. Muesmann, M. S. Wickleder and J. Christoffers, *Synthesis (Stuttg.)*, 2011, **17**, 2775–2780.
- 6 G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401–449.
- 7 N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166.
- 8 S. Neumann, O. S. Wenger and C. Kerzig, *Chem. - Eur. J.*, 2021, **27**, 4115–4123.
- 9 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513–886.
- 10 J. N. Brønsted and C. E. Teeter, *J. Phys. Chem.*, 1924, **28**, 579–587.
- 11 J. N. Brønsted, *Z. Phys. Chem.*, 1922, **102**, 169–207.
- 12 P. Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265.
- 13 K. Miedlar and P. K. Das, *J. Am. Chem. Soc.*, 1982, **104**, 7462–7469.
- 14 F. M. Hörmann, C. Kerzig, T. S. Chung, A. Bauer, O. S. Wenger and T. Bach, *Angew. Chem. Int. Ed.*, 2020, **59**, 9659–9668.
- 15 M. Brautzsch, C. Kerzig and M. Goez, *Green Chem.*, 2016, **18**, 4761–4771.
- 16 C. Kerzig and M. Goez, *Phys. Chem. Chem. Phys.*, 2014, **16**, 25342–25349.
- 17 M. Nemoto, H. Kokubun and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2464–2470.
- 18 I. Carmichael, W. P. Helman and G. L. Hug, *J. Phys. Chem. Ref. Data*, 1986, **16**, 239–260.
- 19 P. Klán and J. Wirz, *Photochemistry of Organic Compounds*, 2009.
- 20 S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini and V. Balzani, *Top. Curr. Chem.*, 2007, **280**, 117–214.
- 21 P. Müller and K. Brettel, *Photochem. Photobiol. Sci.*, 2012, **11**, 632–636.
- 22 C. Kerzig and O. S. Wenger, *Chem. Sci.*, 2018, **9**, 6670–6678.
- 23 S. Neumann, C. Kerzig and O. S. Wenger, *Chem. Sci.*, 2019, **10**, 5624–5633.
- 24 A. M. Funston, S. V Lyman, B. Saunders-Price, G. Czapski and J. R. Miller, *J. Phys. Chem. B*, 2007, **111**, 6895–6902.
- 25 G. E. Adams and R. L. Willson, *Faraday Trans. 1*, 1972, **69**, 719–729.
- 26 E. Hayon, T. Ibata, N. N. Lichtin and M. Simic, *J. Phys. Chem.*, 1972, **76**, 2072–2078.
- 27 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg,

-
- M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian, Inc., Wallingford CT*, 2009.
- 28 T. R. Blum, Z. D. Miller, D. M. Bates, I. A. Guzei and T. P. Yoon, *Science*, 2016, **354**, 1391–1396.
- 29 V. Gray, A. Dreos, P. Erhart, B. Albinsson, K. Moth-Poulsen and M. Abrahamsson, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10931–10939.
- 30 N. Harada, Y. Sasaki, M. Hosoyamada, N. Kimizuka and N. Yanai, *Angew. Chem. Int. Ed.*, 2020, **59**, 10252–10264.
- 31 M. Teders, C. Henkel, L. Anhäuser, F. Strieth-Kalthoff, A. Gómez-Suárez, R. Kleinmans, A. Kahnt, A. Rentmeister, D. Guldi and F. Glorius, *Nat. Chem.*, 2018, **10**, 981–988.
- 32 C. Kerzig and M. Goez, *Chem. Sci.*, 2016, **7**, 3862–3868.
- 33 K. Sandros, *Acta Chem. Scand.*, 1964, **18**, 2355–2374.
- 34 C. Kerzig and O. S. Wenger, *Chem. Sci.*, 2019, **10**, 11023–11029.
- 35 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 258–271.
- 36 S. M. Hubig and J. K. Kochi, *J. Am. Chem. Soc.*, 1999, **121**, 1688–1694.
- 37 C. Kerzig and M. Goez, *Phys. Chem. Chem. Phys.*, 2015, **17**, 13829–13836.
- 38 R. Naumann and M. Goez, *Green Chem.*, 2019, **21**, 4470–4474.
- 39 N. Periasamy and K. S. V. Santhanam, *Proc. Indian Acad. Sci. - Sect. A*, 1974, **80**, 194–206.
- 40 J. J. Warren, T. A. Tronic and J. M. Mayer, *Chem. Rev.*, 2010, **110**, 6961–7001.
- 41 S. Matsuoka, T. Kohzaki, C. Pac, A. Ishida, S. Takamuku, M. Kusaba, N. Nakashima and S. Yanagida, *J. Phys. Chem*, 1992, **96**, 4437–4442.
- 42 M. Zhao, W. Xie and C. Cui, *Chem. - Eur. J.*, 2014, **20**, 9259–9262.
- 43 C. Kerzig, M. Hoffmann and M. Goez, *Chem. - Eur. J.*, 2018, **24**, 3038–3044.

6.9 Supporting Information for Dyads as mechanistic switch between energy and electron transfer (Section 2.3)

Electronic Supplementary Information (ESI) for

**Triplet quenching pathway control with molecular dyads enables
the identification of a highly oxidizing annihilator class**

Maria-Sophie Bertrams,^[a] Katharina Hermainski,^[a] Jean-Marc Mörsdorf,^[b]
Joachim Ballmann,^{*,[b]} and Christoph Kerzig^{*,[a]}

[a] Maria-Sophie Bertrams, Katharina Hermainski, Christoph Kerzig
Department of Chemistry
Johannes Gutenberg University Mainz, Duesbergweg 10-14
55128 Mainz (Germany)
E-mail: ckerzig@uni-mainz.de

[b] Jean-Marc Mörsdorf, Joachim Ballmann
Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 276
69120 Heidelberg, Germany
E-mail: joachim.ballmann@uni-heidelberg.de

Contents

1. General experimental details	3
1.1 Chemicals.....	3
1.2 Steady-state measurements	3
1.3 Time-resolved measurements.....	3
1.4 Calculations of excited-state redox potentials.....	4
2. Synthetic procedures.....	5
2.1 General remarks	5
2.2 Synthesis of 2,2'-bis(diisopropylphosphino)tolane derivatives	5
2.3 Synthesis of phosphonium-bridged ladder stilbene derivatives.....	7
3. NMR spectra of the annihilators P-H²⁺, P-F²⁺, P-Cl²⁺	8
4. X-Ray crystal structure determinations	13
5. DFT calculations	17
6. Quantum yield and lifetime measurements of the annihilators.....	18
7. Additional energy- and electron transfer experiments	19
7.1 Fitting of kinetic absorption and separation of formation and decay kinetics	19
7.2 Ru(bpy) ₃ ²⁺ and P-H ²⁺	21
7.3 RubpyPy ²⁺ and P-H ²⁺	23
7.4 Ru(phen) ₃ ²⁺ and P-H ²⁺	23
7.5 Ru(phen) ₃ ²⁺ and P-F ²⁺ or P-Cl ²⁺	24
7.6 RuphenPy ²⁺ and P-H ²⁺	25
7.7 Ru(bpz) ₃ ²⁺ and P-H ²⁺	26
7.8 Quenching studies with further photosensitizers	27
8. Additional sTTA experiments.....	30
8.1 RubpyPy ²⁺ and P-H ²⁺	30
8.2 Ru(bpz) ₃ ²⁺ and P-H ²⁺	30
8.3 RuphenPy ²⁺ and P-H ²⁺	31
8.4 RuphenPy ²⁺ and P-F ²⁺ or P-Cl ²⁺	32
8.5 Comparison UC vs. direct emission	33
9. Cl⁻ as reductive quencher	34
9.1 P-H ²⁺	35
9.2 P-F ²⁺ and P-Cl ²⁺	35
9.3 Cl ⁻ -quenching with literature-known annihilators.....	36
9.4 Cl ⁻ quenching after sTTA	36
10. Br⁻ as reductive quencher	37
11. Quenching of ¹P-H²⁺* with 1,5-NDS²⁻	40
12. References	41

1. General experimental details

1.1 Chemicals

Unless indicated otherwise, chemicals for optical spectroscopy were used as obtained from the supplier (in the highest available purity) without further purification: Ethanol absolute (VWR, >99 %); 9-(methyaminomethyl)anthracene (Sigma-Aldrich, 99 %); Eosin Y disodium salt (Alfa Aesar, 100 weight %); Erythrosin B disodium salt (TCI, >95 %); NaBr (Merck, extra pure 99 %); NaCl (Fisher Chemicals, ≥99.5 %); NaOH (Sigma Aldrich, ≥98 %); perylene (Thermo Scientific, >98 %); disodium 1,5-naphthalenedisulfonate hydrate (TCI, >98 %); PbO₂ (Acros Organic, >97 %); Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium dichloride (Ru(dpp)₃²⁺, Alfa Aesar); Tris(2,2'-bipyridine)ruthenium dichloride × 6 H₂O (Ru(bpy)₃²⁺, Sigma-Aldrich, 99.95 %); Tris(1,10-phenanthroline)ruthenium dichloride × H₂O (Ru(phen)₃²⁺, Sigma-Aldrich, 97 %); Sulfuric acid (Carl Roth, 96 %, VLSI grade).

Tis(1,10-phenanthroline)osmium(II) hexafluorophosphate (Os(phen)₃²⁺)¹ was synthesized according to a literature procedure. The dyads Ru(bpy)₃-xy₁-Ant²⁺ (as nitrate salt)², bis(2,2'-bipyridine)(5-pyrenyl-1,10-phenanthroline)ruthenium(II) chloride (RubpyPy²⁺)³ and bis(1,10-phenanthroline)(5-pyrenyl-1,10-phenanthroline)ruthenium(II) chloride (RuphenPy²⁺)³ as well as tris(2,2'-bipyrazine)ruthenium dihexafluorophosphate (Ru(bpz)₃²⁺)⁴ were available from recent studies.

The solvent used for optical spectroscopy was 50 mM H₂SO₄ in aqueous solution with ultrapure Millipor MilliQ water (specific resistance 18.2 MΩ cm). All solutions for optical spectroscopy were purged with argon (Nippon Gases 5.0) for at least 10 minutes before the measurements and sealed under inert gas in 1.0 cm pathlength septum cap cuvettes (quartz glass).

1.2 Steady-state measurements

Absorption spectra were recorded using a LAMBDA 365 from Perkin Elmer. Emission spectra for the quantum yield determination were measured using a FL 6500 from Perkin Elmer. All steady-state absorption and emission measurements were performed at room temperature (295 ± 2 K) and the emission spectra were corrected for the wavelength-dependent sensitivity of the emission spectrometer. Very low concentrations of the emissive compounds were employed to avoid filter effects. The *E*₀₀ energies were determined from the intersections of the absorption and emission spectra. The fluorescence quantum yields were measured against a known standard compound (perylene in ethanol⁵). To avoid filter effects, the absorbance was adjusted below 0.1 at the excitation wavelengths and in the overlap area of emission and absorption spectra. The quantum yield was then determined according to Equation S 1⁵ with *Φ* ... quantum yield, *I* ... integrated luminescence intensity, *A* ... optical density at the excitation wavelength, and *η* ... refractive indices of the used solvents. All variables with the index ref correspond to the reference compounds.

$$\Phi = \Phi_{\text{ref}} \times \frac{I}{I_{\text{ref}}} \times \frac{A_{\text{ref}}}{A} \times \frac{\eta^2}{\eta_{\text{ref}}^2}$$

Equation S 1

1.3 Time-resolved measurements

The fluorescence lifetimes of the three annihilator compounds in 50 mM H₂SO₄ were recorded with a mini-τ spectrometer from Edinburgh Instruments (time-correlated single photon counting TCSPC technique), with a pulsed LED (EPLD-300, pulse-width 1020.0 ps, average power 40 μW, *λ*_{exc} = 293 nm) or different lasers (EPL-375, pulse-width 58.3 ps, average power 5 mW, *λ*_{exc} = 371 nm; EPL-450, pulse-width 74.5 ps, average power 5 mW, *λ*_{exc} = 446 nm) for excitation and the built-in band-pass

S3

filters for detection. For the detection of the 1,5-NDS²⁻ lifetime, a 345 nm long-pass filter from Newport was used. The concentrations of all solutions were adjusted such that the optical density at the excitation wavelength was between 0.1 and 0.2.

For the laser flash photolysis (LFP) measurements an LP980-KS apparatus from Edinburgh Instruments was used. The energy of the 532 nm laser pulse (frequency-doubled Nd:YAG laser from Quantel with ~10 ns pulses) was modified by the Q-switch delay (50 μs – 150 μs, corresponding to energies between 50 mJ and 2.4 mJ, further details are given in the figure captions of the ESI). A beam expander (Thorlabs) was used to ensure homogenous excitation in the detection volume (beam diameter in front of the cuvette window, 0.8 cm). Kinetic traces were recorded at a single wavelength with a photomultiplier tube and for measuring transient absorption (TA) or (delayed) emission spectra an iCCD camera from Andor was employed. All TA spectra were time-integrated for 100 ns. The concentrations of the sensitizers were adjusted such that optical densities at the excitation wavelength between 0.017 and 0.034 resulted (except for Figure S 37, where higher concentrations were used). Exact concentrations are given in the figure captions.

To determine quenching rate constants, Stern–Volmer analyses of the quenching experiments were performed. The τ_0/τ values from LFP or TCSPC studies were plotted against the quencher concentration. A linear fit with the intersection fixed at 1 yielded the Stern–Volmer constant (K_{SV}) and division by the known τ_0 lifetime of the respective excited state under given conditions resulted in the bimolecular quenching rate constant.⁵

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q]$$

Equation S 2

The simulated curves for the quenching efficiencies as a function of the quencher concentrations (Figure 5, main paper) were calculated using deviations of the Stern–Volmer equation. The previously determined quenching rate constants (k_q) and lifetimes without quencher present (τ_0) allowed us to calculate the lifetimes at different quencher concentrations according to **Equation S 3**, which is a rearrangement of the Stern–Volmer equation (**Equation S 2**).

$$\tau = \frac{1}{\frac{1}{\tau_0} + k_q \times [Q]}$$

Equation S 3

The efficiency of the resulting lifetimes was calculated using **Equation S 4**, which can also be derived from **Equation S 2**.

$$\eta = \frac{\tau_0 - \tau}{\tau_0}$$

Equation S 4

1.4 Calculations of excited-state redox potentials

The thermodynamic feasibility of a photo-induced redox reaction (Gibbs energy of photoinduced electron transfer) can be predicted using the following equation⁶

$$\Delta G_{ET}^0 = E(D^{*\pm/0}) - E(A^{0/+}) - E_{00} - \omega$$

Equation S 5

with $E(D^{+/0})$... oxidation potential of an electron donor, $E(A^{0/-})$... reduction potential of an electron acceptor, $E_{0,0}$... the excited state energy of the donor or acceptor, and ω ... the Coulomb-term representative for the Coulombic interactions between two ions, which was neglected in the calculation because the corresponding values are small in water⁶. Potentials from literature were often given vs. SCE and could be adjusted to values vs. NHE by the addition of 0.24 V.⁷ The empirical correlation between ΔG^0_{ET} and the observed quenching rate constants was exploited to estimate redox potentials that could not be measured in aqueous solution.^{8,9}

2. Synthetic procedures

2.1 General remarks

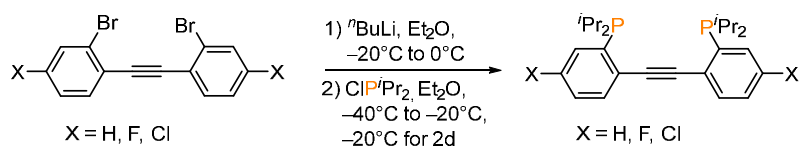
All experiments were conducted under an atmosphere of dry and oxygen-free argon by using standard Schlenk techniques. Argon 5.0 was used and further dried by passing over a column of phosphorus pentoxide. Glassware was heated to 130°C overnight and evacuated while still hot. Dichloromethane, diethylether and pentane were purified using an MBraun Solvent Purification System. Deuterated solvents were dried over sodium (C_6D_6 , toluene- d_8) or over calcium hydride (CD_2Cl_2) and distilled prior to use. Chlorodiisopropylphosphine was purified by simple distillation and stored in a Teflon-valve ampule. All other chemicals for synthesis were purchased from commercial suppliers and used as received. 2,2'-Dibromo-tolane¹⁰, 2,2'-dibromo-4,4'-difluorotolane¹¹ and 2,2'-dibromo-4,4'-dichlorotolane¹² were prepared according to literature-known procedures.

One and two dimensional 1H , ^{13}C , ^{19}F and ^{31}P NMR spectra were recorded on a Bruker Avance DRX 300, a Bruker Avance II 400 MHz or on a Bruker Avance 600 III spectrometer. Unless noted otherwise, all X-nuclei spectra were recorded with 1H broadband or composite pulse decoupling. Residual (undeuterated) solvent served as reference for 1H and ^{13}C NMR spectra. Chemical shifts δ are given in parts per million (ppm), coupling constants J in Hertz (Hz). Signal multiplicities are stated by common abbreviations (e.g. s – singlet, d – doublet, dd – doublet of doublets).

Mass spectra were recorded at the Department of Organic Chemistry at Heidelberg University on a JEOL JMS-700 magnetic sector by liquid injection FD ionization (LIFDI) technique.

Elemental analyses were carried out at the Department of Inorganic Chemistry at Heidelberg University on an Elementar vario MICRO Cube.

2.2 Synthesis of 2,2'-bis(diisopropylphosphino)tolane derivatives



General procedure: A Schlenk flask was charged with the 2,2'-dibromotolane derivative (1.0 eq, X = H, F, Cl) and dissolved in anhydrous Et_2O . The clear solution was cooled to -20°C and $^n\text{BuLi}$ (2.5 M in hexane, 2.0 eq) was added dropwise over 10 min. The solution was stirred for 20 min at -20°C and then placed in an ice bath at 0°C . After 15 min the solution was cooled to -40°C and neat chlorodiisopropylphosphine (2.1 eq) was added dropwise. The mixture was allowed to warm to -20°C and stirred at this temperature for 2d. The resulting suspension (LiCl precipitate) was filtered over a silica plug under inert atmosphere and the plug was washed with Et_2O , while the filtrate was kept in an ice-bath at 0°C . The filtrate was evaporated under reduced pressure and the residue was

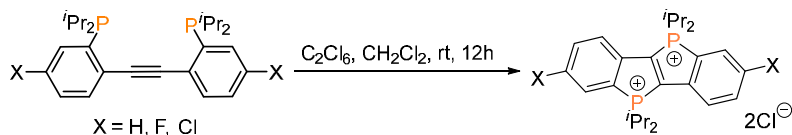
taken up in pentane and filtered over Celite to remove residual amounts of LiCl. The clear filtrate was concentrated under vacuum and the solution was kept at -40°C for crystallization. After 12h, the ensuing colorless crystals were filtered off, washed with a small amount of cold pentane and dried in vacuum. The products are air- and temperature-sensitive, but may be stored indefinitely under an inert atmosphere at -40°C .

Derivative with X=H: This derivative has been reported previously, but the experimental procedure provided here has been improved significantly. The following amounts were used: 4.0 g 2,2'-dibromotolane (11.9 mmol, 1.0 eq) in 120 ml Et_2O , 9.6 ml $n\text{BuLi}$ (2.5 M in hexane, 23.6 mmol, 2.0 eq), 4 ml chlorodiisopropylphosphine (25.1 mmol, 2.1 eq). In the silica filtration step, 200 ml Et_2O were needed for washing the silica plug. The product was obtained in 82% yield (4.0 g, 9.8 mmol). The analytical data are in accordance with literature values. ^1H NMR (600 MHz, CD_2Cl_2 , 22°C): δ (in ppm) = 7.67-7.63 (m, 2H), 7.49-7.45 (m, 2H), 7.36-7.31 (m, 4H), 2.27 (septd, $J_{\text{H-H}} = 7.0$ Hz, $J_{\text{H-P}} = 1.7$ Hz, 4H), 1.16 (dd, $J_{\text{H-H}} = 7.0$ Hz, $J_{\text{H-P}} = 14.5$ Hz, 12H), 0.96 (dd, $J_{\text{H-H}} = 7.0$ Hz, $J_{\text{H-P}} = 11.9$ Hz, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2 , 22°C): δ (in ppm) = 139.0 (d, $J_{\text{C-P}} = 22.0$ Hz, C_q), 133.5 (d, $J_{\text{C-P}} = 2.8$ Hz, CH), 133.3 (d, $J_{\text{C-P}} = 4.5$ Hz, CH), 131.1 (d, $J_{\text{C-P}} = 28.0$ Hz, C_q), 128.8 (s, CH), 127.9 (d, $J_{\text{C-P}} = 1.6$ Hz, CH), 95.2 (dd, $J_{\text{C-P}} = 7.0$ Hz, $J_{\text{C-P}} = 2.6$ Hz, C_q), 23.9 (d, $J_{\text{C-P}} = 13.8$ Hz, CH), 20.4 (d, $J_{\text{C-P}} = 18.4$ Hz, CH_3), 19.7 (d, $J_{\text{C-P}} = 10.9$ Hz, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2 , 22°C): δ (in ppm) = 4.9 (s). MS (LIFDI, toluene): Calcd. for $\text{C}_{26}\text{H}_{36}\text{P}_2$: 410.2292, found: 410.2 $[\text{M}]^+$. Anal. calcd. for $\text{C}_{26}\text{H}_{36}\text{P}_2$ (410.52 g/mol): C 76.07, H 8.84, found: C 75.89, H 9.25.

Derivative with X=F: The following amounts were used: 0.6 g 2,2'-dibromo-4,4'-difluorotolane (1.6 mmol, 1.0 eq) in 40 ml of Et_2O , 1.3 ml $n\text{BuLi}$ (2.5 M in hexane, 3.2 mmol, 2.0 eq), 5.4 μl chlorodiisopropylphosphine (3.4 mmol, 2.1 eq). In the silica filtration step, 50 ml Et_2O were used for washing the silica plug. The product was obtained in 68% yield (0.5 g, 1.1 mmol). ^1H NMR (600 MHz, C_6D_6 , 22°C): δ (in ppm) = 7.67-7.64 (m, 2H), 7.12 (d, $J_{\text{H-H}} = 9.1$ Hz, 2H), 6.65 (td, $J = 8.3$ Hz, $J = 2.6$ Hz, 2H), 1.93 (sept, $J_{\text{H-H}} = 6.9$ Hz, 4H), 1.08 (dd, $J_{\text{H-P}} = 14.4$ Hz, $J_{\text{H-H}} = 7.0$ Hz, 12H), 0.86 (dd, $J_{\text{H-P}} = 11.8$ Hz, $J_{\text{H-H}} = 6.9$ Hz, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 22°C): δ (in ppm) = 162.2 (d, $^1J_{\text{C-F}} = 252$ Hz, C_q), 142.5 (dd, $J = 26.4$ Hz, $J = 4.9$ Hz, C_q), 135.0 (dd, $^3J_{\text{C-F}} = 7.8$ Hz, $^3J_{\text{C-P}} = 4.6$ Hz, CH), 127.4 (dd, $J = 29.7$ Hz, $J = 3.0$ Hz, C_q), 119.4 (d, $^2J_{\text{C-F}} = 20.6$ Hz, CH), 116.0 (d, $^2J_{\text{C-F}} = 22.1$ Hz, CH), 93.9 (d, $^3J_{\text{C-P}} = 4.9$ Hz, C_q), 23.8 (d, $^1J_{\text{C-P}} = 15.3$ Hz, CH), 20.0 (d, $^2J_{\text{C-P}} = 18.3$ Hz, CH_3), 19.4 (d, $^2J_{\text{C-P}} = 11.0$ Hz, CH_3). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, C_6D_6 , 22°C): δ (in ppm) = -111.8 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, C_6D_6 , 22°C): δ (in ppm) = 3.9 (s). MS (EI+): Calcd. for $\text{C}_{26}\text{H}_{34}\text{F}_2\text{P}_2$: 446.2098, found: 446.2089 $[\text{M}]^+$. Anal. calcd. for $\text{C}_{26}\text{H}_{34}\text{F}_2\text{P}_2$ (446.50 g/mol): C 69.94, H 7.68, found: C 69.87, H 7.94.

Derivative with X=Cl: The following amounts were used: 2.5 g 2,2'-dibromo-4,4'-dichlorotolane (5.0 mmol, 1.0 eq) in 120 ml Et_2O , 4.0 ml $n\text{BuLi}$ (2.5 M in hexane, 10.0 mmol, 2.0 eq), 1.7 ml chlorodiisopropylphosphine (10.5 mmol, 2.1 eq). In the silica filtration step, 200 ml Et_2O were used for washing the silica plug. The product was obtained in 80% yield (1.9 g, 3.9 mmol). ^1H NMR (400 MHz, C_6D_6 , 22°C): δ (in ppm) = 7.57 (dd, $J = 8.3$ Hz, $J = 2.8$ Hz, 2H), 7.45 (t, $J = 2.1$ Hz, 2H), 6.95 (dd, $J = 8.3$ Hz, $J = 2.2$ Hz, 2H), 1.92 (hept, $J = 6.9$ Hz, 4H), 1.05 (dd, $J = 14.5$ Hz, $J = 7.0$ Hz, 12 H), 0.85 (dd, $J = 11.8$ Hz, $J = 6.9$ Hz, 12H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 22°C): δ (in ppm) = 4.6 (s). MS (EI+): Calcd. for $\text{C}_{26}\text{H}_{34}\text{P}_2\text{Cl}_2$: 478.1507, found: 478.1530 $[\text{M}]^+$. Anal. calcd for $\text{C}_{26}\text{H}_{34}\text{P}_2\text{Cl}_2$ (479.40 g/mol): C 64.14, H 7.15, found: C 64.08, H 7.39.

2.3 Synthesis of phosphonium-bridged ladder stilbene derivatives



General procedure for the oxidative cyclization with hexachloroethane ($X = \text{H, F, Cl}$): Solid hexachloroethane (1.0 eq) was added to a solution of the 4,4'-substituted ($X = \text{H, F, Cl}$) 2,2'-bis(diisopropylphosphino)tolane (1.0 eq) in 50 ml CH_2Cl_2 under an inert atmosphere and the resulting solution was stirred overnight at room temperature. The resulting precipitate was filtered off (in air) and washed with 10 ml CH_2Cl_2 . The solid was further washed with a solution of three drops NEt_3 in 10 ml CH_2Cl_2 , followed by washing with 10 ml CHCl_3 . The solid was dissolved in methanol and crystallized by layering the solution with an equal amount of Et_2O . After a few days, the crystalline yellow product was collected via filtration and dried in vacuum. The fluorescent products were obtained as air-stable (in the solid state) and water-soluble solids.

Derivative with $X = \text{H}$ (P-H^{2+}): The following amounts were used: 288 mg hexachloroethane (1.22 mmol, 1.0 eq), 500 mg 2,2'-bis(diisopropylphosphino)tolane (1.22 mmol, 1.0 eq). The product was obtained in 97% yield (572 mg, 1.19 mmol). A three-step synthesis of this compound has been reported previously.¹³ The analytical data are accordance with the literature values. ^1H NMR (D_2O , 600 MHz, 22°C): δ (in ppm) = 8.24-8.21 (m, 2H), 8.03-8.00 (m, 2H), 7.96-7.95 (m, 2H), 7.87-7.86 (m, 2H), 3.69-3.65 (m, 4H), 1.44-1.39 (m, 12H), 1.37-1.33 (m, 12H). $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (D_2O , 75 MHz, 25°C): δ (in ppm) = 146.7-146.2 (m, C_q), 138.5 (t, $J = 12.7$ Hz, C_q), 136.9 (s, CH), 134.1 (t, $J = 5.5$ Hz, CH), 132.4 (t, $J = 5.7$ Hz, CH), 127.3 (t, $J = 3.5$ Hz, CH), 120.2-119.5 (m, C_q), 22.6-22.2 (m, CH), 15.2 (bs, CH_3), 14.6 (bs, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (D_2O , 243 MHz, 22°C): δ (in ppm) = 58.4 (s). MS (ESI $^+$): Calcd. for $\text{C}_{26}\text{H}_{37}\text{OP}_2^+$: 427.2314, found: 427.2315 $[\text{M}+\text{OH}]^+$. Anal. calcd. for $\text{C}_{26}\text{H}_{36}\text{Cl}_2\text{P}_2$ (481.42 g/mol): C 64.87, H 7.54, found: C 64.15, H 7.46.

Derivative with $X = \text{F}$ (P-F^{2+}): The following amounts were used: 264 mg hexachloroethane (1.12 mmol, 1.0 eq), 500 mg 2,2'-bis(diisopropylphosphino)-4,4'-difluorotoluene (1.12 mmol, 1.0 eq). The product was obtained in 95% yield (475 mg, 1.06 mmol). ^1H NMR (400 MHz, D_2O , 22°C): δ (in ppm) = 8.04 - 8.00 (m, 2H), 7.90 (dt, $J = 8.0$ Hz $J = 3.8$ Hz, 2H), 7.69 (td, $J = 8.6$ Hz, $J = 2.4$ Hz, 2H), 3.62 (sept, $J_{\text{H-H}} = 7.2$ Hz, 4H), 1.40 - 1.26 (m, 24H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, D_2O , 22°C): δ (in ppm) = 167.7 - 165.9 (m, C_q), 148.1 - 147.6 (m, C_q), 137.5 - 137.3 (m, C_q), 131.9 (dt, $J = 9.0$ Hz, $J = 4.0$ Hz), 126.4 (d, $J = 22.9$ Hz, CH), 125.5 (d, $J = 9.0$ Hz), 125.1 (t, $J = 6.2$ Hz, CH), 125.0 - 124.8 (m, CH), 25.4 - 25.0 (m, CH), 17.5 (dt, $J = 87.4$ Hz, $J = 1.4$ Hz, CH_3). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, D_2O , 22°C): δ (in ppm) = -103.7 (t, $J = 3.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, D_2O , 22°C): δ (in ppm) = 60.1 (s). MS (ESI $^+$): Calcd. for $\text{C}_{26}\text{H}_{33}\text{F}_2\text{P}_2$: 445.2020, found: 445.2018 $[\text{M-H}]^+$, calcd. for $\text{C}_{26}\text{H}_{35}\text{F}_2\text{OP}_2$: 463.2126, found: 463.2123 $[\text{M}+\text{OH}]^+$. Anal. calcd. for $\text{C}_{26}\text{H}_{30}\text{Cl}_2\text{F}_2\text{P}_2 \times 2 \text{H}_2\text{O}$ (553.43 g/mol) C 56.43, H 6.92, found: C 56.35, H 7.19.

Derivative with $X = \text{Cl}$ (P-Cl^{2+}): The following amounts were used: 232 mg hexachloroethane (0.98 mmol, 1.0 eq). 470 mg 2,2'-bis(diisopropylphosphino)-4,4'-dichlorotoluene (0.98 mmol, 1.0 eq). The product was obtained in 87% yield (470 mg, 0.85 mmol). ^1H NMR (400 MHz, D_2O , 22°C): δ (in ppm) = 8.25 (dt, $J = 8.3$ Hz, $J = 2.1$ Hz, 2H), 7.98 - 7.96 (m, 2H), 7.84 (dd, $J = 8.3$ Hz, $J = 3.1$ Hz, 2H), 3.62 (sept, $J = 7.2$ Hz, 4H), 1.40 - 1.26 (m, 24H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, D_2O , 22°C): δ (in ppm) = 145.7 (d, $J = 73.5$

Hz, C_q), 139.1 (t, J = 7.7 Hz), 137.0 – 136.7 (m), 134.2 (t, J = 6.0 Hz, CH), 128.3 (t, J = 3.8 Hz, CH), 122.1 (d, J = 91.6 Hz, C_q), 23.2 – 22.3 (m, CH), 15.3 (s, CH₃), 14.7 (s, CH₃). ³¹P{¹H} NMR (162 MHz, D₂O, 22°C): δ (in ppm) = 60.1 (s). MS (ESI⁺): Calcd. for C₂₆H₃₃Cl₂P₂ [M-H]⁺: 477.1435, found: 477.1430. Calcd. for C₂₆H₃₅Cl₂OP₂ [M+OH]⁺: 495.1540, found: 495.1533. Anal. Calcd. for C₂₆H₃₄Cl₂P₂ × 3 H₂O (446 g/mol) C 51.67, H 6.67. Found: C 52.09, H 6.54.

3. NMR spectra of the annihilators P-H²⁺, P-F²⁺, P-Cl²⁺

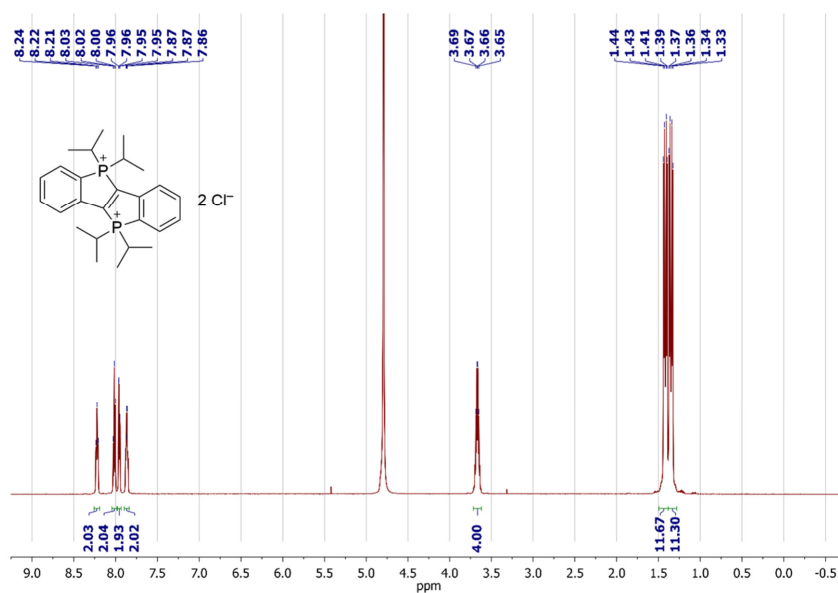


Figure S 1 ¹H NMR spectrum of P-H²⁺ (600 MHz, D₂O, 295 K).

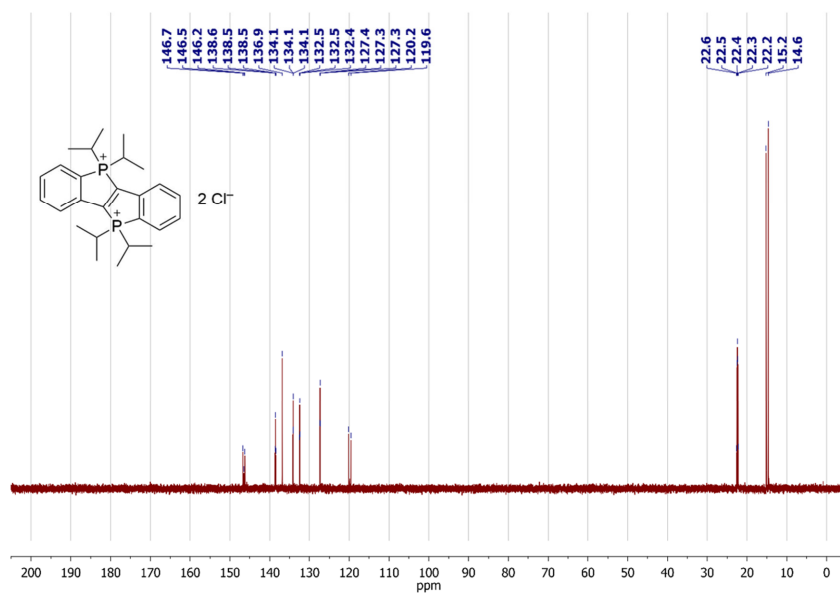


Figure S 2 $^{13}C\{^1H\}$ NMR spectrum of $P-H^{2+}$ (151 MHz, D_2O , 295 K).

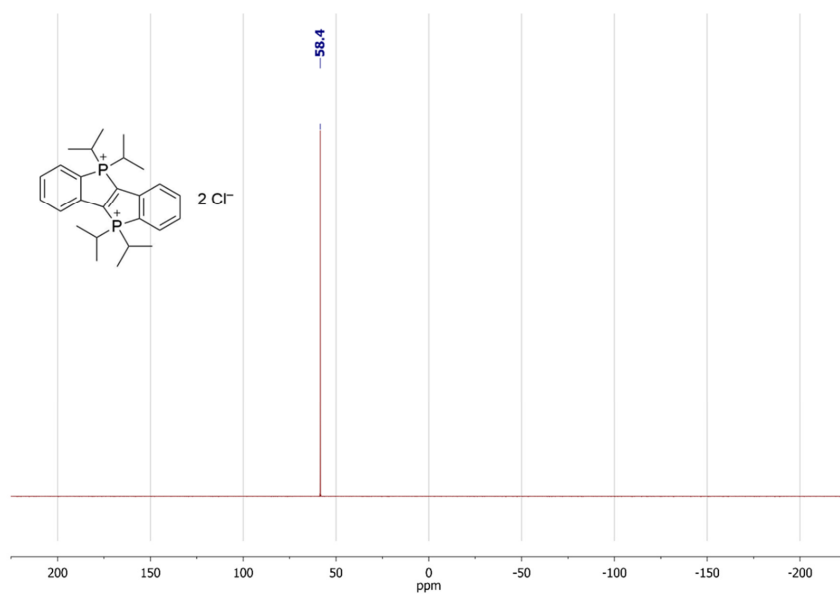


Figure S 3 $^{31}P\{^1H\}$ NMR spectrum of $P-H^{2+}$ (243 MHz, D_2O , 295 K).

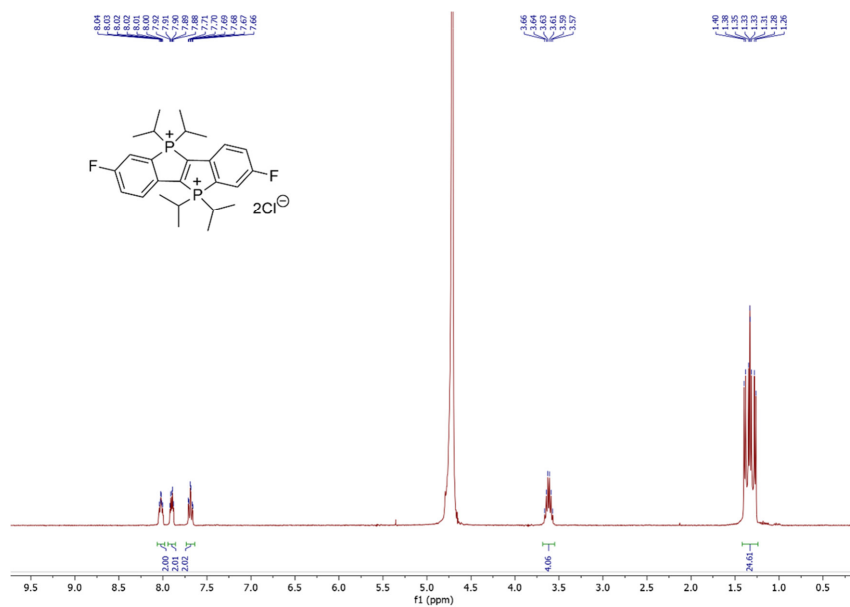


Figure S 4 1H NMR spectrum of $P-F_2^+$ (400 MHz, D_2O , 295 K).

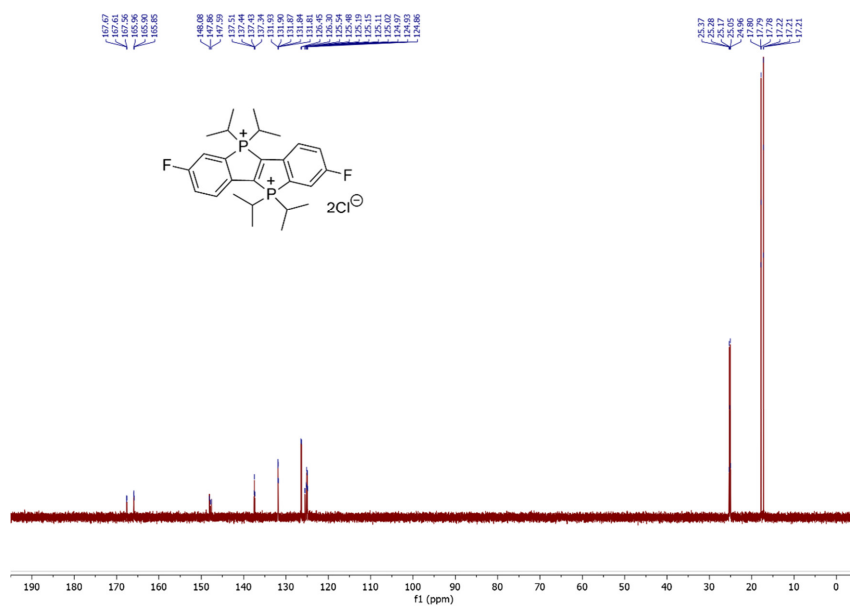


Figure S 5 $^{13}C\{^1H\}$ NMR spectrum of $P-F_2^+$ (151 MHz, D_2O , 295 K).

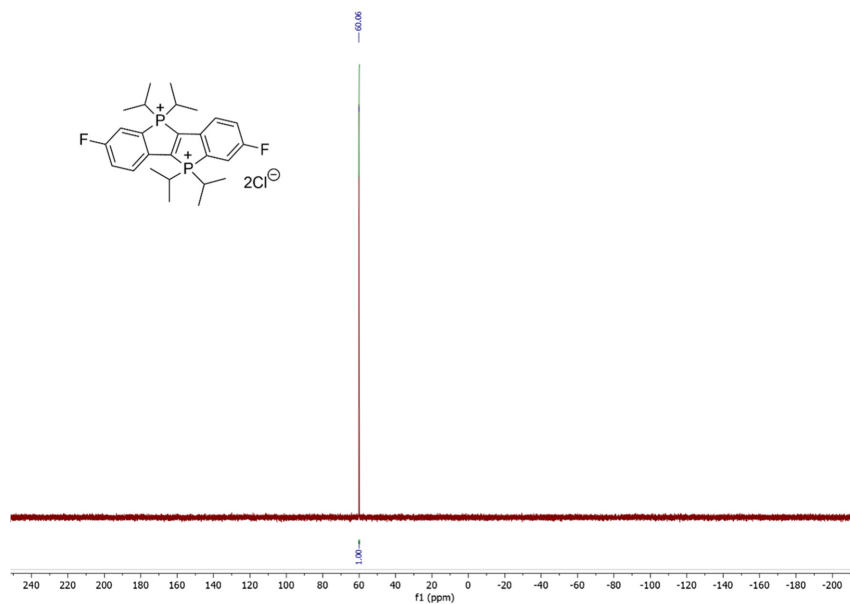


Figure S 6 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of P-F^{2+} (162 MHz, D_2O , 295 K).

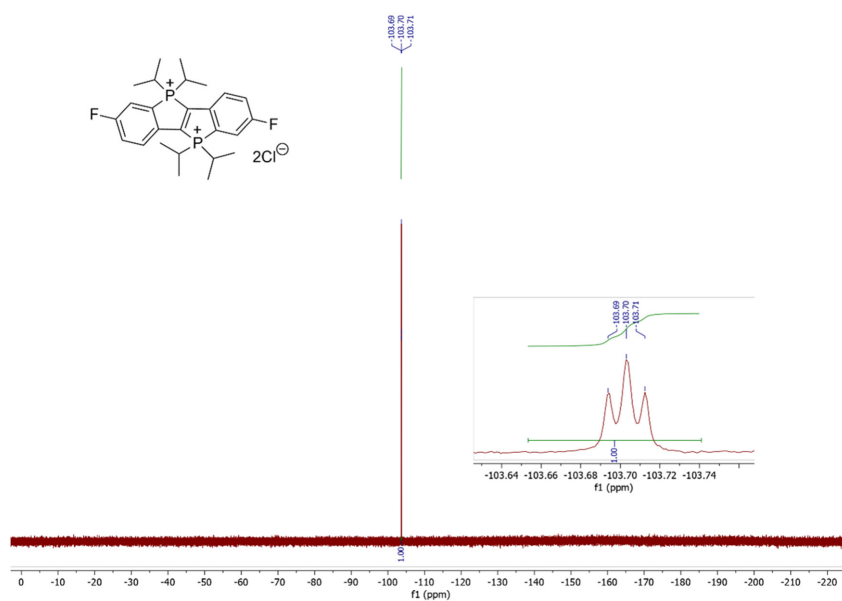
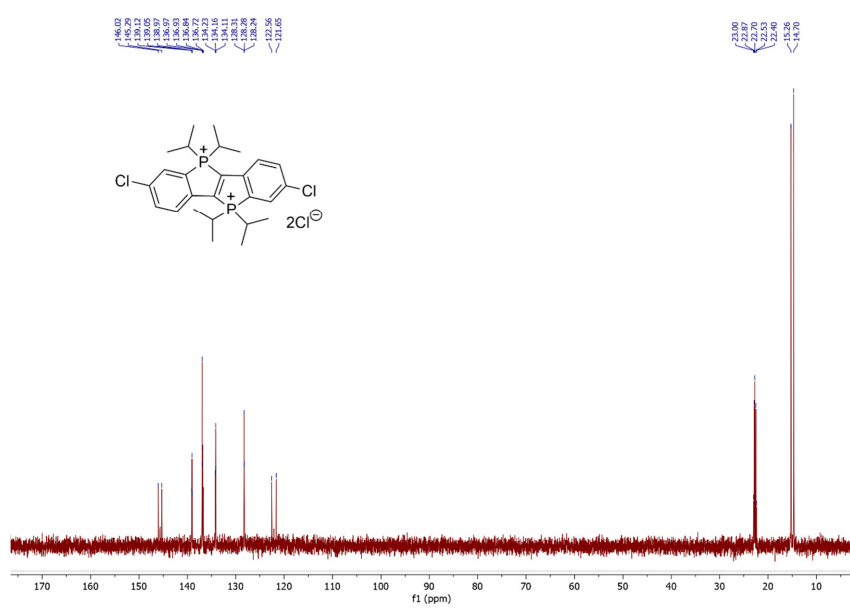
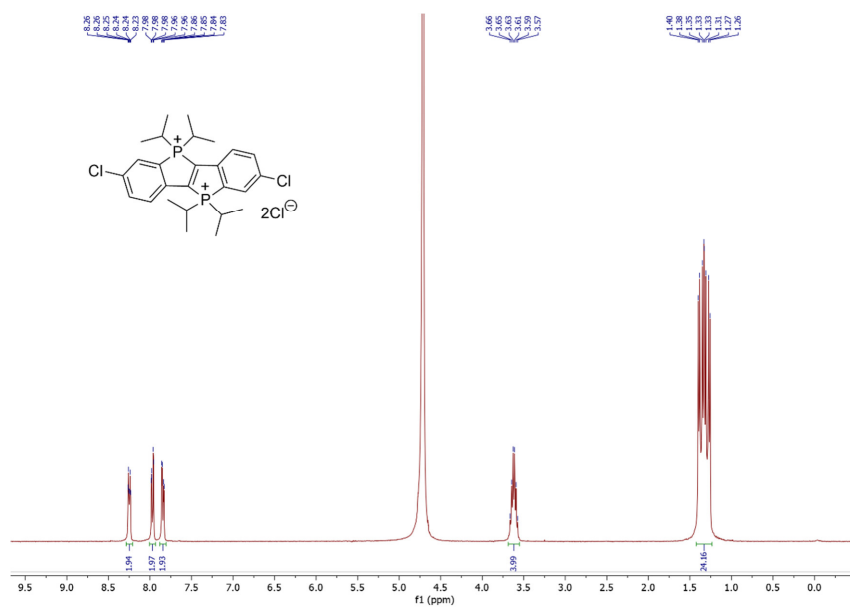


Figure S 7 $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of P-F^{2+} (376 MHz, D_2O , 295 K).



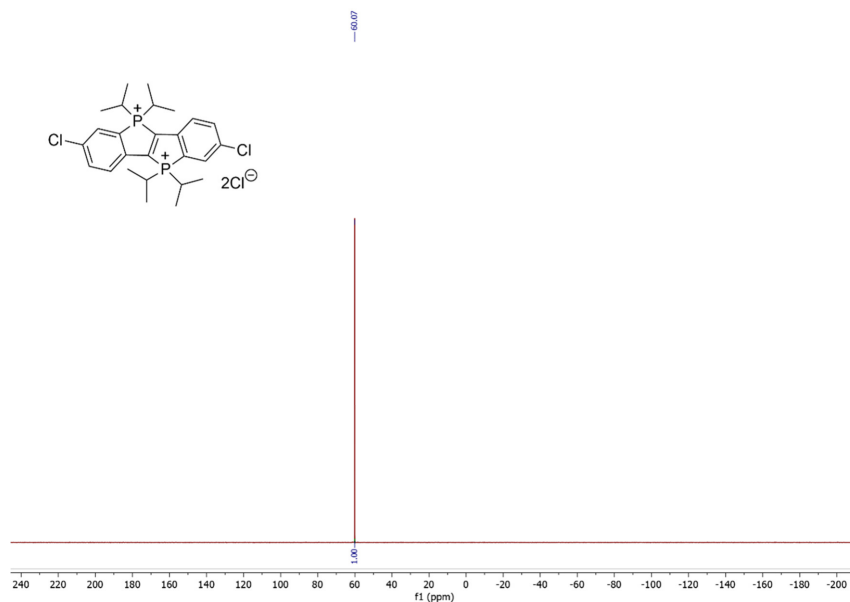


Figure S 10 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of P-F^{2+} (162 MHz, D_2O , 295 K).

4. X-Ray crystal structure determinations

Crystal data and details of the structure determinations are compiled in Table S 1. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer ($\text{Mo-K}\alpha$ or $\text{Cu-K}\alpha$ radiation, microfocus X-ray tube, multilayer mirror optics). Detector frames (typically ω -, occasionally φ -scans, scan width 0.5° for Mo and 1.0° for Cu) were integrated by profile fitting.^{14,15,16} Data were corrected for air and detector absorption, Lorentz and polarization effects^{15,16} and scaled essentially by application of appropriate spherical harmonic functions.^{15–18,19} Absorption by the crystal was treated numerically (Gaussian grid).^{15–20} An illumination correction was performed as part of the numerical absorption correction.^{17,18} Using Olex2²¹, the structures were solved with SHELXT²² (intrinsic phasing) and refined with SHELXL²³ by full-matrix least squares methods based on F^2 against all unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. The H_2O hydrogen atoms in $\text{X} = \text{Cl} \cdot 1.5 \text{H}_2\text{O}$ were located in the difference Fourier map and refined (in part by applying a SADI restraint)

CCDC 2224633 and 2224634 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via <https://www.ccdc.cam.ac.uk>.

Table S 1 Crystal data and details of the structure determinations for **X = F** · 4 MeOH and **X = Cl** · 1.5 H₂O.

Compound	X = F · 4 MeOH	X = Cl · 1.5 H ₂ O
Empirical Formula	C ₂₆ H ₃₄ Cl ₂ F ₂ P ₂ · 4 (H ₃ COH)	2 (C ₂₆ H ₃₄ Cl ₄ P ₂), 3 (H ₂ O)
Formula Weight	645.54	1154.59
Crystal system	monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> /Å	7.68726(3)	11.9371(8)
<i>b</i> /Å	16.93199(8)	15.3069(7)
<i>c</i> /Å	13.38321(7)	17.4558(6)
α /°	90	78.259(4)
β /°	94.5657(4)	76.680(4)
γ /°	90	69.650(5)
<i>V</i> /Å ³	1736.440(14)	2883.3(3)
<i>Z</i>	2	2
<i>F</i> ₀₀₀	688	1212
<i>d</i> _c /Mg·m ⁻³	1.235	1.330
μ /mm ⁻¹	2.900	0.541
max, min transmission factors	1.000, 0.625	1.000, 0.745
X-ray radiation, λ /Å	Cu-K α , 1.54184	Mo-K α , 0.71073
data collect. temperature /K	120(1)	120(1)
θ range /°	4.2 to 71.1	2.4 to 34.2
index ranges <i>h</i> , <i>k</i> , <i>l</i>	±9, ±20, ±16	±18, ±24, -26 to +27
reflections measured	95360	92290
unique [<i>R</i> _{int}]	3356 [0.0315]	22576 [0.0886]
observed [<i>I</i> > 2 σ (<i>I</i>)]	3239	14083
parameters refined [restraints]	199 [0]	644 [1]
GooF on <i>F</i> ²	1.069	1.041
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] <i>R</i> ₁ , <i>wR</i> ₂	0.0269, 0.0730	0.0571, 0.1081
<i>R</i> indices (all data) <i>R</i> ₁ , <i>wR</i> ₂	0.0277, 0.0736	0.1079, 0.1304
difference density: max, min /e·Å ⁻³	0.33, -0.23	0.69, -0.48
deposition number CCDC	2224633	2224634

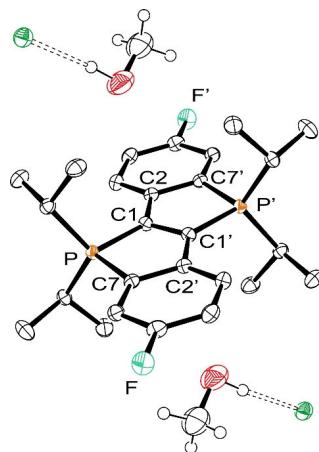


Figure S 11 ORTEP plot of the molecular structure of $X = F \cdot 4 \text{ MeOH}$ (displacement ellipsoids drawn at 50% probability, CH and CH_3 hydrogen atoms omitted for clarity, only two of the four co-crystallized MeOH molecules are shown for clarity). Selected bond lengths (Å) and angles ($^\circ$): P–C1 1.7984(12), P–C7 1.7964(12), C1–C1' 1.358(2), C1–C2 1.4663(16), C2–C7' 1.4118(17), C7–P–C1 93.04(6), C1'–C1–P 108.56(11), C1'–C1–C2 117.16(13), C2–C1–P 134.27(9), C7'–C2–C1 111.59(10), C2'–C7–P 109.55(9).

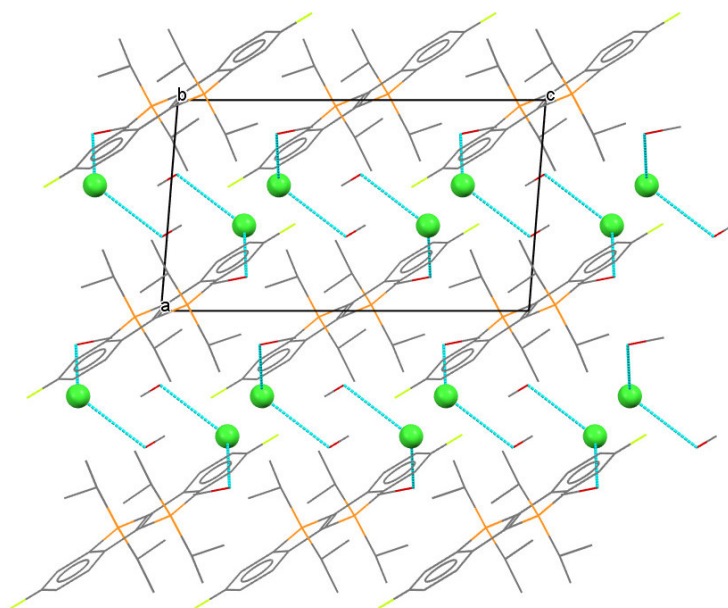


Figure S 12 Packing diagram of $X = F \cdot 4 \text{ MeOH}$ (hydrogen atoms omitted for clarity, view along the b axis).

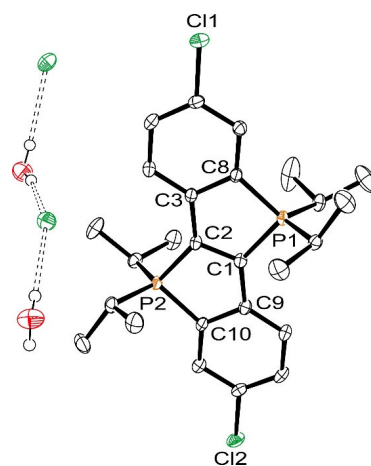


Figure S 13 ORTEP plot of the molecular structure of $X = \text{Cl} \cdot 1.5 \text{H}_2\text{O}$ (displacement ellipsoids drawn at 50% probability, CH and CH_3 hydrogen atoms omitted for clarity, only one independent molecule and two out of three co-crystallized water molecules are shown for clarity). Selected bond lengths (Å) and angles (°): P1–C1 1.802(2), P2–C2 1.796(2), P1–C8 1.8031(19), P2–C10 1.8069(19), C1–C2 1.366(3), C1–P1–C8 92.40(9), C2–P2–C10 92.38(9), C1–C2–C3 116.66(17), C2–C1–C9 115.97(17), C2–C1–P1 109.12(14), C1–C2–P2 109.76(14). For the two other half-molecules in the asymmetric unit (each completed to a full molecule by symmetry), very similar metrical parameters were found.

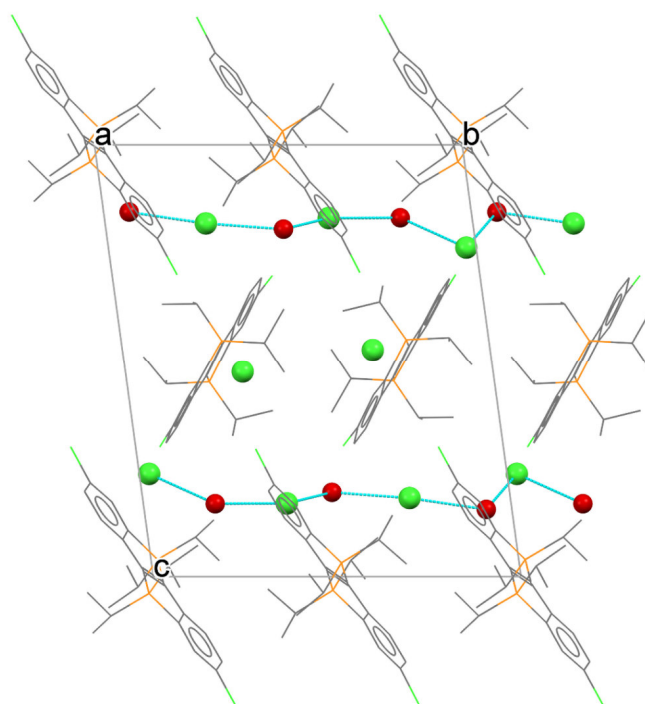


Figure S 14 Packing diagram of $X=\text{Cl} \cdot 1.5 \text{H}_2\text{O}$ (hydrogen atoms omitted for clarity, view along the a axis).

5. DFT calculations

The DFT calculations for structure optimization and frequency analysis were carried out with the Gaussian 09 software package²⁴ using the B3LYP functional combined with the 6-311++G(d,p) basis set and the ieefpcm model with water as the solvent. No negative vibrational frequencies were observed in the optimized structures indicating the successful convergence on minimum structures. Initially, P-H²⁺ was optimized in its singlet ground state. This structure served as the starting point for the corresponding triplet state calculations and those for the one electron reduced species. The calculated triplet energy, $E_T(\text{DFT})$, was determined by comparing the energies of the optimized singlet ground state to that of the corresponding triplet state (Figure S 15), which has been done successfully in previous studies.²⁵

Time-dependent DFT calculations with identical functional and basis set (30 states) were used to calculate the vertical excitation energies for simulating the triplet-triplet absorption spectrum and that of the radical cation. The predicted transitions and their oscillator strengths are displayed in Figure S 16 and Figure S 17. The spin density maps of both species are plotted as insets in the corresponding spectrum, and they were obtained by single point calculations.

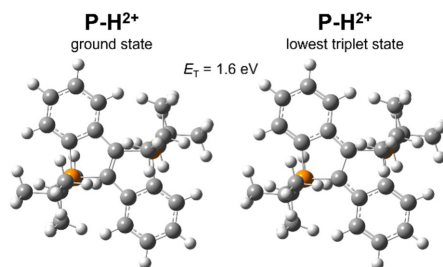


Figure S 15 Optimized structures of the P-H²⁺ ground state and the lowest triplet state together with their energy difference, calculated using the B3LYP functional and the 6-311++G(d,p) basis set.

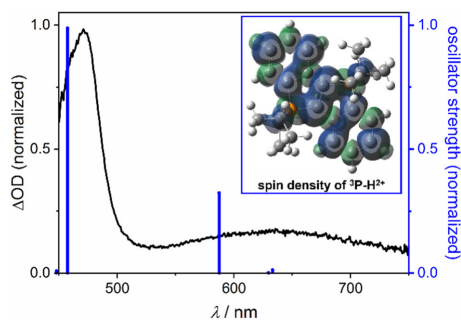


Figure S 16 Spectrum of ³P-H²⁺ (black) together with the predicted transitions (blue), calculated using TD-DFT with the B3LYP functional and the 6-311++G(d,p) basis set. The inset displays the corresponding spin density map.

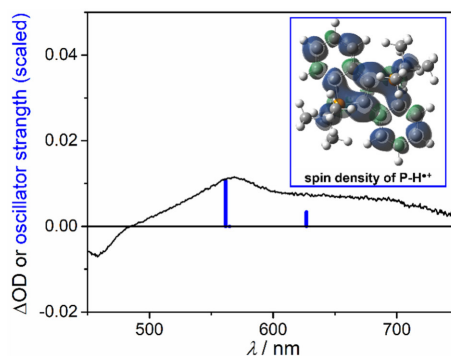


Figure S 17 Spectrum of P-H^{••} (black) together with the predicted transitions (blue), calculated using TD-DFT with the B3LYP functional and the 6-311++G(d,p) basis set. The experimental absorption signals above 530 nm correspond to the pure P-H^{••} spectrum. The spectrum below 530 nm is a superposition of P-H^{••} and Ru(bpy)₃³⁺ (with P-H²⁺ and Ru(bpy)₃²⁺ serving as baseline). The inset displays the spin density map calculated for P-H^{••}.

6. Quantum yield and lifetime measurements of the annihilators

The lifetimes of the three annihilator compounds were determined in 50 mM H₂SO₄ using the mini-τ apparatus (compare, Section 1). To obtain a high accuracy, the lifetimes were measured under different excitation and detection conditions. The measurements were performed under air and after 10 minutes of argon purging.

P-H²⁺ was excited with the EPL-375 nm and the EPLED-300 nm using filters F3 and F4 of the mini-τ, P-F²⁺ and P-Cl²⁺ were excited with the EPL-375 nm using filters F3 and F4, and EPL-450 nm using filter F4. The resulting lifetimes were averaged and summarized in Table S 2. One sample measurement of each annihilator compound is shown in Figure S 18.

Table S 2 Summary of the annihilator lifetimes in 50 mM H₂SO₄ in air-saturated solution and after 10 min of purging with argon.

	P-H ²⁺ [a]	P-F ²⁺ [b]	P-Cl ²⁺ [b]
τ ₀ / ns (purged)	14.7 ± 0.09	16.4 ± 0.04	11.4 ± 0.4
τ ₀ / ns (air)	14.5 ± 0.05	16.2 ± 0.1	11.3 ± 0.01

[a] averaged from measurements upon excitation at 371 nm or 293 nm using filters F3 and F4.

[b] averaged from measurements upon excitation at 371 nm using filters F3 or F4 and upon excitation at 446 nm using filter F4.

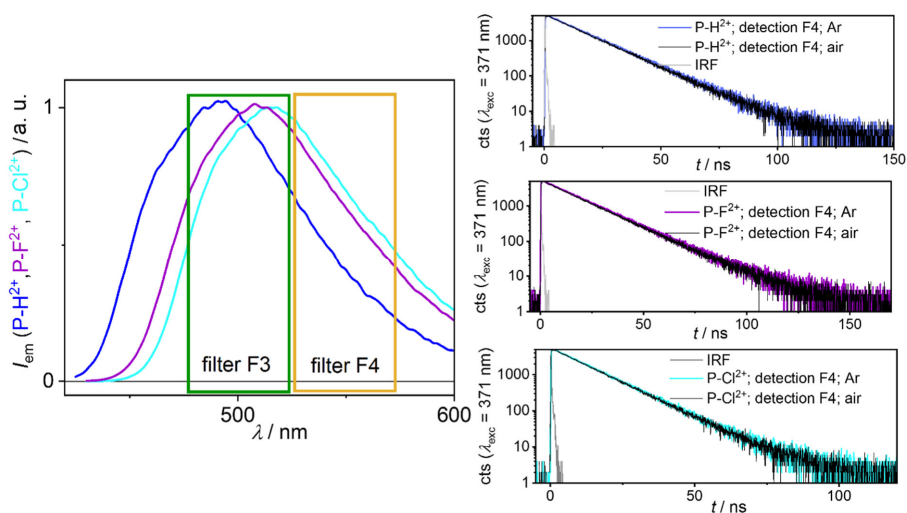


Figure S 18 Left: Emission spectra together with the detection window of the band-pass filters that were used for the lifetime measurements. Right: Sample lifetime measurements of all three annihilator compounds. For each annihilator the sample data set for the excitation with the LED-375 nm combined with detection filter F4 under air and argon are shown.

The fluorescence quantum yields of the annihilator compounds were determined in Ar-saturated 50 mM H₂SO₄. An Ar-saturated solution of perylene in ethanol (reference quantum yield, 0.92)⁵ was employed as reference. The relative quantum yields were measured at three excitation wavelengths and the absolute values were determined according to **Equation S 1** out of those three measurements.

Table S 3 Summary of fluorescence quantum yields of all annihilator compounds in 50 mM H₂SO₄ after 10 min degassing with argon. The given values are averaged from measurements at three different excitation wavelengths: 380 nm, 408 nm and 418 nm.

Reference compound	P-H ²⁺	P-F ²⁺	P-Cl ²⁺
perylene in ethanol	0.87 ± 0.019	0.85 ± 0.020	0.87 ± 0.023

7. Additional energy- and electron transfer experiments

7.1 Fitting of kinetic absorption and separation of formation and decay kinetics

The quenching rate constants for ET or EnT from the Ru photosensitizers were determined with Stern–Volmer plots. The corresponding kinetic traces were detected at two or three different wavelengths and from the resulting quenching rate constants (k_q) the averaged values are given in the main paper.

The formation of a new species after electron or energy transfer quenching is usually observed at a wavelength where only the newly formed species absorbs, or at an isosbestic point. The TA spectra of the triplet-excited dyads and follow-up species overlap over the entire spectrum and consequently, the kinetic absorption traces always show two superimposed species: Initially the unquenched dyad triplet, which is converted into the less absorbing ³P-H²⁺. Those kinetic traces were fitted using a biexponential function (Figure S 23, detection wavelength 486 nm) to obtain the dyad triplet lifetime under given conditions.

Because the formation kinetics of the EnT product cannot be measured isolated from the initial sensitizer triplet, the contribution of the sensitizer was subtracted from the biexponential decay trace. This was done by normalizing the (isolated) emission kinetic of the sensitizer at a given quencher concentration to the kinetic trace of the absorption at the same quencher concentration. Using the “subtract” function in the program Origin 9, the emission data (Figure S 19, red trace) was subtracted from the absorption data (violet trace), allowing to extract the formation kinetic (blue trace) out of the original absorption trace. A similar separation was carried out for the $^3\text{Ru}(\text{phen})_3^{2+}$ quenching with P-H^{2+} displayed in Figure S24.

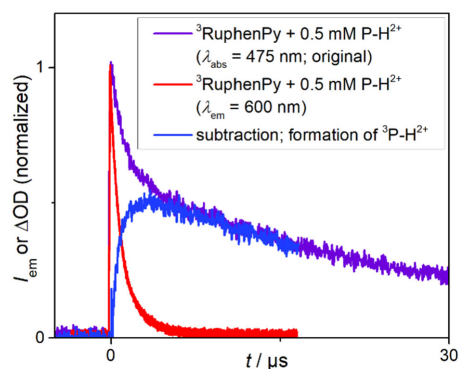


Figure S 19 Example for the process of isolating the formation kinetics of a species (blue trace) from the recorded absorption trace (violet) by subtracting the corresponding emission kinetic trace (red).

7.2 Ru(bpy)₃²⁺ and P-H²⁺

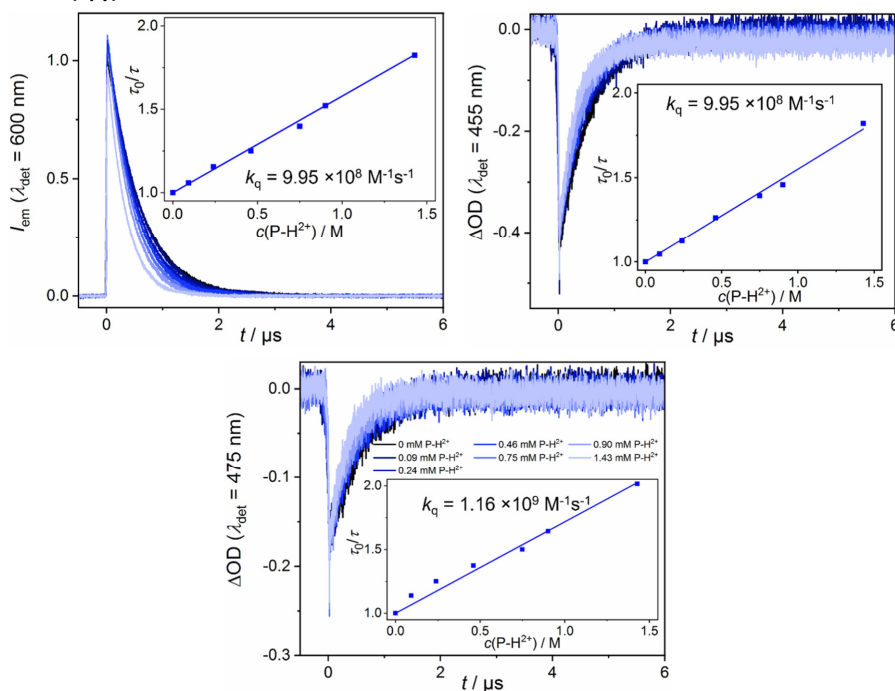


Figure S 20 Stern–Volmer ET quenching of ³Ru(bpy)₃²⁺ by P-H²⁺: The samples with 35 μM Ru(bpy)₃²⁺ in 50 mM H₂SO₄ were excited at 532 nm using an average pulse energy of 7.5 mJ. The main plots show the kinetic traces at three different detection wavelengths (sensitizer emission at 600 nm, absorption at 455 nm and 475 nm; for the transient absorption (TA) spectra of the sensitizer triplet and the quenching products, see Figure 4 of the main paper), the insets show the corresponding Stern–Volmer plots including the quenching rate constants (*k_q*).

For a more reliable assignment of the TA bands after ET from ³Ru(bpy)₃²⁺ to P-H²⁺, we independently oxidized Ru(bpy)₃²⁺ (32 μM) using an acidic (H₂SO₄ 11.0 mL, 0.7 M) solution with PbO₂ (excess) added.²⁶ A simulated ΔOD spectrum of the oxidized Ru(bpy)₃³⁺ (Figure S 21, lower part) shows a bleach in the very same spectral region as has been observed in a delayed TA spectrum of Ru(bpy)₃²⁺ and P-H²⁺ (same figure, middle part). For the assignment of the resulting reduced P-H^{•+} species, a UV/vis absorption spectrum of the chemically prepared P-H^{•+}¹³ was recorded in MeOH (H₂O is impossible for stability reasons) were performed and the resulting spectrum was compared to the delayed TA spectra, which were measured after ET from ³Ru(bpy)₃²⁺ or ³Ru(phen)₃²⁺ (Figure S 22). The overlap of all three (scaled) spectra is excellent for wavelengths above 550 nm (at lower wavelengths, the uncorrected bleach of the oxidized ruthenium species superimposes the spectrum; furthermore, the TA spectra have a P-H²⁺ baseline, whereas the P-H^{•+} spectrum was recorded with a solvent baseline, which is why the spectra cannot be compared below 450 nm).

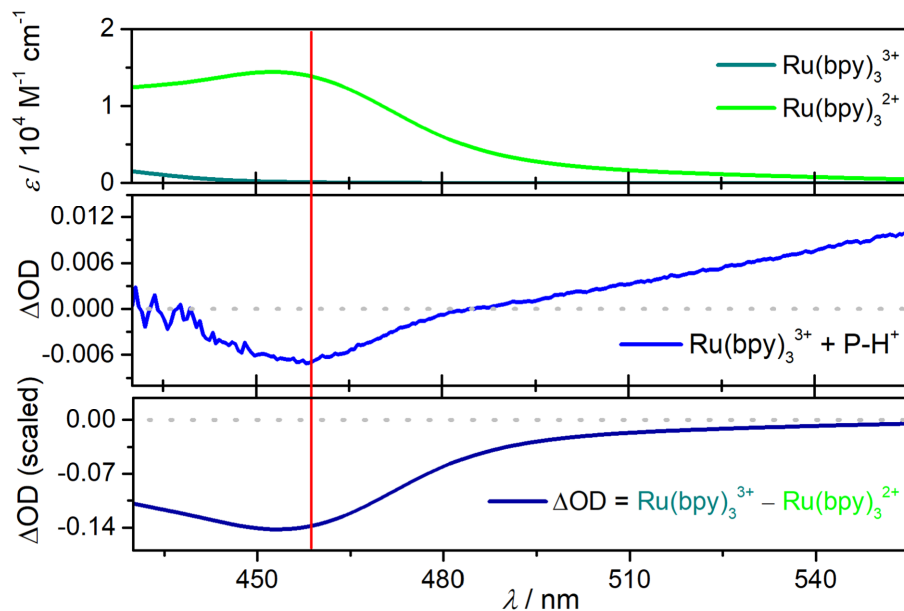


Figure S 21 Upper: Calibrated absorption spectra of $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^{2+}$. Middle: Delayed TA spectrum after ET from $^3\text{Ru}(\text{bpy})_3^{2+}$ to P-H^{2+} (for experimental conditions, see Figure 4 of the main paper). Lower: Spectral difference between $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^{2+}$. The red line serves as a visual aid to follow the bleach observed in the delayed TA spectrum.

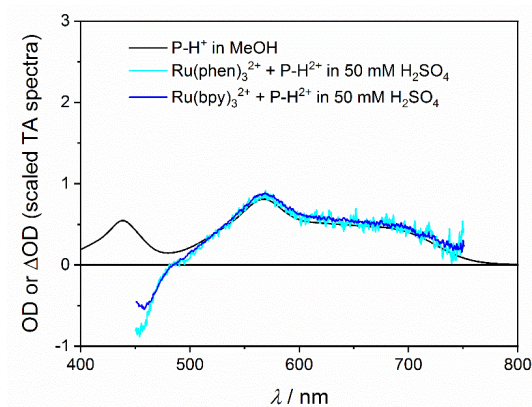


Figure S 22 Overlaid spectra of chemically generated P-H^{*+} (chemically prepared as in ref.¹³ and with chloride counter ion, the solvent MeOH was refluxed over Mg, distilled and degassed prior to use), and TA spectra after ET from triplet excited Ru-sensitizer ($^3\text{Ru}(\text{bpy})_3^{2+}$ or $^3\text{Ru}(\text{phen})_3^{2+}$) to P-H^{2+} ; for experimental conditions see main part Figure 4, and Figure S 24.

7.3 RubpyPy²⁺ and P-H²⁺

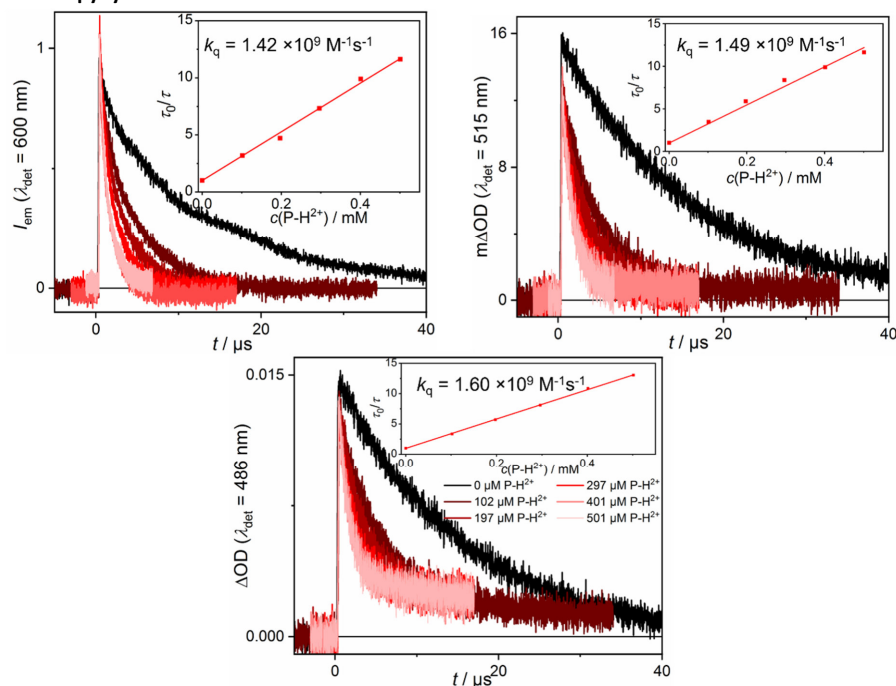


Figure S 23 Stern–Volmer ET quenching of ³RubpyPy²⁺ by P-H²⁺: The samples with 35 μM RubpyPy²⁺ in 50 mM H₂SO₄ were excited at 532 nm using an average pulse energy of 8.4 mJ. The main plots show the kinetic traces at three different detection wavelengths (sensitizer emission at 600 nm, absorption at 515 nm and 486 nm; data sets at the latter wavelength were fitted carefully such that the resulting annihilator-derived offsets do not contribute to the initial kinetics; for TA spectra see Figure 4 of the main paper), the insets show the corresponding Stern–Volmer plots including the quenching rate constants (k_q).

7.4 Ru(phen)₃²⁺ and P-H²⁺

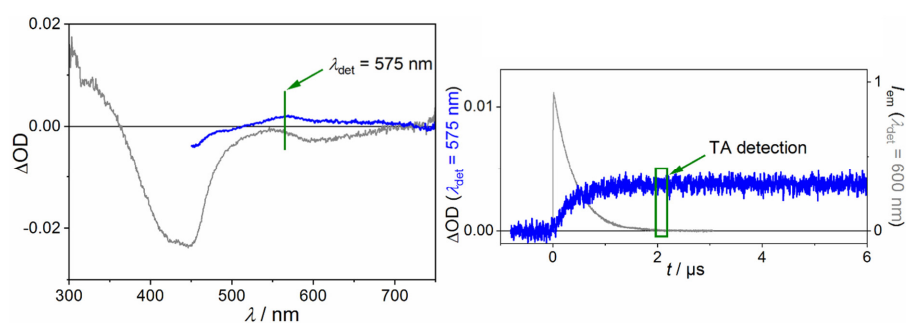


Figure S 24 Electron transfer reactivity of ³Ru(phen)₃²⁺ with P-H²⁺, after 532 nm excitation (19.8 mJ) Left: TA spectra of ³Ru(phen)₃²⁺ (grey, time delay 200 ns) and of oxidized Ru(phen)₃³⁺ and 1.2 mM P-H²⁺ after the electron transfer (blue, time delay 2 μs). Right: Kinetic traces of ³Ru(phen)₃²⁺ (dark grey) and the formation of P-H^{*} (blue, subtracted kinetic trace).

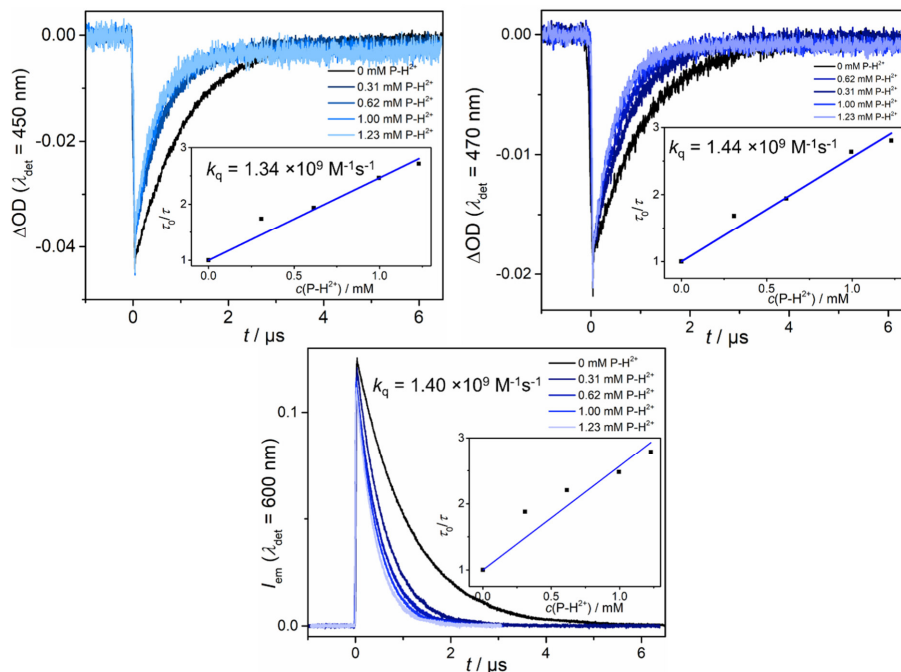


Figure S 25 Stern–Volmer ET quenching of ${}^3\text{Ru}(\text{phen})_3^{2+}$ by P-H^{2+} : The samples with $24\ \mu\text{M}$ $\text{Ru}(\text{phen})_3^{2+}$ in $50\ \text{mM}$ H_2SO_4 were excited at $532\ \text{nm}$ using an average pulse energy of $14.6\ \text{mJ}$. The main plots show the kinetic traces at three different detection wavelengths (sensitizer emission at $600\ \text{nm}$, absorption at $450\ \text{nm}$ and $470\ \text{nm}$, for corresponding TA spectra see Figure S 24), the insets show the resulting Stern–Volmer plots including the quenching rate constants (k_q).

7.5 $\text{Ru}(\text{phen})_3^{2+}$ and P-F^{2+} or P-Cl^{2+}

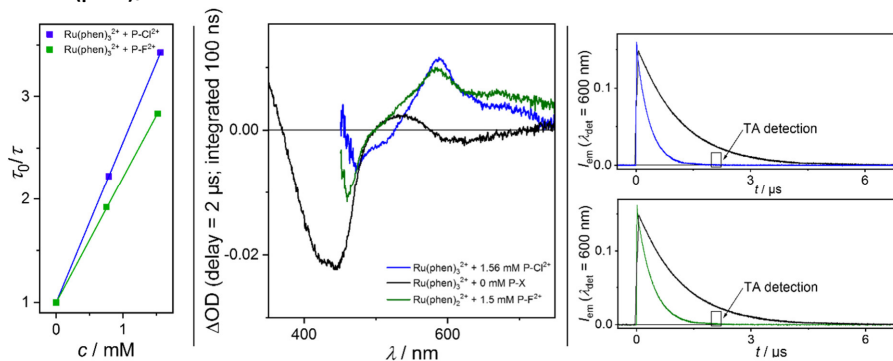


Figure S 26 Quenching of ${}^3\text{Ru}(\text{phen})_3^{2+}$ by P-Cl^{2+} (blue) and P-F^{2+} (green, same color-code throughout the figure, all measured with $\lambda_{\text{exc}} = 532\ \text{nm}$, $25\ \text{mJ}$) with preliminary Stern–Volmer plots (left), the TA spectra of ${}^3\text{Ru}(\text{phen})_3^{2+}$ (black) and with one of the annihilators present (all after a time delay of $2\ \mu\text{s}$). The right part of the figure contains the kinetic traces for the quenching of ${}^3\text{Ru}(\text{phen})_3^{2+}$ with the two annihilators; the same solutions as for the TA spectra were used.

7.6 RuphenPy²⁺ and P-H²⁺

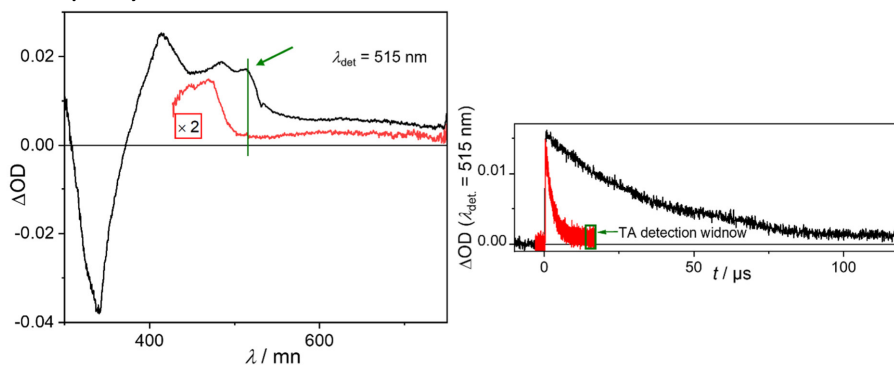


Figure S 27 Energy transfer reactivity of ³RuphenPy²⁺ with P-H²⁺ (initial concentrations 39 μM RuphenPy²⁺, 0.3 mM P-H²⁺) after 532 nm excitation (14.6 mJ). Left: TA spectra of ³RuphenPy²⁺ (black, time delay 100 ns) and ³P-H²⁺ after the energy transfer (red, time delay 15 μs). Right: Kinetic traces ($\lambda_{\text{exc}} = 532$ nm, 8.4 mJ) of ³RuphenPy²⁺ without (black) and with 0.3 mM P-H²⁺ added to the solution (red).

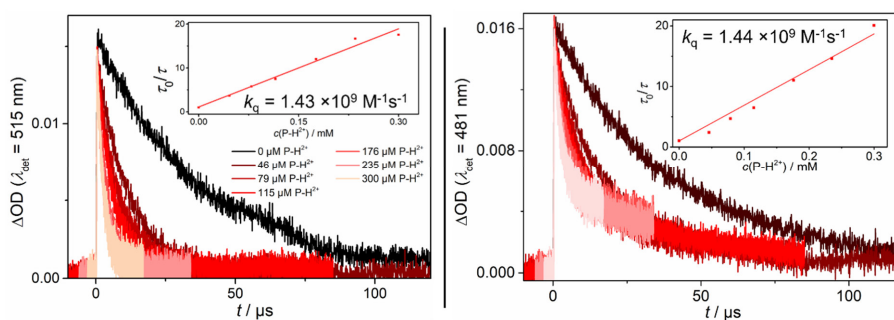


Figure S 28 Stern–Volmer EnT quenching of ³RuphenPy²⁺ with P-H²⁺: The samples with 39 μM RuphenPy²⁺ in 50 mM H₂SO₄ were excited at 532 nm using an average pulse energy of 8.4 mJ. The main plots show the kinetic traces at two different detection wavelengths (absorption 515 nm and 481 nm, for corresponding TA spectra see Figure S 27), the insets show the resulting Stern–Volmer plots including the quenching rate constants (k_q).

7.7 Ru(bpz)₃²⁺ and P-H²⁺

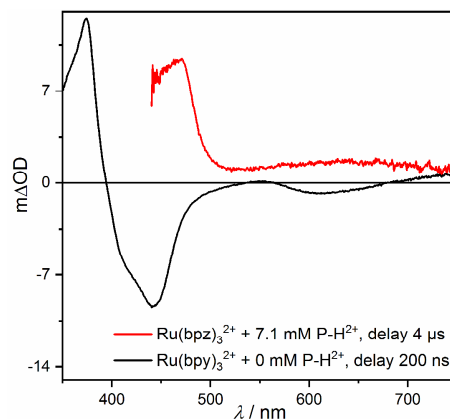


Figure S 29 Energy transfer reactivity of $^3\text{Ru}(\text{bpz})_3^{2+}$ (46 μM) with P-H^{2+} (7.1 mM) after 532 nm excitation (25 mJ). TA spectra of $^3\text{Ru}(\text{bpz})_3^{2+}$ (black, time delay 200 ns) and $^3\text{P-H}^{2+}$ (red, time delay 4 μs) after the energy transfer are shown.

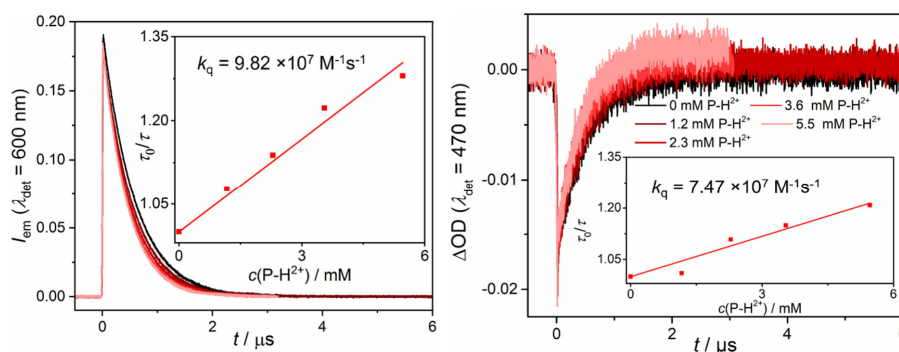


Figure S 30 Stern–Volmer EnT quenching of $^3\text{Ru}(\text{bpz})_3^{2+}$ by P-H^{2+} : The samples with 20 μM $\text{Ru}(\text{bpz})_3^{2+}$ in H_2O were excited at 532 nm using an average pulse energy of 25 mJ. The main plots show the kinetic traces at two different detection wavelengths (sensitizer emission at 600 nm and TA at 470 nm, corresponding TA spectra are shown in Figure S 29), the insets show the resulting Stern–Volmer plots including the quenching rate constants (k_q).

Non-coordinated heteroatoms of the bipyrazine ligands can be protonated, which leads to a shift in the UV/vis absorption, and a change in optical properties.²⁷ For that reason, all measurements involving $\text{Ru}(\text{bpz})_3^{2+}$ were performed in neat H_2O (MilliQ). To estimate the kinetic salt effect caused by the addition of 50 mM H_2SO_4 , which is present in all other solutions and serves as ionic strength buffer due to the high degree of acid dissociation, we compared the EnT quenching constants of the dyads RuphenPy^{2+} and RubpyPy^{2+} in pure water with those measured in 50 mM H_2SO_4 (see main paper Table 1). EnT between the two cationic species is faster in the acidic solution and the resulting factor is similar.

Table S 4 Rate constants (k_q) for EnT quenching of $^3[\text{Ru}]^{2+}$ with P-H^{2+} in neat water and 50 mM H_2SO_4 .

	RuphenPy $^{2+}$	RubpyPy $^{2+}$	Ru(bpz) $_3^{2+}$
$k_q(\text{H}_2\text{O}) / 10^9 \text{ M}^{-1}\text{s}^{-1}$	0.47	0.63	0.09
$k_q(\text{H}_2\text{SO}_4 \text{ 50 mM}) / 10^9 \text{ M}^{-1}\text{s}^{-1}$	1.44	1.50	≈ 0.25
factor	$3.06^{[a]}$	$2.38^{[a]}$	$2.72^{[b]}$

^[a] $k_q(\text{H}_2\text{O}) \times \text{factor} = k_q(\text{H}_2\text{SO}_4 \text{ 50 mM})$

^[b] averaged from dyads.

7.8 Quenching studies with further photosensitizers

The following table contains the additional sensitizers that have been tested with the quencher P-H^{2+} , along with their triplet energies and calculated quenching efficiencies under our experimental conditions. Key observations are summarized and explained in more detail in the following paragraphs. The concentrations of the metal-based sensitizers were chosen such that the absorption at the excitation wavelength 532 nm was between 0.02-0.03 and for the organic dyes the absorption was set to 0.2.

Table S 5 Literature known photosensitizers together with their triplet energies, the calculated efficiencies for the excited state quenching with P-H^{2+} (in Ar-saturated H_2O) and the spectral changes observed after quenching.

Sensitizer ^[a]	E_T / eV	$\eta_q^{[b]} ([\text{P-H}^{2+}] / \text{mM})$	Observation ^[a]
Os(phen) $_3^{2+}$	1.8^{28}	0.18 (5.0)	ET, bleach indicating Os $^{3+}$ formation
Rubpy-xy-Ant $^{2+}$	$\sim 1.84^2$	>0.99 (1.2)	ET, bleach indicating Ru $^{3+}$ formation
Ru(dpp) $_3^{2+}$	$2.0\text{-}2.2^{29}$	0.74 (1.2)	ET, bleach indicating Ru $^{3+}$ formation
Eosin Y (EY $^{2-}$)	1.9^{30}	>0.99 (0.6)	ET, absorption of EY $^{*-}$ and bleach for EY $^{2-}$
Erythrosin B (ETB $^{2-}$)	$1.8\text{-}2.0^{31}$	>0.99 (0.3)	ET, absorption of ETB $^{*-}$ and bleach for ETB $^{2-}$

^[a] For chemical structures of the sensitizers, corresponding spectra and kinetic traces see Figure S 31 - Figure S 35.

^[b] Under our experimental conditions: In Ar-saturated H_2O , concentration of the quencher P-H^{2+} is given in brackets.

Os(phen) $_3^{2+}$ + P-H^{2+}

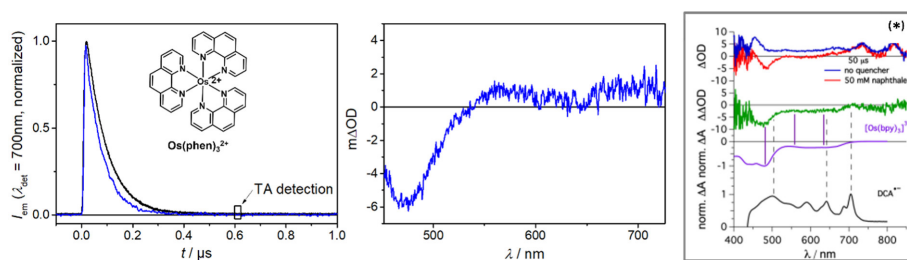


Figure S 31 Left: Emission decay traces of $^3\text{Os(phen)}_3^{2+}$ without (black trace) and with 5.0 mM P-H^{2+} (blue trace) together with the structure of the sensitizer (all solutions were measured in Ar-saturated H_2O , after excitation with 532 nm, 30 mJ); Middle: TA spectrum of the Os(phen)_3^{2+} P-H^{2+} (5.0 mM) solution after 600 ns time delay; Right: (*)Picture taken from ref. ³², with the simulated (purple trace) and measured (green trace) spectrum of Os(bpy)_3^{3+} .

Excited $^3\text{Os(phen)}_3^{2+}$ is evidently quenched by P-H^{2+} and the TA spectrum after quenching shows a bleach between 450-530 nm (Figure S 31). P-H^{2+} does not absorb in that spectral region and the

corresponding triplet would show a positive absorption band (main part, Figure 4). Therefore, the bleach can be unambiguously assigned to the oxidized Os-species³² (right part of Figure S 31) originating from oxidative quenching of $^3\text{Os}(\text{phen})_3^{2+}$ by P-H^{2+} (ET reactivity).

Rubpy-xy-Ant²⁺ + P-H²⁺

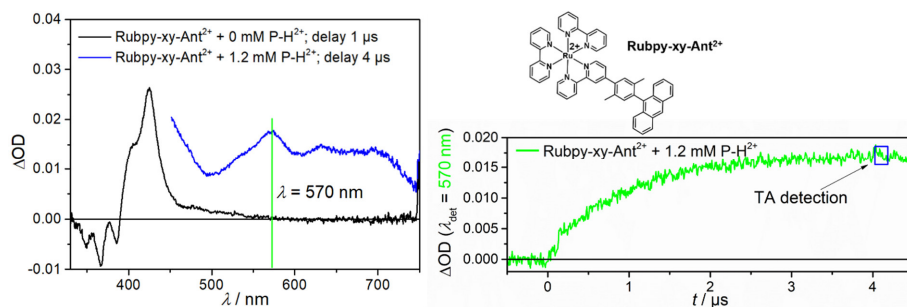


Figure S 32: Left: TA spectra of $^3\text{Rubpy-xy-Ant}^{2+}$ (black)² and the sensitizer with 1.2 mM P-H^{2+} added (blue), after a 4 μs time delay (after 532nm excitation, 30 mJ); Upper right: Structure of the sensitizer; Lower right: TA measurement of the sensitizer (green) with 1.2 mM P-H^{2+} detected at 570 nm.

The quenching product for the system $^3\text{Rubpy-xy-Ant}^{2+}$ (whose initial $^3\text{MLCT}$ is converted to triplet anthracene on a sub-nanosecond timescale)² and P-H^{2+} has a broad absorption above 500 nm, which strongly resembles the spectrum of the reduced P-H^+ species (Figure S 17 and Figure S 22). The maximum at 570 nm is essentially identical to the one observed for electron transfer reactions with $^3\text{Ru}(\text{bpy})_3^{2+}$ (see main part Figure 4) or $^3\text{Ru}(\text{phen})_3^{2+}$ (Figure S 24). The absence of the $^3\text{P-H}^{2+}$ absorption maximum provided further evidence that the dyad $^3\text{Rubpy-xy-Ant}^{2+}$ reduces the P-H^{2+} and does not undergo energy transfer but rather an electron transfer as main quenching pathway.

$\text{Ru}(\text{dpp})_3^{2+}$ + P-H²⁺

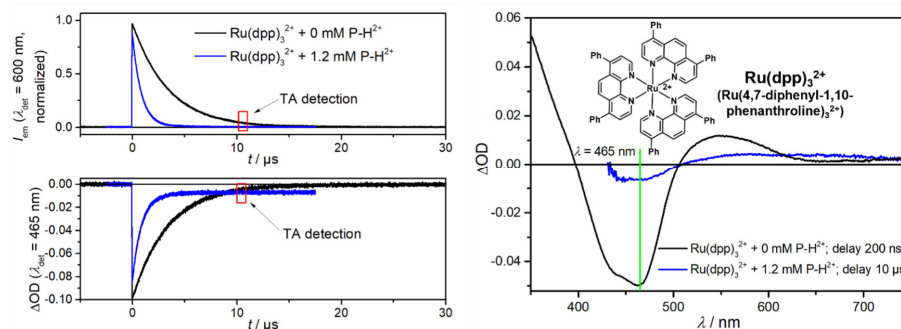


Figure S 33 Upper left: Emission decay of $^3\text{Ru}(\text{dpp})_3^{2+}$ without (black trace) and with 1.2 mM P-H^{2+} added (after 532 nm excitation, 30 mJ); same color code throughout the figure; Lower left: Absorption decay traces detected at 465 nm; Right: TA spectra of $^3\text{Ru}(\text{dpp})_3^{2+}$ (black) and after the quenching with P-H^{2+} (time delay 10 μs indicated by red boxes in the kinetic traces of the left part of the figure), together with the structure of the sensitizer.

The kinetic traces of absorption and emission show quenching of $^3\text{Ru}(\text{dpp})_3^{2+}$ by P-H^{2+} . The bleach at 465 nm in the TA spectrum after quenching can be assigned to the oxidized Ru-species (compare Figure 4 main part and Figure S 24 and Figure S 21). This, together with the absence of the $^3\text{P-H}^{2+}$

absorption band (expected in the same spectral region, around 470 nm), points to an electron transfer reaction between $^3\text{Ru}(\text{dpp})_3^{2+}$ and P-H^{2+} .

$\text{EY}^{2-} + \text{P-H}^{2+}$

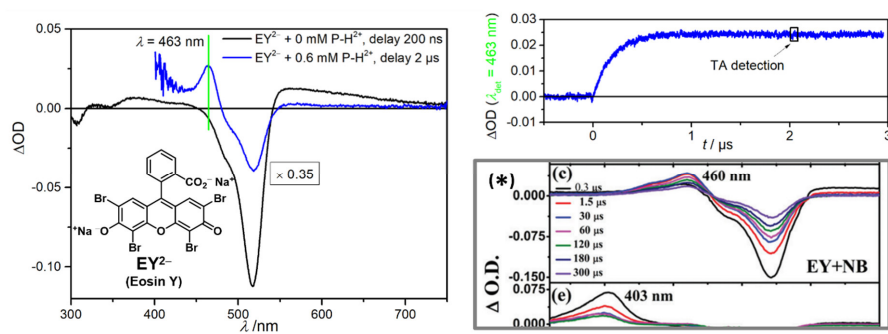


Figure S 34 Left: TA spectrum of EY^{2-} (black, scaled, structure shown as inset) and post-quenching spectrum with P-H^{2+} (0.6 mM, blue), after excitation with 532 nm, 30 mJ; Upper right: Kinetic absorption trace for the formation of the oxidized form $\text{EY}^{\bullet-}$; Lower right: (*) TA spectra at different delay times taken from 33 , which show the formation of $\text{EY}^{\bullet-}$ in the presence of an oxidative quencher (NB = nitrobenzene, in $\text{H}_2\text{O}:\text{EtOH}$ mixture).

The oxidized form of EY^{2-} shows two significant transient signatures: the bleach around 515 nm and a new absorption band around 460 nm.^{33,34} Both bands are also observed in our quenching studies (left part of Figure S 34) with P-H^{2+} , confirming an electron transfer between the excited EY^{2-} and P-H^{2+} .

$\text{ETB}^{2-} + \text{P-H}^{2+}$

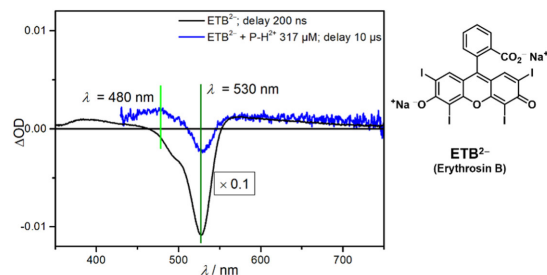


Figure S 35 Left: TA spectra of ETB^{2-} without (black, scaled) and with (blue) P-H^{2+} after quenching, in Ar-saturated H_2O , excitation with 532 nm pulses, 30 mJ; Right: Structure of the photosensitizer Erythrosin B (ETB^{2-}).

As observed for the structurally related EY^{2-} , the quenching product of $^3\text{ETB}^{2-}$ with P-H^{2+} shows the ground state bleach (530 nm) and a new absorption band in the blue/green spectral region (480 nm). Owing to the similarity of EY^{2-} and ETB^{2-} (identical structure, only the bromo substituents have been replaced by iodine), and again the lack of the absorption band of $^3\text{P-H}^{2+}$ despite high quenching efficiencies, we conclude that an electron transfer between the excited ETB^{2-} and P-H^{2+} takes place.

8. Additional sTTA experiments

8.1 RubpyPy²⁺ and P-H²⁺

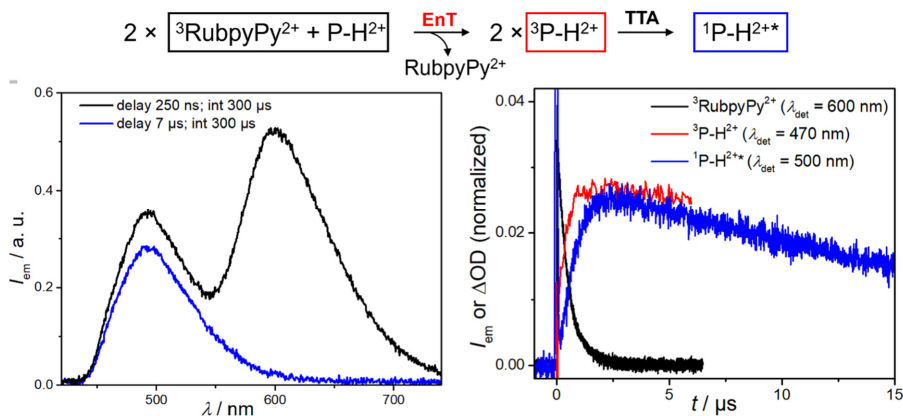


Figure S 36 Top: Reaction scheme of sTTA with RubpyPy²⁺ (22 μM) and P-H²⁺ (1.2 mM). Left: Time-gated emission spectra (excitation at $\lambda = 532 \text{ nm}$, 25 mJ) of ${}^3\text{RubpyPy}^{2+}$ and ${}^1\text{P-H}^{2+*}$ (black, delay 250 ns integrated over 300 μs), the isolated spectrum after sTTA (blue, delay 7 μs integrated over 300 μs). The control measurement with only P-H²⁺ in solution after 532 nm excitation (no emission observed) is shown in Figure 6 of the main paper. Right: Relative kinetic traces (excitation at $\lambda = 532 \text{ nm}$, 27 mJ) of ${}^3\text{RubpyPy}^{2+}$ with 1.2 mM P-H²⁺ (black, $\lambda_{\text{det}} = 600 \text{ nm}$), formation of ${}^3\text{P-H}^{2+}$ (red, $\lambda_{\text{det}} = 470 \text{ nm}$, subtracted kinetic trace, for details see page S19-S20) and the formation and decay of ${}^1\text{P-H}^{2+*}$ after sTTA (blue, $\lambda_{\text{det}} = 500 \text{ nm}$).

8.2 Ru(bpz)₃²⁺ and P-H²⁺

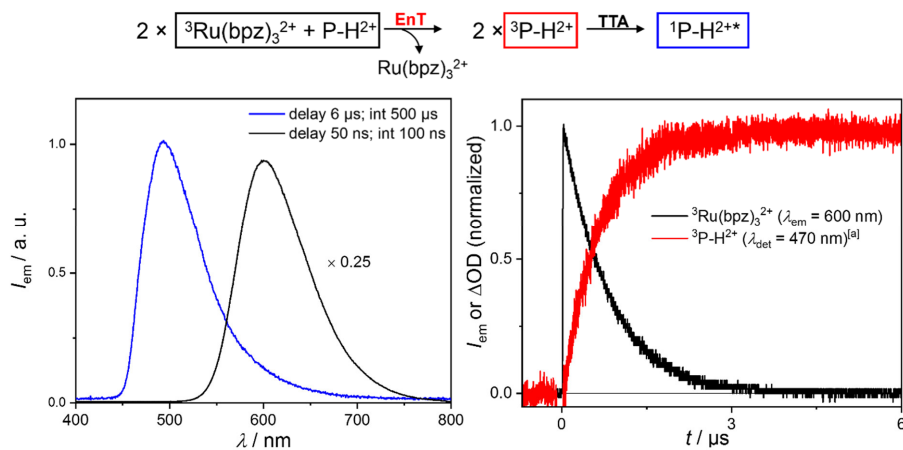


Figure S 37 Top: Reaction scheme of sTTA with Ru(bpz)₃²⁺ (80 μM) and P-H²⁺ (8.3 mM) in neat water. Left: Time-gated emission spectra (excitation at $\lambda = 532 \text{ nm}$, 25 mJ) of ${}^3\text{Ru}(\text{bpz})_3^{2+}$ (black, delay 50 ns integrated over 100 ns), the isolated spectrum after sTTA (blue, delay 6 μs integrated over 500 μs). Right: Normalized kinetic traces (excitation at $\lambda = 532 \text{ nm}$, 25 mJ) of ${}^3\text{Ru}(\text{bpz})_3^{2+}$ with 10 mM P-H²⁺ (black, $\lambda_{\text{det}} = 600 \text{ nm}$) and formation of ${}^3\text{P-H}^{2+}$ (red, $\lambda_{\text{det}} = 470 \text{ nm}$, subtracted kinetic trace, for details see page S19-S20).

8.3 RuphenPy²⁺ and P-H²⁺

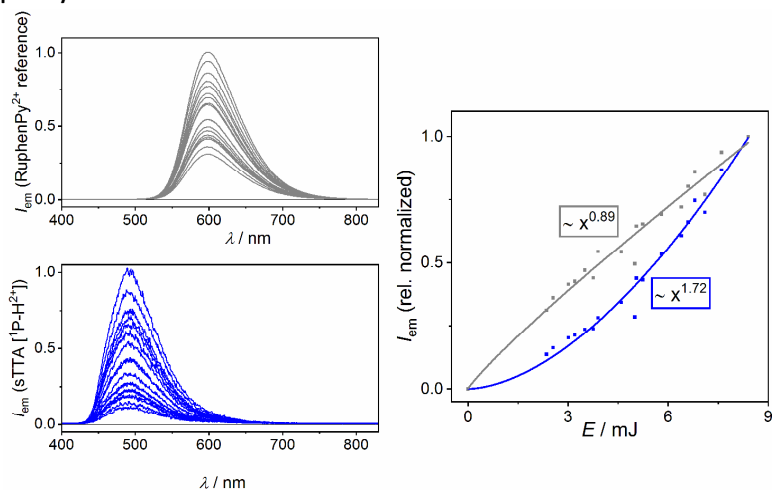


Figure S 38 Comparison of direct (reference, grey data sets for 26 μM RuphenPy²⁺) sensitizer emission and delayed annihilator emission after sTTA (blue data sets, 26 μM RuphenPy²⁺ and 511 μM P-H²⁺) at different excitation intensities. Upper left: Normalized emission of the sensitizer RuphenPy²⁺ as reference, almost linear intensity dependence (right plot, the exponent of the power function is 0.89). Lower left: Normalized emission of ¹P-H²⁺* after sTTA-UC. The intensity dependence is almost quadratic (right plot, the exponent of the power function is 1.72).

8.4 RuphenPy²⁺ and P-F²⁺ or P-Cl²⁺

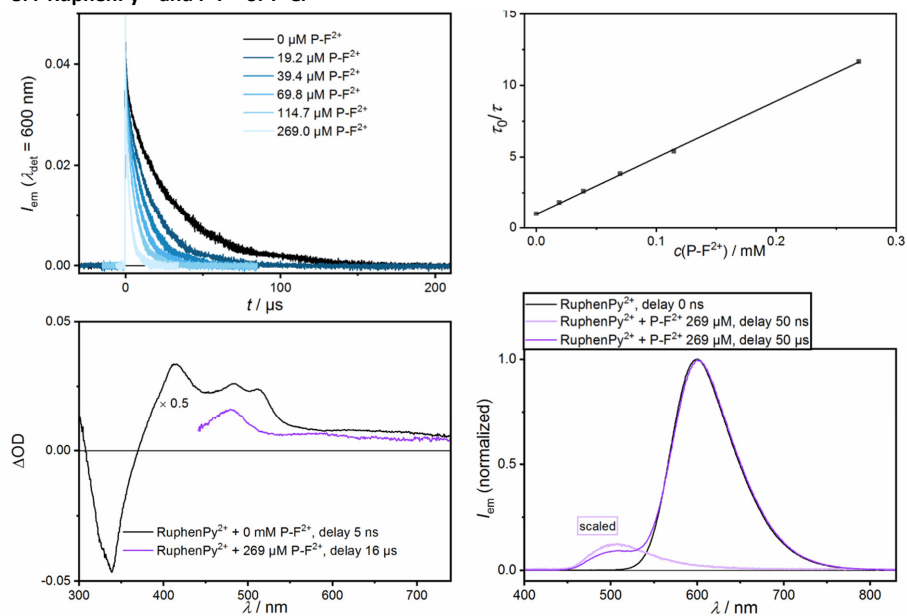


Figure S 39 Upper panel: Energy transfer quenching between ³RuphenPy²⁺ (52 μM) and P-F²⁺ after excitation at $\lambda = 532$ nm (46 mJ for spectra, 20 mJ for kinetics); left, kinetic traces of the ³RuphenPy²⁺ emission with increasing P-F²⁺ concentrations; right, Stern–Volmer plot resulting in $k_q = 1.07 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Lower panel, left: TA spectra of ³RuphenPy²⁺ and ³P-F²⁺ before and after EnT; right: Emission spectra of ³RuphenPy²⁺ without P-F²⁺ (time delay 50 ns, black), and ³RuphenPy²⁺ with 0.27 mM P-F²⁺ after 50 ns time delay (dark violet), and the isolated emission after STTA, with a time delay of 50 μs (light violet). All emission spectra were integrated over 200 μs.

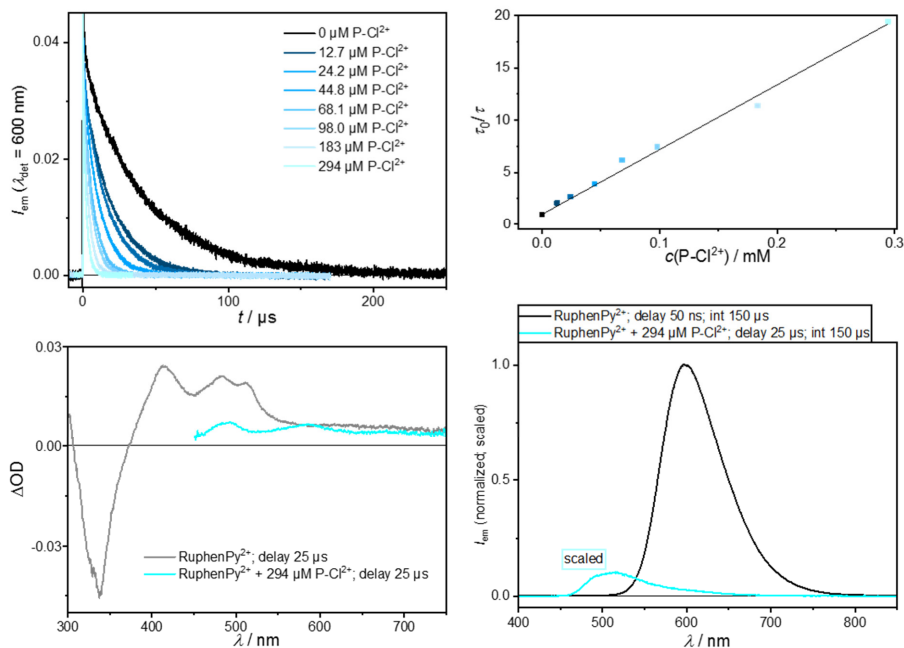


Figure S 40 Upper panel: Energy transfer quenching between $^3\text{RuphenPy}^{2+}$ (initial sensitizer concentration 17 μM) and P-Cl^{2+} after excitation at $\lambda = 532\text{ nm}$ (25 mJ for spectra, 20 mJ for kinetics); left, kinetic traces of the $^3\text{RuphenPy}^{2+}$ emission with increasing P-Cl^{2+} concentrations; right, Stern–Volmer plot resulting in $k_q = 1.30 \times 10^9\text{ M}^{-1}\text{s}^{-1}$. Lower panel, left: TA spectra of $^3\text{RuphenPy}^{2+}$ and $^3\text{P-Cl}^{2+}$ (after EnT); right: Emission spectra of $^3\text{RuphenPy}^{2+}$ without P-Cl^{2+} (time delay 50 ns, black) and the isolated emission after sTTA, with a time delay of 25 μs and with 0.3 mM P-Cl^{2+} (turquoise trace).

8.5 Comparison UC vs. direct emission

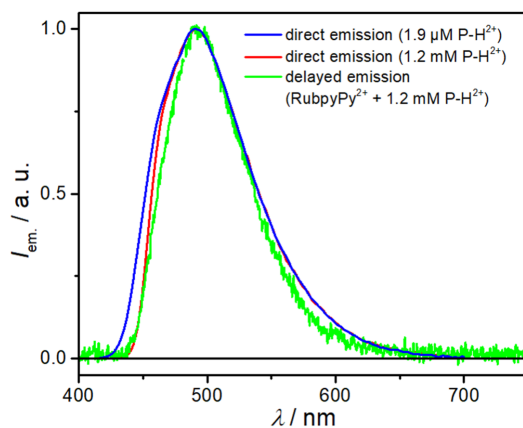


Figure S 41 Comparative $^1\text{P-H}^{2+*}$ emission spectra upon direct excitation in diluted solution (blue spectrum, measured on the FL6500; in 50 mM H_2SO_4 , $\lambda_{\text{exc}} = 386\text{ nm}$, 1.9 μM P-H^{2+}), and at the concentration used for sTTA (red spectrum, measured on the FL6500; in 50 mM H_2SO_4 , $\lambda_{\text{exc}} = 355\text{ nm}$, 1.2 mM P-H^{2+}), together with the delayed emission after sTTA with the corresponding sensitizer (green spectrum, measured on the LP980 setup (detection with ICCD camera, in 50 mM H_2SO_4 , $\lambda_{\text{exc}} = 532\text{ nm}$, 8.4 mJ, 26 μM RubpyPy $^{2+}$ and 1.2 mM P-H^{2+}).

As a proof for no natural triplet formation, the annihilator structure was excited directly (355 nm) and TA as well as delayed emission spectra were measured. Both did not show any signals, which is why the observed emission with the complete UC system and the TA signals can only result from sensitization. For comparison, the spectra after ET or EnT are given in Figure S 42.

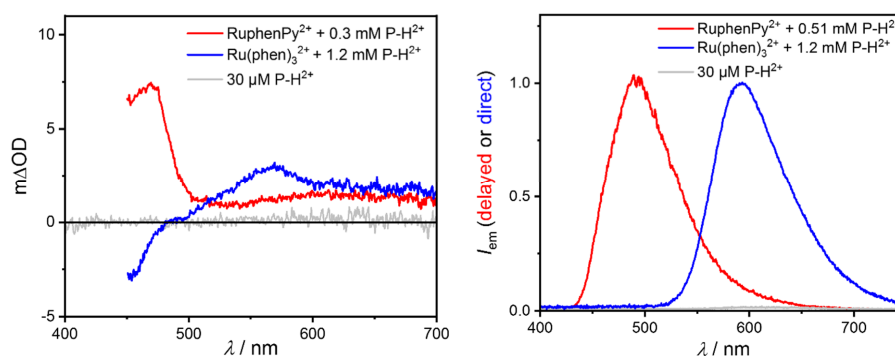


Figure S 42 Control measurements of the annihilator P-H²⁺ without (gray spectrum, 355 nm excitation, 14 mJ) or with either of the photosensitizers RuphenPy²⁺ (red) or Ru(bpy)₃²⁺ (blue) in 50 mM H₂SO₄. Left: TA spectrum of only P-H²⁺ with a time delay of 100 ns (grey), and under sensitization conditions for the ET and EnT processes as detailed in Figure S 24 and Figure S 27. Right: delayed emission spectra of the pure annihilator solution (gray, time delay 250 ns, integrated over 800 μs, 355 nm excitation), a spectrum after sTTA (red, RuphenPy²⁺ 26 μM, excitation at 532 nm with 8.4 mJ, time delay 20 μs, integrated over 250 μs), and a spectrum of Ru(phen)₃²⁺ (24 μM) and 1.2 mM P-H²⁺ after 532 nm excitation (integrated over 100 μs, time delay 100 ns).

9. Cl⁻ as reductive quencher

This section contains the raw data sets and resulting Stern–Volmer plots for the chloride quenching of directly excited water-soluble annihilators. The summary of the corresponding rate constants is given in the main paper (Table 2). All experiments were conducted after 10 min purging with argon gas.

The solutions for MAMA⁺, P-Cl²⁺, P-F²⁺ and P-H²⁺ were prepared in 50 mM H₂SO₄, thereby ensuring identical ionic strengths of the solutions. For 1,5-NDS²⁻, we selected 50 mM NaOH to avoid the protonation of sulfonate groups, which would change the redox potentials that are literature-known for the dianion drastically. To get insights into the kinetic salt effects that strongly depend on the charge of the ionic emitter, 1,5-NDS²⁻ was measured in pure H₂O and in 50 mM NaOH. The effective Coulombic repulsion between the dianion 1,5-NDS²⁻ and the chloride is reduced at higher ionic strengths, which would accelerate the quenching kinetics. 1,5-NDS²⁻ is clearly not quenched by chloride, regardless of the ionic strength of the solution.

At very high quencher concentrations, the Stern–Volmer plots show either a downward or an upward curvature. This is due to additional kinetic salt effects caused by the ionic quencher, which accelerate (e.g. in Figure S 53) or decelerate (e.g. in Figure S 43) the second-order rate constants, depending on the charge of the emitter. For the rate constant determinations, only the linear regions of the Stern–Volmer plots have been used.

9.1 P-H²⁺

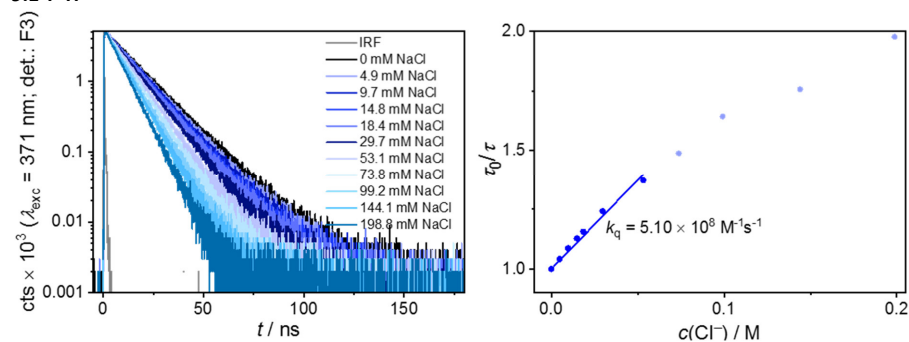


Figure S 43 Left: Kinetic emission traces of ${}^1\text{P-H}^{2+}$ with increasing NaCl concentrations in 50 mM H_2SO_4 , after 371 nm excitation. Right: Resulting Stern–Volmer plot. See Figure S 18 for the spectrum of filter F3 in the detection path.

9.2 P-F²⁺ and P-Cl²⁺

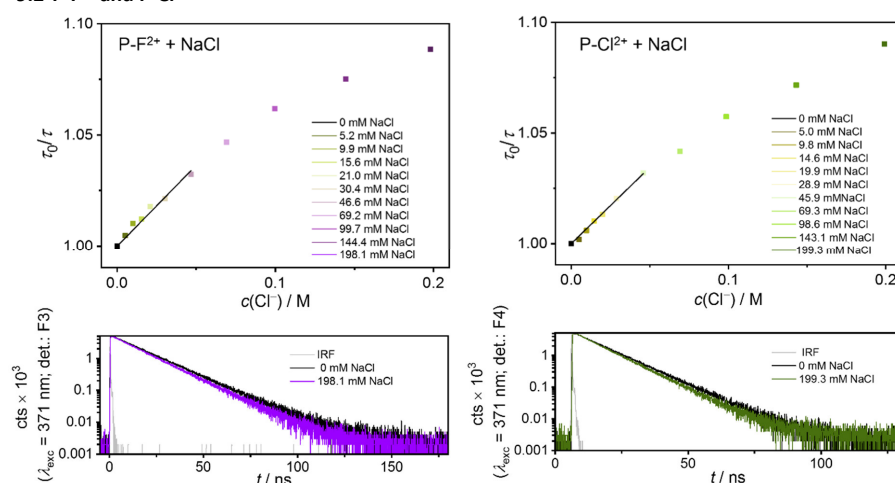


Figure S 44 Left: Stern–Volmer plot (upper) and sample kinetic traces (lower) for ${}^1\text{P-F}^{2+}$ quenching by NaCl in 50 mM H_2SO_4 . Only two kinetic traces (without NaCl and with 198.1 mM NaCl) are shown for better visibility. Right: Stern–Volmer plot (upper) and sample kinetic traces (lower) for ${}^1\text{P-Cl}^{2+}$ quenching by NaCl in 50 mM H_2SO_4 . Only two kinetic traces (without NaCl and with 199.3 mM NaCl) are shown for better visibility. See Figure S 18 for the spectra of filters F3 and F4 that were used in the detection path. Excitation occurred at 371 nm.

9.3 Cl^- -quenching with literature-known annihilators

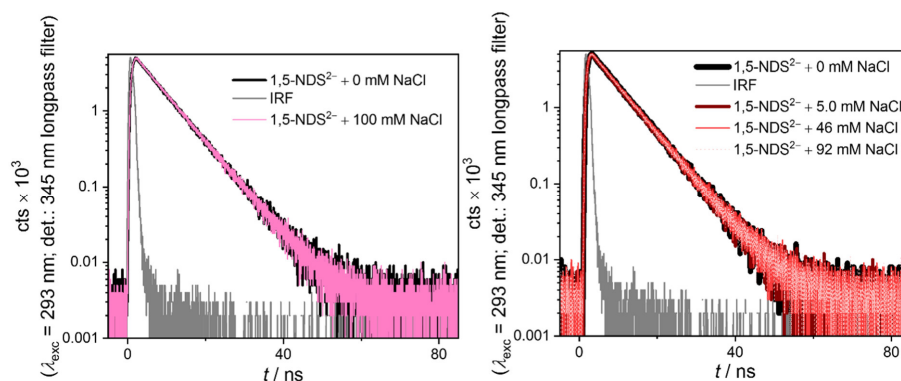


Figure S 45 Left: Kinetic emission traces of 1,5-NDS²⁻* in 50 mM aqueous NaOH with (pink) and without (black) NaCl added. Right: Kinetic emission traces of 1,5-NDS²⁻* in pure H₂O without (black) and with different concentrations of NaCl (color-coded data sets) added.

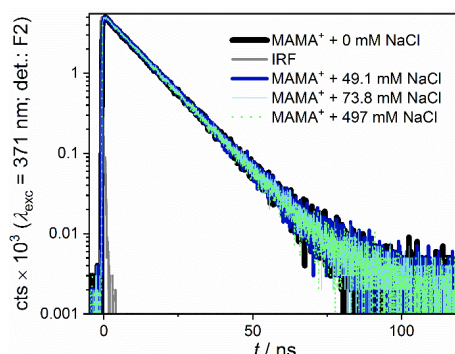


Figure S 46 Kinetic emission traces of ¹MAMA⁺* without (black) and with NaCl (different concentrations, color-coded) added. The solutions were prepared in 50 mM H₂SO₄ and excited at 371 nm.

9.4 Cl^- quenching after sTTA

Figure S 47 indicates that quenching with chloride ions is similarly possible after annihilation. All data sets in the figure follow the same color code with the black spectra or kinetic traces referring to the upconversion system without chloride ions as quencher, whereas the red spectra and kinetic traces correspond to solutions with chloride as quencher added. The triplet is essentially unaffected by the presence of the quencher (see kinetic traces on the left side of the figure, detection at 471 nm). Similarly, the rise and decay kinetics of the delayed emission do not change upon NaCl addition (lower right part of the figure). However, a significant decrease of the delayed emission intensity is observed (upper right part of the figure). The impact of Cl^- on the emission intensity after sTTA resembles that of the direct (lifetime) quenching of ¹P-H²⁺*.

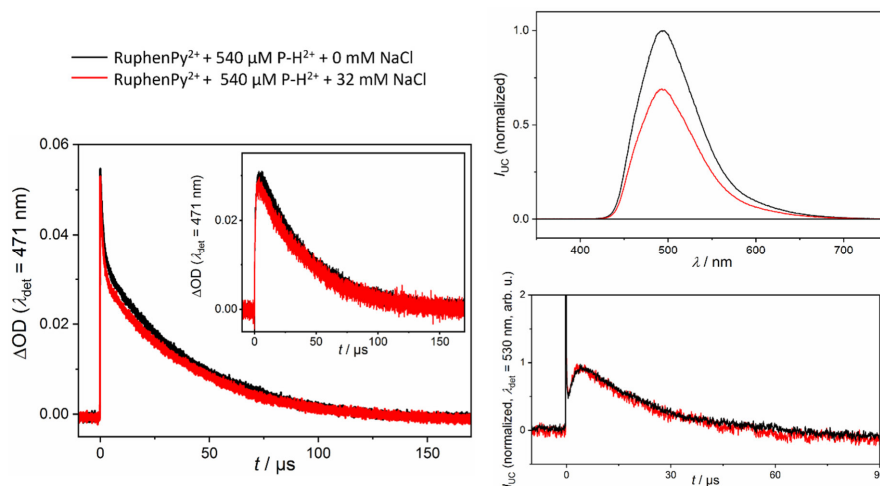


Figure S 47 Quenching of chloride after STTA: The two solutions, with chloride (red data) added as quencher or without the quencher (black data) in 50 mM H_2SO_4 , were investigated under identical measuring conditions (Ruphen $^{2+}$ 30 μM , P-H $^{2+}$ 540 μM , excited with 532 nm, 50 mJ). The kinetic traces of the $^3\text{P-H}^{2+}$ (left part, detection at 471 nm, compare TA-spectra of Figure S 27) show an identical intensity regardless of the presence or absence of the quencher. The inset shows the kinetic traces after subtraction of the initial sensitizer signals. Also, the duration of the delayed emission (kinetic traces lower right part) is not affected by the presence or absence of NaCl. Upper right: Spectra of delayed $^1\text{P-H}^{2+*}$ emission, delayed 10 μs and integrated over 70 μs .

10. Br^- as reductive quencher

This section contains the raw data sets and resulting Stern–Volmer plots for the bromide quenching of directly excited, water-soluble annihilators. The singlet states of our novel annihilators $^1\text{P-H}^{2+*}$, $^1\text{P-F}^{2+*}$, and $^1\text{P-Cl}^{2+*}$ are all quenched with diffusion-controlled kinetics by bromide, whereas the rate constants of literature-known annihilators are clearly below the diffusion limit. The summary of the corresponding rate constants is given in the main paper (Table 2). All experiments were conducted after 10 min purging with argon gas. The same considerations as for chloride quenching (see above) hold true regarding the selected additives and salt effects.

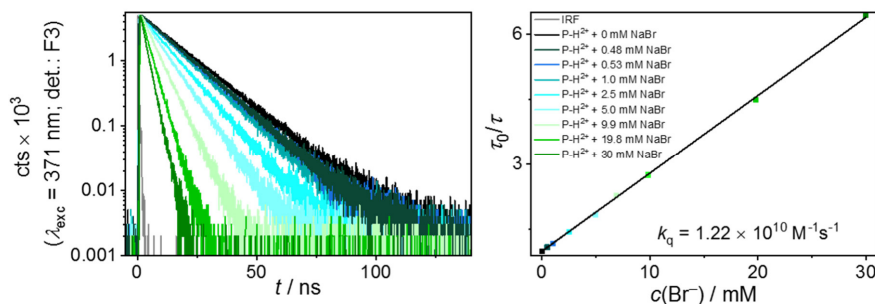


Figure S 48 Kinetic emission traces of $^1\text{P-H}^{2+*}$ (black) with increasing NaBr concentrations in 50 mM H_2SO_4 , after 371 nm excitation. Right: Stern–Volmer plot of $^1\text{P-H}^{2+*}$ quenching by NaBr together with the resulting quenching rate constant. See Figure S 18 for the spectrum of filter F3 in the detection path.

S37

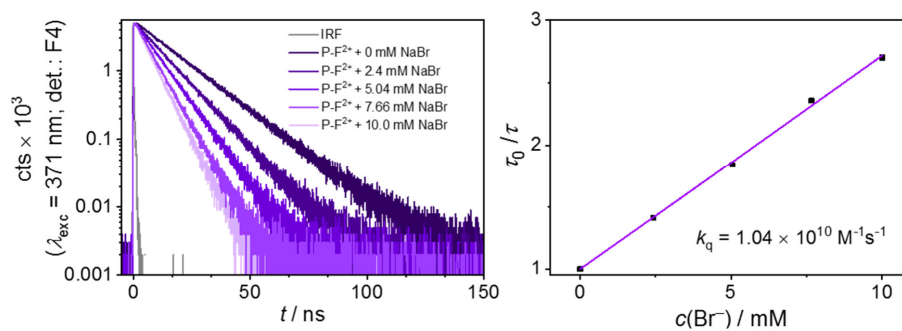


Figure S 49 Kinetic emission traces of ${}^1\text{P-F}^{2+*}$ (black) with increasing NaBr concentrations in 50 mM H_2SO_4 , after 371 nm excitation. Right: Stern–Volmer plot of ${}^1\text{P-F}^{2+*}$ quenching by NaBr together with the resulting quenching rate constant. See Figure S 18 for the spectrum of filter F4 in the detection path.

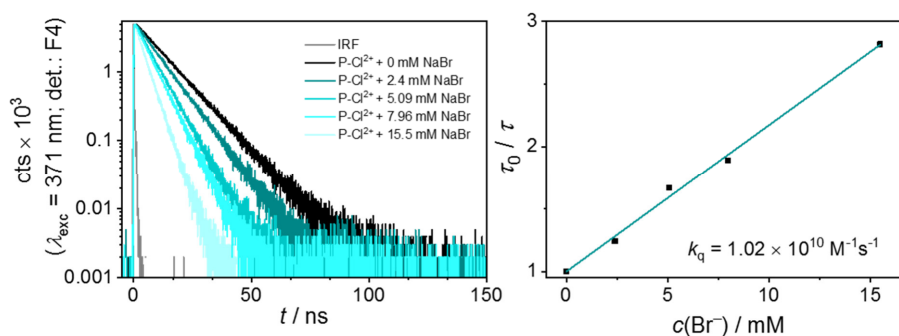


Figure S 50 Kinetic emission traces of ${}^1\text{P-Cl}^{2+*}$ (black) with increasing NaBr concentrations in 50 mM H_2SO_4 , after 371 nm excitation. Right: Stern–Volmer plot of ${}^1\text{P-Cl}^{2+*}$ quenching by NaBr together with the resulting quenching rate constant. See Figure S 18 for the spectrum of filter F4 in the detection path.

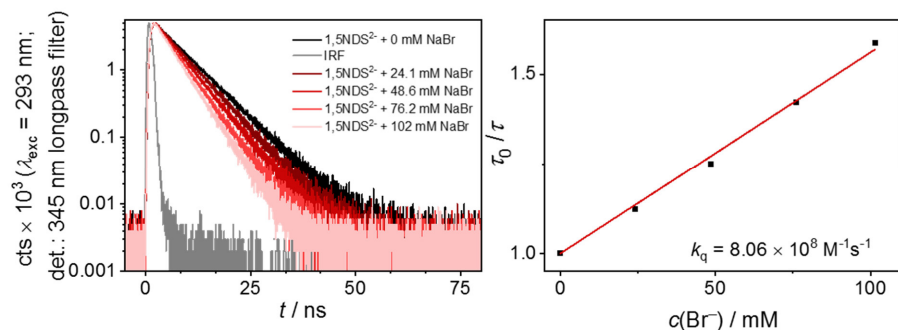


Figure S 51 Kinetic emission traces of $^1\text{1,5-NDS}^{2-*}$ (black) in 50 mM NaOH with increasing NaBr concentrations, after 293 nm excitation using a 345 nm long-pass filter to exclude excitation stray light. Right: Stern-Volmer plot of $^1\text{1,5-NDS}^{2-*}$ quenching by NaBr together with the resulting quenching rate constant.

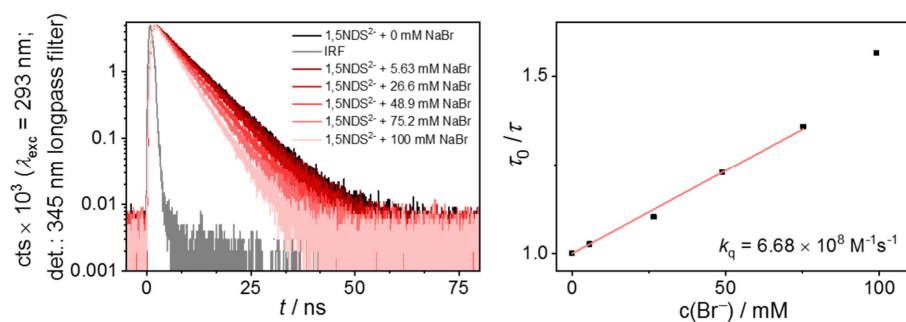


Figure S 52 Kinetic emission traces of $^1\text{1,5NDS}^{2-*}$ (black) in H_2O with increasing NaBr concentrations, after 293 nm excitation using a 345 nm long-pass filter to exclude excitation stray light. Right: Stern-Volmer plot of $^1\text{1,5NDS}^{2-*}$ quenching by NaBr together with the resulting quenching rate constant.

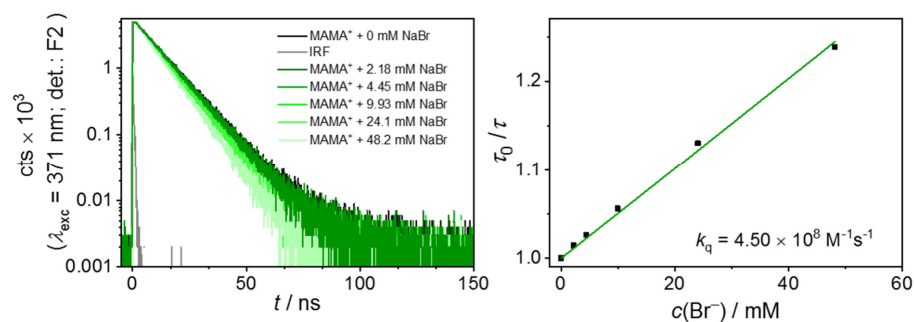


Figure S 53 Kinetic emission traces of $^1\text{MAMA}^{*}$ (black) with increasing NaBr concentrations in 50 mM H_2SO_4 , after 371 nm excitation. Right: Stern-Volmer plot of $^1\text{MAMA}^{*}$ quenching by NaBr together with the resulting quenching rate constant.

11. Quenching of $^1\text{P-H}^{2+*}$ with 1,5-NDS $^{2-}$

Further quenching experiments were performed for a more precise estimation of the (excited state) reduction potential of P-H^{2+} . The water-soluble naphthalene 1,5-NDS $^{2-}$ with known oxidation potential ($E(\text{NDS}^{\bullet-}/2-) = 2.03 \text{ V vs. NHE}^{35}$) was used in acidic 1,5-NDS $^{2-}$ solution. However, the solubility of 1,5-NDS $^{2-}$ at 50 mM H_2SO_4 is insufficient, which is why this quenching experiment was performed in diluted sulfuric acid (1 mM, see Figure S 54).

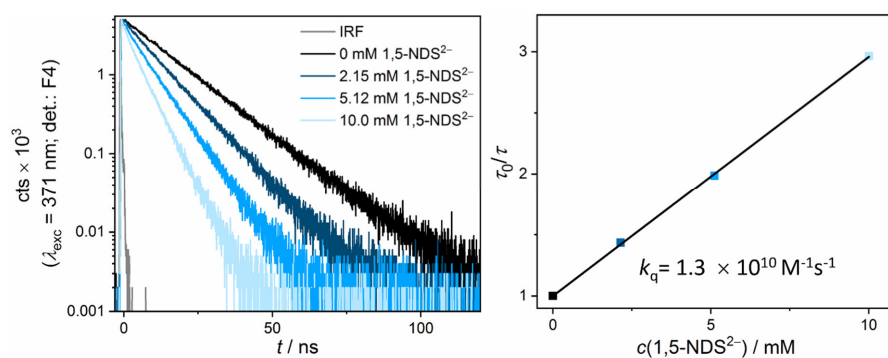


Figure S 54 Kinetic traces of $^1\text{P-H}^{2+*}$ without (black) and with 1,5-NDS $^{2-}$ (different concentrations) after 371 nm excitation in 1 mM H_2SO_4 . Right: Corresponding Stern–Volmer-plot together with the resulting quenching rate constant.

12. References

- 1 Y. Wei, Y. Li, M. Zheng, X. Zhou, Y. Zuo and C. Yang, *Adv. Opt. Mater.*, 2020, **8**, 1902157.
- 2 S. Neumann, O. S. Wenger and C. Kerzig, *Chem. Eur. J.*, 2021, **27**, 4115–4123.
- 3 A. C. Sell, J. C. Wetzel, M. Schmitz, A. W. Maijenburg, G. Woltersdorf, R. Naumann and C. Kerzig, *Dalton Trans.*, 2022, **51**, 10799–10808.
- 4 F. M. Hörmann, C. Kerzig, T. S. Chung, A. Bauer, O. S. Wenger and T. Bach, *Angew. Chem. Int. Ed.*, 2020, **59**, 9659–9668.
- 5 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of photochemistry*, CRC/Taylor & Francis, Boca Raton, 3rd edn., 2006.
- 6 G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401–449.
- 7 N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart and J. L. Dempsey, *J. Chem. Educ.*, 2018, **95**, 197–206.
- 8 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259–271.
- 9 S. Farid, J. P. Dinnocenzo, P. B. Merkel, R. H. Young, D. Shukla and G. Guirado, *J. Am. Chem. Soc.*, 2011, **133**, 11580–11587.
- 10 A. Orita, N. Yoshioka, P. Struwe, A. Braier, A. Beckmann and J. Otera, *Chem. Eur. J.*, 1999, **5**, 1355–1363.
- 11 H.-K. Chang, S. Datta, A. Das, A. Odedra and R.-S. Liu, *Angew. Chem. Int. Ed.*, 2007, **46**, 4744–4747.
- 12 J. Nejedlý, M. Šámal, J. Rybáček, I. G. Sánchez, V. Houska, T. Warzecha, J. Vacek, L. Sieger, M. Buděšínský, L. Bednářová, P. Fiedler, I. Císařová, I. Starý and I. G. Stará, *J. Org. Chem.*, 2020, **85**, 248–276.
- 13 P. Federmann, H. K. Wagner, P. W. Antoni, J.-M. Mörsdorf, J. L. Pérez Lustres, H. Wadepohl, M. Motzkus and J. Ballmann, *Org. Lett.*, 2019, **21**, 2033–2038.
- 14 K. Kabsch, in Rossmann and M. G. Arnold, eds., *"International Tables for Crystallography"*, Vol. F, Ch. 11.3, Kluwer Academic Publishers, Dordrecht, The Netherlands, 11th edn., 2001.
- 15 *Rigaku Oxford Diffraction*, Rigaku Polska Sp.z.o.o., Worclaw, 2015–2020.
- 16 *CrysAlisPro*, Agilent Technologies UK Ltd., Oxford, UK, 2011–2014.
- 17 *SCALE3 ABSPACK. CrysAlisPro*, Agilent Technologies UK Ltd., 2011–2014.
- 18 *Rigaku Oxford Diffraction*, Rigaku Polska Sp.z.o.o., Poland, 2015–2020.
- 19 R. H. Blessing, *Acta. Cryst.*, 1995, **A51**, 33–38.
- 20 W. R. Busing and H. A. Levy, *Acta. Cryst.*, 1957, **10**, 180–182.
- 21 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- 22 a) G. M. Sheldrick, *SHELXT*, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany, 2012–2018; b) M. Ruf and B. C. Noll, *Application Note SC-XRD 503*, Bruker AXS GmbH, Karlsruhe, Germany, 2014; c) G. M. Sheldrick, *Acta. Cryst.*, 2015, **A71**, 3–8.
- 23 a) G. M. Sheldrick, *Acta. Cryst.*, 2008, **A64**, 112–122; b) G. M. Sheldrick, *Acta. Cryst.*, 2015, **C71**, 3–8; c) G. M. Sheldrick, *SHELXL-20xx*, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany, 2012–2018.
- 24 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-

-
- Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian, Inc.*, Gaussian, Inc., Wallingford CT, 2016.
- 25 a) C. Fischer, C. Kerzig, B. Zilate, O. S. Wenger and C. Sparr, *ACS Catal.*, 2010, **10**, 210–215; b) V. Gray, A. Dreos, P. Erhard, B. Albinsson, K. Moth-Poulsen and M. Abrahamsson, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10931–10939; c) L. Vaghi, F. Rizzo, J. Pedrini, A. Mauri, F. Meinardi, U. Cosentino, C. Greco, A. Moguzzi and A. Papagini, *Photochem. Photobiol. Sci.*, 2022, **21**, 913–921.
- 26 a) M. Goez, M. Schiewek and M. H. O. Musa, *Angew. Chem. Int. Ed.*, 2002, **41**, 1535–1538; b) C. Creutz and N. Sutin, *Proc. Nat. Acad. Sci. USA*, 1975, **72**, 2858–2862.
- 27 a) R. J. Crutchley, N. Kress and A. B. P. Lever, *J. Am. Chem. Soc.*, 1983, 1170–1178; b) O. S. Wenger, *Coord. Chem. Rev.*, 2015, **282–283**, 150–158.
- 28 Y. Wei, Y. Li, Z. Li, X. Xu, X. Cao, X. Zhou and C. Yang, *Inorg. Chem.*, 2021, **60**, 19001–19008.
- 29 a) A. Juris and V. Balzani, *Coord. Chem. Rev.*, 1988, **84**, 85–277; b) C. T. Lin, W. Boettcher, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1976, **98**, 6536–6544.
- 30 a) N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166; b) D. P. Hari, T. Hering and B. König, *Org. Lett.*, 2012, **14**, 5334–5337.
- 31 T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, Hiresaki Tatsuro, H. Furuuchi, H. Zengm, H. Sakuragi and K. Tokumaru, *Pure & Appl. Chem.*, 1988, **7**, 989–998.
- 32 F. Glaser and O. S. Wenger, *Chem. Sci.*, 2022, **14**, 149–161.
- 33 X.-J. Yang, B. Chen, L.-Q. Zheng, L.-Z. Wu and C.-H. Tung, *Green Chem.*, 2014, **16**, 1082–1086.
- 34 V. Kasche and L. Lindquist, *Photochem. Photobiol.*, 1965, **4**, 923–933.
- 35 a) S. M. Hubig, *J. Lumin.*, 1990, **47**, 137–145; b) C. Kerzig and M. Goez, *Phys. Chem. Chem. Phys.*, 2014, **16**, 25342–25349.

6.10 Supporting Information for Molybdenum complex as triplet sensitizer for upconversion and as photoredox catalyst (Section 3.1)

A stable molybdenum(0) carbonyl complex for upconversion and photoredox catalysis

Supporting Information

Winald R. Kitzmann^{a,*}, Maria-Sophie Bertrams^a, Pit Boden^b, Alexander C. Fischer^a, René Klauer^a, Johannes Sutter^c, Robert Naumann^a, Christoph Förster^a, Gereon Niedner-Schatteburg^b, Nicolas H. Bings^a, Johannes Hunger^c, Christoph Kerzig^a, Katja Heinze^{a,*}

^a W. R. Kitzmann, M.-S. Bertrams, A. C. Fischer, R. Klauer, Dr. R. Naumann, Dr. C. Förster, Prof. Dr. N. H. Bings, JProf. Dr. C. Kerzig, Prof. Dr. K. Heinze, Department of Chemistry, Johannes Gutenberg-University of Mainz, Duesbergweg 10–14, 55128 Mainz, Germany; E-Mail: kitzmann@uni-mainz.de and katja.heinze@uni-mainz.de

^b Dr. P. Boden, Prof. Dr. G. Niedner-Schatteburg, Department of Chemistry and Research Center Optimas, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern, Germany

^c J. Sutter, Dr. J. Hunger, Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Table of Contents

1. Materials and Methods	2
2. Synthetic Procedures	9
3. NMR- and FTIR spectroscopy, APCI-MS, XRD	12
4. Cyclic voltammetry, square-wave voltammetry and chemical oxidation of 1	16
5. Absorption and emission spectroscopy, luminescence lifetimes, TD-DFT	22
6. Transient absorption spectroscopy	40
7. ns-Step-scan FTIR spectroscopy	44
8. Fs-VIS-pump-IR-probe spectroscopy	51
9. Stability in the dark and under irradiation	53
10. Quantum chemical calculations	56
11. Photon upconversion with DPA	66
12. Catalysis	69
13. Emission spectra of excitation sources	72
13. DFT-optimized structures	73

1. Materials and Methods

General procedures. All reagents were used as received from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer, Sigma-Aldrich and TCI). Dry solvents were either obtained from Acros Organics and degassed by purging with argon for 20 min or dried by distillation: Acetonitrile and methylene chloride were distilled from CaH₂. Diethylether was distilled from sodium. THF and toluene were distilled from potassium. Air-sensitive substances were handled in a glovebox (MBraun).

UV-Vis spectra were recorded using a JASCO V770 spectrometer using 1.0 cm quartz cells with a PTFE capping or with a Schott valve for measurements under inert conditions.

¹H NMR spectra were recorded on a Bruker AV2-400 spectrometer at 400 MHz or on a Bruker AV300 spectrometer at 300 MHz (¹H). All resonances are reported in ppm versus the solvent signal as an internal standard (CDCl₃, δ = 7.26; CD₃CN, δ = 1.94; d₇-DMF, δ = 8.93, 2.92, 2.75).¹ (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (m)=multiplet.

APCI mass spectra were recorded on an Agilent 6545 QTOF-MS spectrometer.

ATR-IR spectra were recorded with a Bruker ALPHA II FT-IR spectrometer with a Platinum Di-ATR module inside an argon filled glovebox.

Elemental analyses were performed by the central analytic service of the department of chemistry of the University of Mainz using an Elementar vario EL Cube.

Electrochemical experiments were carried out on a BioLogic SP-200 voltammetric analyzer using platinum wires as counter and working electrodes and 0.01 M Ag/AgNO₃ as the reference electrode. The measurements were carried out at a scan rate of 100 mV s⁻¹ for cyclic voltammetry experiments and at 50 mV s⁻¹ for square-wave voltammetry experiments using 0.1 M [ⁿBu₄N][PF₆] as the supporting electrolyte. Potentials are referenced to the ferrocene/ferrocenium couple using ferrocene as an internal standard and recalculated to a SCE reference according to Table S1.

Table S1: Potentials used to convert the reference of electrochemical data from vs. FcH/FcH⁺ to vs. SCE.

Solvent	conducting salt (0.1 M)	$E(\text{FcH}/\text{FcH}^+) / \text{V vs. SCE}$	Ref.
MeCN	[ⁿ Bu ₄ N][PF ₆]	+0.40	2
MeCN	[ⁿ Bu ₄ N][BF ₄]	+0.60	3
DCM	[ⁿ Bu ₄ N][PF ₆]	+0.46	2
DMF	[ⁿ Bu ₄ N][PF ₆]	+0.45	2
DMSO	[ⁿ Bu ₄ N][PF ₆]	+0.45	4
THF	[ⁿ Bu ₄ N][PF ₆]	+0.56	2

X-Ray Diffraction

Intensity data for crystal structure determination were collected with a STADIVARI diffractometer from STOE & CIE GmbH using Mo-K α radiation (λ = 0.71073 Å). The diffraction frames were integrated using the STOE X-Area software package⁵ and were corrected for absorption with STOE LANA^{6,7} of the STOE X-Area software package.⁵ The structures were solved with SHELXT⁸ and refined by the full-matrix method based on F^2 using the SHELXL⁹ of the SHELX software package¹⁰ and the ShelXle graphical interface.¹¹ All non-hydrogen atoms were refined anisotropically while the positions of all hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent atoms with fixed isotropic thermal parameters. Crystallographic data for the structures

reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2251140 for **1**.

Emission and excitation spectra were recorded using an Edinburgh Instruments FLS1000 spectrofluorometer with a xenon lamp (Xe2) as excitation source. **Luminescence lifetime** measurements on ns-timescale were determined with a time-correlated single-photon counting system (TCSPC, FLS1000) in reverse mode using a picosecond-pulsed laser (NKT-FIU-6 SuperK Fianium FIU-6) as excitation source. Luminescence lifetimes on μ s-timescale were determined with a multichannel scaling time-resolved single-photon counting (multichannel scaling, MCS, FLS1000) system with a microsecond xenon flashlamp as excitation source (μ F2). Measurements were performed at 20.0°C in a Peltier-cooled holder if not stated otherwise. **Low-temperature measurements** were performed in an Optistat-DN from Oxford Instruments at 77 K. **Absolute quantum yields** were determined using an integrating sphere at room temperature or in a Cryosphere at 77 K. Luminescence decays were fitted using the software Fluoracle (Edinburgh Instruments). The photomultipliers N-G11 PMT-980 (250–980 nm), N-G05exd high speed PMT and liquid nitrogen cooled N-G09 PMT-1700 (500–1700 nm) were used for detection. Samples for measurements in absence of oxygen were prepared in a glovebox using degassed solvents and measured in airtight cuvettes.

Determination of relative quantum yields using a reference

Isoabsorptive solutions of **1** in the deaerated solvent of interest and [Ru(bpy)₃]Cl₂ in aerated water were prepared. Emission spectra were recorded using excitation at the wavelength where both samples are isoabsorptive ($A \approx 0.001$ – 0.05). Then the relative quantum yield of **1** was calculated using Eq. S1:

$$\Phi_{rel} = \frac{I_{Mo}}{I_{Ru}} \left(\frac{n_{Mo}}{n_{Ru}} \right)^2 \Phi_{Ru} \quad (S1)$$

Where I_{Mo} and I_{Ru} are the integrated emission intensities of the sample and the reference, respectively, n_{Mo} is the refractive index of the solvent used to dissolve **1** and n_{Ru} the refractive index of water. Φ_{Ru} is the quantum yield of [Ru(bpy)₃]Cl₂ in aerated water determined absolutely using an integrating sphere in the same setup (4.23 %, consistent with previous reports¹²).

Estimation of the triplet energy of **1**

In literature the energy of triplet states is extracted from low-temperature phosphorescence spectra, either taking the band maximum¹³ or the energy where the high energy tail hits 10 %.¹⁴ Due to the pronounced rigidochromism of **1** which prohibits the use of emission spectra taken in frozen solution for this purpose, luminescence spectra were recorded in 2-MeTHF at –130°C (143 K, Figure S29) just above the glass point of the solvent. The band maximum lies at 712 nm (1.74 eV) and the high energy tail at 10 % at 630 nm (1.97 eV). Both values do not seem to be good estimates for the ³MLCT energy of **1**. With a triplet energy at 1.74 eV an energy transfer equilibrium is expected with DPA ($E_T \approx 1.77$ eV)¹⁵ similar to a recently published Cr(III) complex.¹⁶ However, such an equilibrium has not been observed for **1**/DPA (Figure 6a). A triplet energy of 1.97 eV derived from the high-energy tail of the low-temperature emission on the other hand would enable energy transfer to *trans*-stilbene to induce the *trans-cis* isomerization.¹³ However, we did not observe any quenching of the emission of **1** in MeCN with *trans*-stilbene (65 mM) nor did we see the formation of *cis*-stilbene after irradiation of a solution of **1** and *trans*-stilbene in MeCN with green light. Hence we estimate the ³MLCT state energy of **1** to be in between both values and around 1.85 eV.

Ns-Transient Absorption spectroscopy

For the laser flash photolysis (LFP) measurements an LP980-KS apparatus from Edinburgh Instruments was used. The energy of the 532 nm laser pulse (frequency-doubled Nd:YAG laser from Quantel with ~10 ns pulses) was modified by the Q-switch delay (further details are given in the figure captions of the SI). Kinetic traces were recorded at a single wavelength with a photomultiplier tube and for measuring transient absorption (TA) or (delayed) emission spectra an ICCD camera from Andor was employed. All TA spectra were time-integrated for 100 ns if not stated otherwise. The concentrations of the sensitizers were adjusted such that the optical density at the excitation wavelength is between 0.1 and 0.2. The LFP experiments were carried out at 20°C using a cuvette holder that permits temperature control.

Fs-Transient absorption experiments were conducted using a Helios-Fire pump-probe setup from *Ultrafast Systems* paired with a regeneratively amplified 1030 nm laser (Pharos, *Light Conversion*, 1030 nm, 200 fs, 200 μ J). The effective laser repetition rate of 1 kHz was set via an internal pulse picker. A small portion of the 1030 nm fundamental was directed to the optical delay line and was subsequently used to generate broadband probe light by focusing the beam onto a sapphire (vis/NIR range) crystal. The pump pulse was generated with an optical parametric amplifier (Orpheus-F, *Light Conversion*). The samples were measured in a 2 mm quartz cuvette under argon with excitation at 480 nm with 400 nJ pulse energy.

Time-resolved step-scan FTIR spectroscopy

All the time-resolved FTIR experiments were performed with the FTIR spectrometer Bruker Vertex 80v, operated in the step-scan mode. A liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector (Kolmar Tech., Model KV100-1-B-7/190) with a rise time of 25 ns, connected to a fast preamplifier and a 14-bit transient recorder board (Spectrum Germany, M3I4142, 400 MS/s), was used for signal detection and processing. The laser setup used for the measurements includes a Q-switched Nd:YAG laser (Innolas SpitLight Evo I) generating pulses with a duration of about 6 ns at a repetition rate of 100 Hz. The second harmonic (532 nm) of the Nd:YAG laser was used directly for sample excitation. The diameter of the VIS pump beam was limited to 9 mm and the laser power was attenuated to 1.5 mJ and 1.0 mJ per shot for investigations on KBr pellets and solutions, respectively. The beam was directed onto the sample and adjusted to have a maximal overlap with the IR beam of the spectrometer. The sample chamber was equipped with anti-reflection-coated germanium filters to prevent the entrance of laser radiation into the detector and interferometer compartments.

The KBr pellets were prepared as described in the section on luminescence spectroscopy, however, with a smaller amount of sample of ca. 0.2 mg and 180 mg KBr. The strongest peak in the ground state spectrum showed an absorption of about 0.6 OD with the mentioned concentration. The measurements were performed at a constant temperature of 290 K or 20 K using a closed-cycle helium cryostat (ARS Model DE-202A). The cryocooler was equipped with a pellet holder (copper) and CaF₂ windows.

Step-scan investigations in solution were performed by dissolving the complex in argon purged DMSO-d₆ (2 mM, 0.2 OD for the strongest absorption peak) and using an optical cell (Specac Omni-Cell®) with a thickness of 200 μ m.

The temporal resolution of the 14-bit transient recorder board was chosen to 50 ns and 10000 time slices were recorded to cover a time range of 500 μ s for investigations on KBr pellets. Measurements on solutions were performed with a time resolution of 20 ns and 5000 time slices, covering a time span of 100 μ s. The time when the laser pulse reached the sample was set as zero point in all spectra. The time delay between the start of the experiment and the laser pulse was controlled with a Stanford Research Systems DG535 delay generator and set to 1.3 μ s before the laser excitation of the sample.

The spectral region was limited by undersampling to 2634–0 cm^{-1} with a spectral resolution of 4 cm^{-1} (1481 interferogram points) and 8 cm^{-1} (741 interferogram points) for measurements on solid samples and solutions, respectively. An IR long pass filter (no IR transmission < 2400 cm^{-1}) prevented problems when performing a Fourier transformation (i.e. no IR intensity outside the measured region should be observed). FTIR ground state spectra were recorded systematically to check if there is no sample degradation. Estimated uncertainties for the excited state lifetimes are on the order of 10%.

Fs-VIS-pump-IR-probe spectroscopy

Femtosecond VIS pump-IR probe experiments were based on a Ti:sapphire regenerative amplifier (Spitfire Ace, Spectra-Physics) generating 800 nm pulses with a duration of ~35 fs at a repetition rate of 1 kHz. A fraction of the 800 nm beam was used to generate 400 nm pulses with ~12 μJ pulse energy via frequency doubling of the 800 nm light in a BBO crystal ($\beta\text{-BaB}_2\text{O}_4$). The 400 nm light was sent through a delay stage to control the timing and focused into the sample to pump the sample.

A second part of the 800 nm light was used to generate signal and idler beams by pumping an optical parametric amplifier (TOPAS Prime, Spectra-Physics). Signal and idler beams were recombined in a NDFG (non-collinear difference frequency generation) stage based on a GaSe crystal to generate tunable IR pulses (~100 fs). We used the front and the back reflection of the IR beam at a wedged CaF_2 window to generate a reference and a probe beam, respectively. The probe beam was focused into the sample using an off-axis parabolic mirror and spatially overlapped with the pump beam. After the sample, the pump pulse was blocked. The probe beam was re-collimated and reference and probe beams were focused onto the entrance slit of a monochromator (Triax 180, Horiba Scientific). To resolve the probing frequency, ν , both beams were spectrally dispersed using a grating with 150 grooves/mm onto two lines of a 2x32 pixel MCT (mercury cadmium telluride) line detector (InfraRed Associates) resulting in a spectral resolution of ~5 cm^{-1} . The frequency dependent intensity of the reference beam, $T^{\text{ref}}(\nu)$, was used to account for pulse-to-pulse energy fluctuations. The pump beam was modulated using a mechanical chopper at 500 Hz to measure the pump-induced changes in the frequency-dependent transmission of the probe beam, $T^{\text{probe}}(\nu)$, on a shot-to-shot basis. The transmitted intensities were used to obtain the waiting time (t_w)-dependent transient absorption spectra $\Delta\alpha$ using Eq. S2.

$$\Delta\alpha(\nu, t_w) = -\ln \frac{T^{\text{probe}}(\nu, t_w) T_0^{\text{ref}}(\nu, t_w)}{T_0^{\text{probe}}(\nu, t_w) T^{\text{ref}}(\nu, t_w)} \quad (\text{S2})$$

Where subscripts '0' denote the intensities in the absence of the pump pulse.

The KBr powder (180 mg) was homogeneously pestled with the sample (0.2 mg) and then pressed for 15 minutes at 10 t pressure using a hydraulic press (Perkin-Elmer) to form a pellet. The KBr pellet containing the sample was held between two CaF_2 windows in a rotating cell to avoid photodegradation. The saturated DMSO solutions were prepared in an argon-filled glovebox in a sample chamber with a path length of 200 μm .

Determination of absolute decomposition quantum yields using continuous laser irradiation

The method to determine the absolute decomposition quantum yields Φ_{degr} was adapted from a previously published procedure¹⁷ using the following setup: A 514 nm cw-laser ($P = 827 \text{ mW}$, emission spectrum: Figure S90) was used for irradiation of the isoabsorptive samples ($A_{514} = 0.165$, sample volume: 2.5 mL) of **1** (23 μM) and **2** (51 μM) in unstabilized THF and $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ in MeCN (129 μM) under stirring in a temperature controlled cell-holder at 20°C for 2 h each (see Table S9 for details), while measuring the emission intensity of the samples at their respective emission maxima every 5 s. The emission intensity was assumed to be proportional to the concentration of the

complexes under investigation. The photodegradation quantum yield Φ_{degr} is defined as the number of decomposed molecules N_{degr} divided by the number of absorbed photons N_{abs} (Eq. S3).

$$\Phi_{\text{degr}} = \frac{N_{\text{degr}}}{N_{\text{abs}}} \quad (\text{S3})$$

The energy of one photon with a wavelength of 514 nm can be calculated using Eq. 4:

$$E_{514} = \frac{hc}{\lambda} = 3.8647 \cdot 10^{-19} \text{ J} \quad (\text{S4})$$

The photon flux F of a cw-laser with a power P of 827 mW can be calculated using Eq. S5 with N_A being the Avogadro number:

$$F = \frac{P}{E_{514} \cdot N_A} = 3.5534 \frac{\mu\text{M}}{\text{s}} \quad (\text{S5})$$

Since the laser showed a warm-up period of ca. 30 s, we chose the time interval Δt between 90 and 80 % of the initial intensity values as the basis of our evaluation and assumed the absorbance to be constant at the average value of the interval ($A_{514,\text{avg}} = 0.85 \cdot A_{514,0} = 0.14$). In this time period the samples absorbed N_{abs} photons (Eq. 6).

$$N_{\text{abs}} = (1 - 10^{-A_{514,\text{avg}}}) \cdot F \cdot \Delta t \quad (\text{S6})$$

The number of molecules N_{degr} that decomposed after irradiation for the time Δt can be calculated from the initial concentrations c_0 with Eq. S7.

$$N_{\text{degr}} = 0.1c_0 \quad (\text{S7})$$

Now Eq. S3 can be used to calculate the photodegradation quantum yield. The results are summarized in Table S10. UV/Vis absorption and emission spectra were recorded before and after the photostability measurements (Figure S67–68) to exclude the formation of emissive impurities.

Photon upconversion experiments

Prior to the upconversion experiments, yellow 9,10-diphenylanthracene was purified by sublimation to yield a white solid. A stock solution of **1** in deaerated THF was prepared with an extinction of 0.1 at 520 nm. DPA was added to a part of this stock solution to yield concentrations of 10 mM. Photon upconversion quantum yields Φ_{UC} of **1**/DPA in deaerated THF were determined relative to an isoabsorptive sample of the stock solution of **1** without DPA. Both samples were excited using a green cw-laser with adjustable power (514 nm, $P_{\text{max}} = 827$ mW, Roithner Lasertechnik, beam size = 3.0 mm², emission spectrum: Figure S89) inside of a spectrometer (FLS1000) and emission spectra of the upconverted blue emission (**1**/DPA) and red phosphorescence (**1**) were recorded using the same spectrometer settings for each measurement. At intense laser powers, the emission signal was attenuated using neutral density filters and the resulting spectra were corrected for the known extinction profiles of the filters. Upconversion quantum yields were calculated using Eq. S8 (I_{UC} = integrated upconverted emission, I_{Mo} = integrated emission of **1** without DPA, Φ_{Mo} = quantum yield of **1** without DPA determined as 0.62 % (Table 3)):

$$\Phi_{\text{UC}} = \frac{I_{\text{UC}}}{I_{\text{Mo}}} \Phi_{\text{Mo}} \quad (\text{S8})$$

Spectra of the upconverted emission with a green LED as excitation source were recorded on a EL 6500 spectrometer from Perkin Elmer at 295±2 K and the emission spectra were corrected for the wavelength dependent sensitivity of the emission spectrometer. A 525 nm LED (Kessil Science, PR160L) was used for excitation. This light source has four power settings (25%, 50%, 75% and 100%) and the

average intensity (at 100% output power) is reported as 352 mW cm^{-2} (measured from 1 cm distance).¹⁸

Determination of Mo concentrations via ICP-MS

To accurately determine the extinction coefficients of **1** in solution, mass spectrometrical determinations of the precise molybdenum concentrations in five different solvents (MeCN, DCM, DMSO, THF, DMF) were performed by the Laboratory for Inorganic Trace Analysis and Plasma Spectrometry, University of Mainz. The molybdenum concentrations were determined by microwave assisted acid digestion and subsequent ICP-MS (inductively coupled plasma-mass spectrometry). Prior to analysis, 5 mL of each filtered solution were pipetted into three PTFE digestion vessels together with 100 μL of a 50 mg L^{-1} Rh solution as internal standard to compensate for analyte loss during evaporation and digestion. A blank sample containing the pure solvent was prepared in the same way but without the internal standard. The organic solvents were evaporated under reduced pressure using the evaporation rotor MMR-12 together with the Ethos 2000plus microwave assisted digestion system (Milestone Inc, Shelton, USA). After cooling to room temperature, 5 mL of nitric acid (70 % p.a. grade, Fisher Scientific GmbH, Dreieich, Germany) and 2 mL of hydrogen peroxide (30 % p.a. grade, Carl Roth GmbH, Karlsruhe, Germany) were added to each vessel. The subsequent digestions were performed using the following two-step heating program: 1) Temperature ramp to 220°C within 10 min (max. power 900 W). 2) Holding step at this temperature for 15 min (max. power 900 W). After cooling to room temperature, the obtained colorless solutions were each diluted to 25 mL with ultrapure water (Millipore, Merck KGaA, Darmstadt, Germany). ICP-MS measurements were performed using an Agilent 7800 quadrupole MS together with a concentric MicroMist nebulizer and a double pass spray chamber (all from Agilent Technologies, Santa Clara, USA). As calibration strategy, external calibration was chosen due to Mo recovery rates of near 100 % in prior performed analyses. For these experiments, the Mo complex was accurately weighted into a volumetric flask, filled up with THF, and stored until the dissolution was optically completed. Decomposition of the complex would not have effected these measurements. The optimum instrumental parameters of the ICP-MS method were as follows: plasma power: 1550 W, plasma gas flow rate: 15 L min^{-1} , auxiliary gas flow rate: 0.9 L min^{-1} , nebulizer gas flow rate: 1.00 L min^{-1} , sampler and skimmer cone: Ni, monitored isotopes: $^{95}\text{Mo}^+$, $^{103}\text{Rh}^+$, data acquisition: 0.1 s integration time, 10 replicates, 30 sweeps per replicate.

The resulting molybdenum concentrations were:

In MeCN: $(0.993 \pm 0.032) \mu\text{g/L}$ (U ; $k=2$)

In THF: $(2.765 \pm 0.098) \mu\text{g/L}$ (U ; $k=2$)

In DCM: $(7.49 \pm 0.24) \mu\text{g/L}$ (U ; $k=2$)

In DMSO: $(2.772 \pm 0.087) \mu\text{g/L}$ (U ; $k=2$)

In DMF: $(4.61 \pm 0.14) \mu\text{g/L}$ (U ; $k=2$)

Quantum chemical calculations were performed using the quantum computing suite ORCA 4.2.1.¹⁹ Geometry optimization was performed using (un-)restricted Kohn-Sham orbitals DFT (RKS/UKS) and the B3LYP functional^{20,21} in combination with Ahlrichs' split-valence triple-zeta basis set TZVP for all atoms.^{22,23} Tight convergence criteria were chosen for DFT calculations (keywords *tightscf* and *tightopt*).

All DFT calculations make use of the resolution of identity (Split-RI-J) approach for the Coulomb term in combination with the chain-of-spheres approximation for the exchange term (keyword *RIJCOSX*).^{24,25} The zeroth order regular approximation was used to describe relativistic effects in all calculations

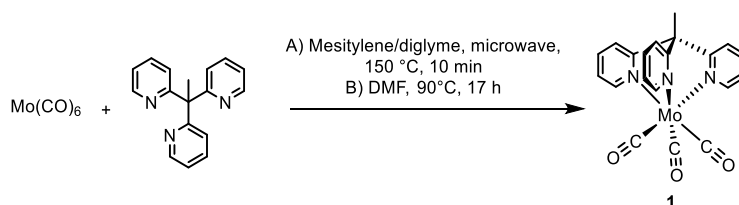
(keyword *ZORA*).²⁶ To account for solvent effects, a conductor-like screening model (keyword *CPCM*) was used in all calculations.^{27,28} Atom-pairwise dispersion correction was performed with the Becke-Johnson damping scheme (keyword *D3BJ*).^{29,30} A numerical frequency calculation confirmed that the optimized geometry corresponds to a minimum structure. Explicit counter ions and/or solvent molecules were not taken into account. 50–100 spin-allowed transitions were calculated by TD-DFT. The charge transfer number analyses of the TD-DFT calculated transitions were done using TheoDORÉ 2.4.³¹

To identify a good guess for the optimization of ³MLCT–³MC transition states, a nudged elastic band calculation (NEB) was performed that optimized the minimum energy path between the ³MLCT and ³MC geometry. For the NEB calculations, 7 intermediate images were calculated with initial path generation via the image dependent pair potential (IDPP) method³² and optimized using the Limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) algorithm.³³ Default values were used for the tolerance for the maximum component of the atomic force perpendicular to the path (1.0×10^{-3} Eh a_0^{-1}), its root-mean-square (5.0×10^{-4} Eh a_0^{-1}) and the spring constant (1.0×10^{-1} Eh a_0^{-2}). The highest energy image of the NEB calculation was used as a initial guess to optimize a transition state (*OptTS*).

2. Synthetic Procedures

The ligand tpe was synthesized according to a literature procedure.³⁴

Synthesis of Mo(CO)₃(tpe) (**1**)



Route A) Microwave

Mo(CO)₆ (30 mg, 0.11 mmol) and tpe (33 mg, 0.13 μmol, 1.1 eq.) were suspended in a mixture of dry mesitylene (3 mL) and diglyme (1.5 mL) in a 10 mL microwave tube under inert conditions. The reaction mixture was heated to 150 °C with a microwave (300 W) under stirring for 10 min. After the reaction cooled to room temperature, the product was isolated as red needles by filtration, washed with petroleum ether (3x7 mL) and diethyl ether (3x10 mL). The bright red crystals were dried under reduced pressure. Yield: 49.9 mg (0.113 mmol, >99 %).

Route B) Heating under reflux in a flask

Mo(CO)₆ (303 mg, 1.15 mmol) and tpe (300 mg, 1.15 mmol) were suspended in molecular sieve dried DMF (20 mL) in a Schlenk flask equipped with an air cooler under inert conditions. The reaction mixture was heated to 90 °C for 17 h. The solution turned red, small red crystals formed at the flask wall and a small amount of colorless Mo(CO)₆ sublimed in the cooler. The flask was introduced in a glove box where the deep red supernatant solution was removed with a syringe. The crystals were washed with diethyl ether (4x10 mL), finely grounded using a mortar and washed again with diethyl ether (5x8 mL) to remove residual free ligand. The bright red powder of **1** was dried under reduced pressure. Yield: 425 mg (0.963 mmol, 84 %).

¹H NMR (400 MHz, DMF-d₇): δ/ppm = 9.26 (d, *J* = 5.5 Hz, 3H), 8.13 (d, *J* = 8.4 Hz, 3H), 8.08 – 7.98 (m, 3H), 7.41 (t, *J* = 6.4 Hz, 3H), 2.82 (s, 3H, CH₃). MS (HR-APCI): calcd for [C₂₀H₁₅MoN₃O₃+H]⁺: *m/z* = 444.0246. Found: *m/z* = 444.0253. Elem. anal. calcd for C₂₀H₁₅MoN₃O₃: C, 54.43; H, 3.43; N, 9.52. Found: C, 54.40; H, 3.71; N, 9.53. IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 1890 (s, ν(CO)), 1750 (s, ν(CO)), 1729 (sh, ν(CO)), 1589 (w), 1566 (w), 1457 (m), 1436 (m), 1395 (w), 1302 (w), 1288 (w), 1241 (w), 1166 (m), 1144 (w), 1115 (w), 1053 (m), 1020 (w), 999 (w), 966 (w), 899 (w), 888 (w), 849 (w), 771 (m), 754 (s), 709 (w), 659 (m), 645 (m), 624 (m), 581 (w), 556 (w), 523 (m), 505 (m), 484 (m), 451 (w), 429 (m), 418 (w), 408 (w). CV (THF, vs. FcH/FcH⁺): *E*_{1/2}/V = −0.31 (rev.), +0.48 (irrev.). CV (CH₃CN, vs. FcH/FcH⁺): *E*_{1/2}/V = −0.23 (rev.), +0.74 (irrev.). CV (DCM, vs. FcH/FcH⁺): *E*_{1/2}/V = −0.29 (rev.), +0.74 (irrev.). CV (DMF, vs. FcH/FcH⁺): *E*_{1/2}/V = −0.20 (rev.), +0.58 (irrev.). CV (DMSO, vs. FcH/FcH⁺): *E*_{1/2}/V = −0.16 (rev.), +0.56 (irrev.). UV/Vis (CH₃CN): λ_{max}/nm (ε/M^{−1} cm^{−1}) = 209 (40 500), 249 (19 400), 289 (7570), 438 (8870). UV/Vis (THF): λ_{max}/nm (ε/M^{−1} cm^{−1}) = 251 (21 700), 265 (13 200, sh), 299 (7970), 474 (11 100). UV/Vis (DCM): λ_{max}/nm (ε/M^{−1} cm^{−1}) = 250 (16 700), 265 (9230, sh), 295 (5860), 455 (8060). UV/Vis (DMF): λ_{max}/nm (ε/M^{−1} cm^{−1}) = 273 (9940, sh), 292 (7470), 447 (9200). UV/Vis (DMSO): λ_{max}/nm (ε/M^{−1} cm^{−1}) = 266 (9340, sh), 291 (6830), 442 (8440). UV/Vis (2-MeTHF): λ_{max}/nm = 479, 301, 266, 250. UV/Vis (2,5-Me₂THF): λ_{max}/nm = 484, 303. UV/Vis (Benzene): λ_{max}/nm = 486, 301. UV/Vis (Toluene): λ_{max}/nm = 491, 304. UV/Vis (Xylene): λ_{max}/nm = 493. UV/Vis (Mesitylene): λ_{max}/nm = 495, 304. UV/Vis (2-MeTHF, 77 K): λ_{max}/nm = 451. Absorptance (KBr Pellet): λ_{max}/nm = 450.

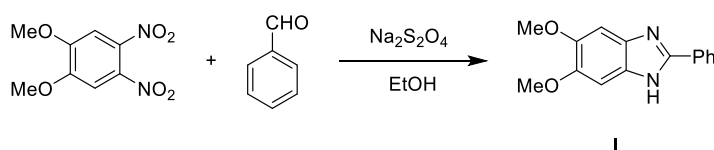
Synthesis of Mo(CO)₄(bpy) (**2**)

The complex was synthesized following a literature procedure³⁵ and was crystallized for purification by storing a concentrated solution of **2** in MeCN/toluene (10/3, v/v) at -20 °C for 4 d. The ¹H NMR spectrum of **2** in CD₂Cl₂ agreed with literature values of chemical shifts.³⁶

Synthesis of sacrificial donor (BIH)

The synthesis of **BIH** was derived from a previously reported procedure with ¹H NMR spectra matching those previously reported.³⁷

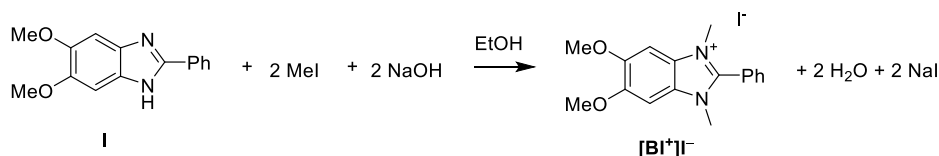
Step 1: 5,6-dimethoxy-2-phenyl-1H-benzo[d]imidazole (**I**)



1,2-Dimethoxy-4,5-dinitrobenzene (6.38 g, 28 mmol) and Na₂S₂O₄ (11.4 g, 65.8 mmol, 2.35 eq) were suspended in dry ethanol (250 mL) under inert conditions. Freshly distilled benzaldehyde (3.4 mL, 33 mmol, 1.18 eq.) was added dropwise under stirring. The yellow mixture was heated under reflux and the reaction was followed via TLC. After 4 d the mixture had turned orange and additional benzaldehyde (3.4 mL, 33 mmol) and Na₂S₂O₄ (11.4 g, 65.8 mmol) was added. After additional 6 d with heating under reflux the suspension had turned yellow. The solvent was removed under reduced pressure. The residue was dissolved in aqueous NH₄OH solution (1 M, 170 mL) yielding a brownish red solution and extracted with ethyl acetate (7x 150 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure to yield an orange solid (ca. 8.5 g). The crude product was recrystallized from ethyl acetate/petrol ether (27 mL/7.5 mL) under reflux. After cooling back to room temperature a precipitate formed, that was filtered off and washed with cold ethyl acetate (2x 2 mL) yielding 1.04 g (4.09 mmol) of **I** as an off-white powder. The filtrate was concentrated under reduced pressure and the red to black solid was purified using column chromatography (SiO₂, petrol ether/ethyl acetate 8:2 → ethyl acetate) yielding two fractions with protonated **I** (A: light blue solid, 1.7 g; B: light purple solid, 2.3 g, ¹H-NMR (400 MHz, CD₃CN) δ/ppm = 10.68 (s, 1H, broad), 8.38–7.82 (m, 2H), 7.85–7.24 (m, 3H), 7.12 (s, 2H, broad), 3.86 (s, 6H)). The two fractions were deprotonated by vigorously stirring the solid in aqueous NaOH solution (1 M, 150 mL) layered with ethyl acetate 100 mL. The aqueous phase was extracted with ethyl acetate (5x 50 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure to yield **I** as a pale purple solid from fraction A (1.22 g, 4.8 mmol) and B (2.00 g, 7.9 mmol). The total yield of the reaction was 4.26 g (60 %).

¹H NMR (400 MHz, CD₃CN): δ/ppm = 8.13–7.97 (m, 2H), 7.59–7.39 (m, 3H), 7.12 (s, 2H), 3.86 (s, 6H).

Step 2: 5,6-dimethoxy-1,3-dimethyl-2-phenyl-1H-benzo[d]imidazol-3-ium iodide ([BI⁺]⁻)

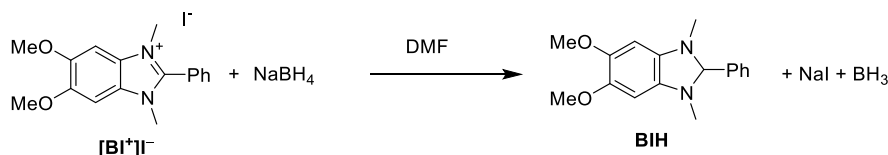


I (1.88 g, 7.4 mmol), ground NaOH (355 mg, 8.88 mmol, 1.2 eq.), methyl iodide (1.4 mL, 22.2 mmol, 3.5 eq.) and dry ethanol (30 mL) were introduced to a sealed PTFE tube (inner diameter 2.5 cm, height 12 cm) with a stirring bar. The mixture was heated to 160°C over 15 h. After additional 8 h, the mixture had cooled to room temperature. The product (off-white powder and red crystals) was filtered off, washed with ethanol (20 mL) and diethyl ether (5 mL) and dried under air. Yield: 1.88 g (62 %).

The red crystals are likely the I_3^- salt of the product, the formation of which can be avoided by using fresh MeI.

1H NMR (400 MHz, DMSO- d_6) δ 7.92–7.83 (m, 2H), 7.84–7.70 (m, 3H), 7.67 (s, 2H), 3.95 (s, 6H), 3.87 (s, 6H).

Step 3: 5,6-dimethoxy-1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH)



In an open flask, $[BI^*]I^-$ (523 mg, 1.27 mmol) was suspended in DMF (12 mL) forming an orange suspension. $NaBH_4$ (144 mg, 3.66 mmol, 3 eq.) was added in portions under stirring. The suspension initially lost color and after stirring for 30 min turned light yellow. The solvent was removed under reduced pressure and the residue was dissolved in water/ethyl acetate (30 mL/20 mL). The organic layer was separated and the aqueous phase was extracted with ethyl acetate (2x 15 mL). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4 , filtered and the solvent was removed under reduced pressure. **BIH** was obtained as a crystalline white solid and was dried under reduced pressure over night. Yield: 330 mg (92 %).

We chose this procedure because our starting material $[BI^*]I^-$ did not fully dissolve in water as described in the literature³⁷ leading to very low yields (<20 %) for the reduction to **BIH** in our experiments.

The product should be stored under inert gas.

1H NMR (400 MHz, Chloroform- d) δ 7.61 – 7.52 (m, 2H), 7.46 – 7.36 (m, 3H), 6.25 (s, 2H), 4.64 (s, 1H), 3.84 (s, 6H), 2.53 (s, 6H).

3. NMR- and FTIR spectroscopy, APCI-MS, XRD

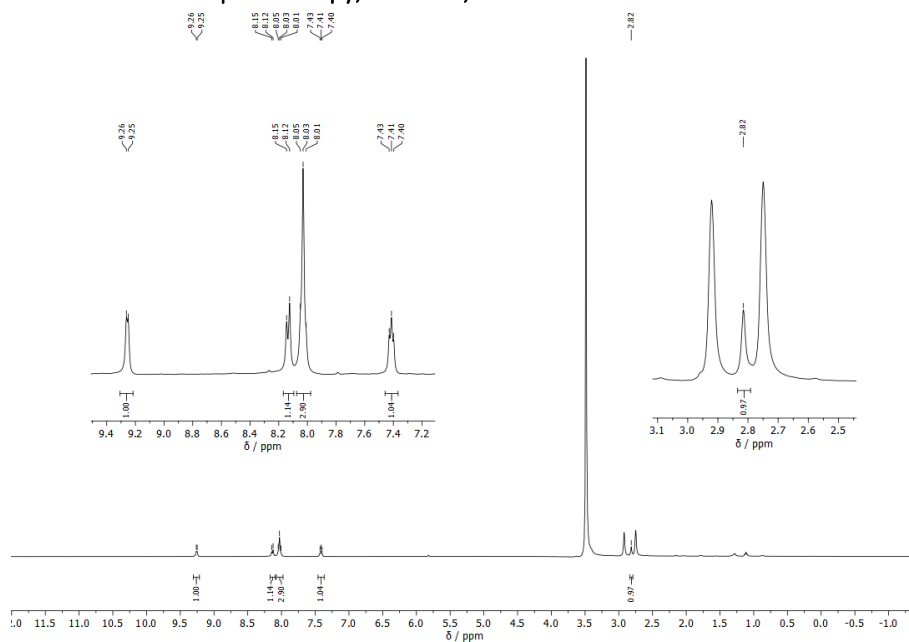


Figure S1: ^1H NMR spectrum of **1** in DMF-d_7 . The resonance at 8.03 ppm overlaps with a residual signal of undeuterated DMF.

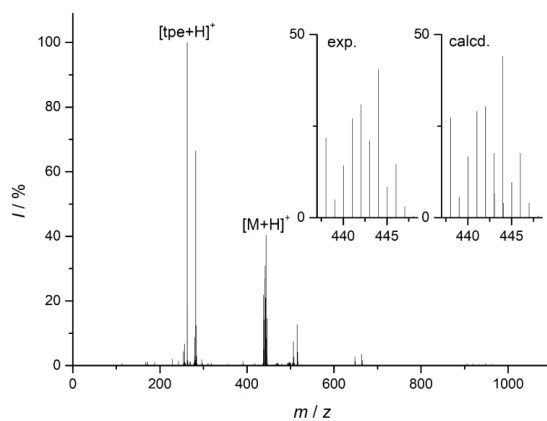


Figure S2: APCI-MS spectrum of **1** in MeCN with comparison of experimental and calculated isotope patterns of the $[\text{M}+\text{H}]^+$ peak.

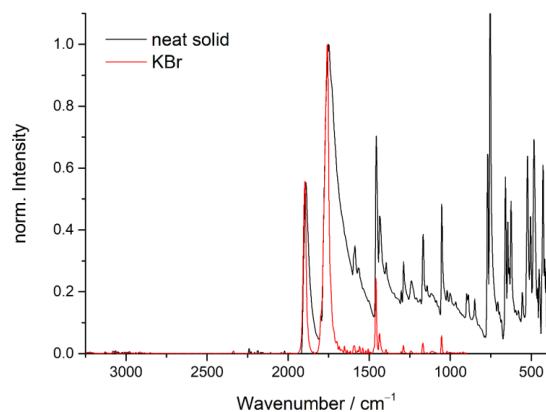


Figure S3: ATR-IR spectra of **1** as neat solid and in a KBr pellet.

Table S2: Summary of XRD data for **1**.

	Mo(CO)₃(tpe) 1
Empirical formula	C ₂₀ H ₁₅ MoN ₃ O ₃
Formula weight	441.29
Crystal color / habit	orange plate
<i>T</i> / K	120(2)
Crystal dimensions / mm	0.100 x 0.061 x 0.032
Crystal system	Monoclinic
Space group	Cc
<i>a</i> / Å	16.928(2)
<i>b</i> / Å	8.0401(11)
<i>c</i> / Å	13.848(2)
<i>α</i> / °	90
<i>β</i> / °	108.570(11)
<i>γ</i> / °	90
<i>V</i> / Å³	1786.6(4)
<i>Z</i>	4
<i>F</i>(000)	888
Density (calcd) / g cm⁻³	1.641
Absorption coefficient <i>μ</i> / mm⁻¹	0.76
Theta range / °	2.539 - 25.997
Index ranges	-19 ≤ <i>h</i> ≤ 20 -9 ≤ <i>k</i> ≤ 9 -16 ≤ <i>l</i> ≤ 16
Reflections collected	2808
Independent reflections	2808
Observed reflections	2808
Parameters/restraints	247/14
Min. / max. transmission	0.1495 / 0.9897
Goodness-of-fit	1.001
Largest difference peak and hole / e Å⁻³	4.286 / -1.412
<i>R</i>₁ (<i>I</i> > 2σ(<i>I</i>))	0.0763
<i>R</i>₁ (all data)	0.0944
<i>wR</i>₂ (<i>I</i> > 2σ(<i>I</i>))	0.1755
<i>wR</i>₂ (all data)	0.1844

Table S3: Bond lengths / Å and angles / deg of **1** determined from a crystal structure and an optimized geometry calculated via density functional theory (B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN)). For the numbering the reader is referred to Figure 1a.

	Bond lengths			Bond angles	
	XRD	DFT		XRD	DFT
Mo–C ¹	1.933(17)	1.954	C ¹ –Mo–C ²	88.3(7)	86.85
Mo–C ²	1.949(16)	1.957	C ¹ –Mo–C ³	88.4(6)	89.02
Mo–C ³	1.962(17)	1.958	C ² –Mo–C ³	90.5(7)	88.25
Mo–N ²	2.211(14)	2.236	C ¹ –Mo–N ²	97.5(6)	94.05
Mo–N ¹	2.248(12)	2.243	C ² –Mo–N ²	173.0(6)	176.11
Mo–N ³	2.258(13)	2.247	C ³ –Mo–N ²	93.4(6)	95.55
			C ¹ –Mo–N ¹	174.8(7)	173.54
			C ² –Mo–N ¹	95.1(6)	97.97
			C ³ –Mo–N ¹	95.4(6)	95.4
			N ² –Mo–N ¹	78.8(5)	80.86
			C ¹ –Mo–N ³	95.2(6)	94.88
			C ² –Mo–N ³	95.9(6)	94.68
			C ³ –Mo–N ³	172.8(6)	175.24
			N ² –Mo–N ³	79.9(5)	81.47
			N ¹ –Mo–N ³	80.6(4)	80.49

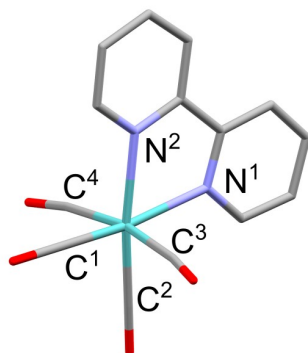


Figure S4: Crystal structure of **2** (from ref. ³⁸) with atom numbering used in Table S4. Hydrogen atoms omitted for clarity.

Table S4: Bond lengths / Å and angles / deg of **2** determined from a crystal structure³⁸ and an optimized geometry calculated via density functional theory (B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN)).

	Bond lengths			Bond angles	
	XRD	DFT		XRD	DFT
Mo–C ¹	1.952(4)	1.974	C ¹ –Mo–C ²	90.12(15)	90.65
Mo–C ²	1.962(3)	1.973	C ¹ –Mo–C ³	85.14(15)	88.76
Mo–C ³	2.056(3)	2.046	C ² –Mo–C ³	88.35(14)	90.44
Mo–C ⁴	2.022(4)	2.050	C ¹ –Mo–N ²	99.13(12)	99.81
Mo–N ¹	2.241(3)	2.235	C ² –Mo–N ²	170.67(13)	169.49
Mo–N ²	2.249(3)	2.23	C ³ –Mo–N ²	93.56(12)	88.77
			C ¹ –Mo–N ¹	171.35(12)	172.98
			C ² –Mo–N ¹	98.43(13)	96.37
			C ³ –Mo–N ¹	93.79(12)	91.25
			N ¹ –Mo–N ²	72.34(10)	73.17
			C ¹ –Mo–C ⁴	84.26(15)	86.34
			C ² –Mo–C ⁴	85.73(14)	90.68
			C ³ –Mo–C ⁴	167.85(15)	174.98
			C ⁴ –Mo–N ²	93.99(12)	91.02
			C ⁴ –Mo–N ¹	97.58(12)	93.49

4. Cyclic voltammetry, square-wave voltammetry and chemical oxidation of **1**

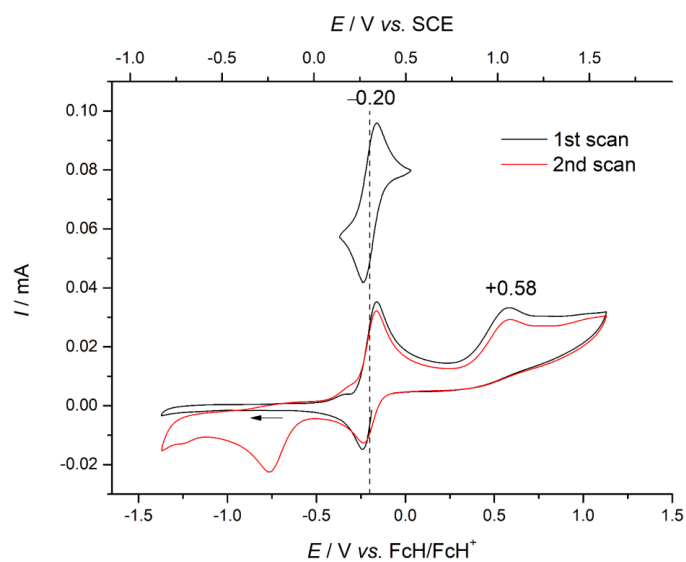


Figure S5: Cyclic voltammogram of **1** in DMF (1 mM). The arrow denotes the scan direction. The redox events are labeled with potentials vs. FcH/FcH^+ .

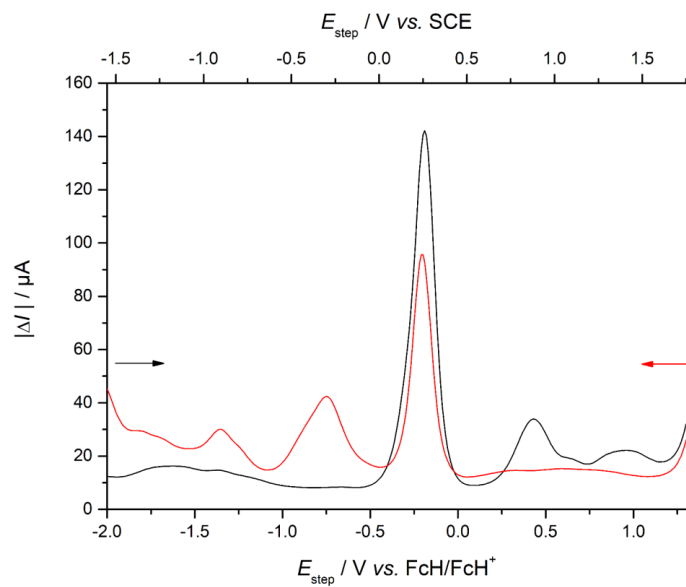


Figure S6: Square-wave voltammogram of **1** in DMF (1 mM). The arrows denote the scan direction.

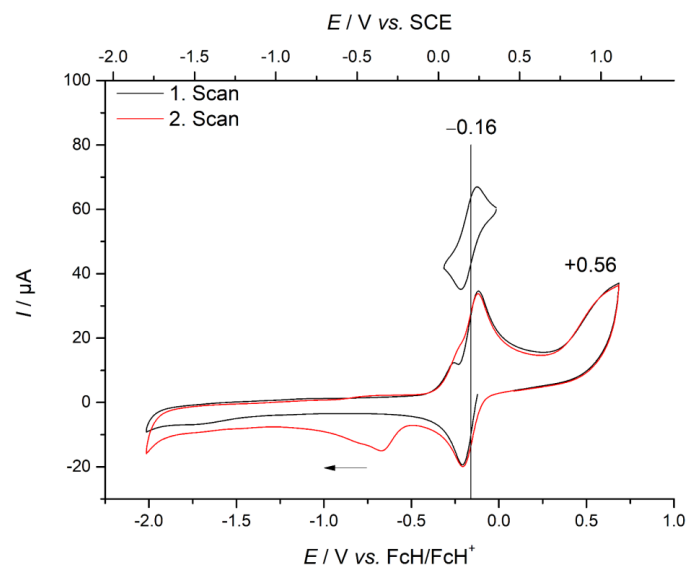


Figure S7: Cyclic voltammogram of **1** in DMSO (1 mM). The redox events are labeled with potentials vs. FcH/FcH^+ .

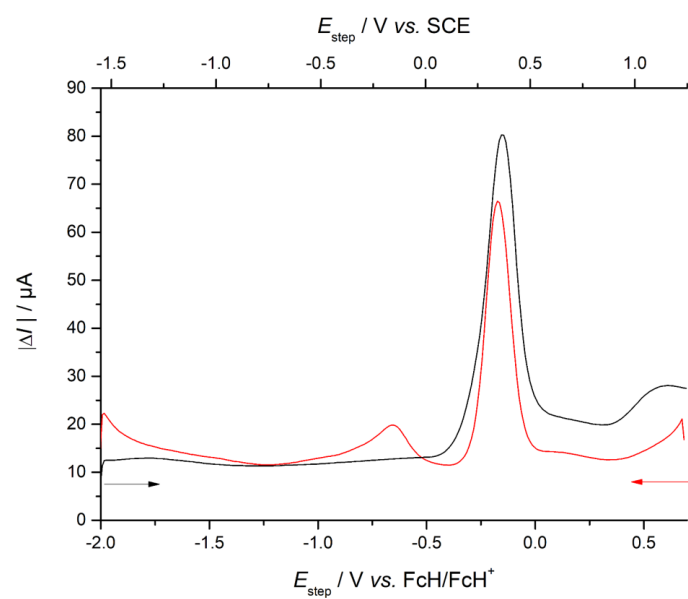


Figure S8: Square-wave voltammogram of **1** in DMSO (1 mM). The arrows denote the scan direction.

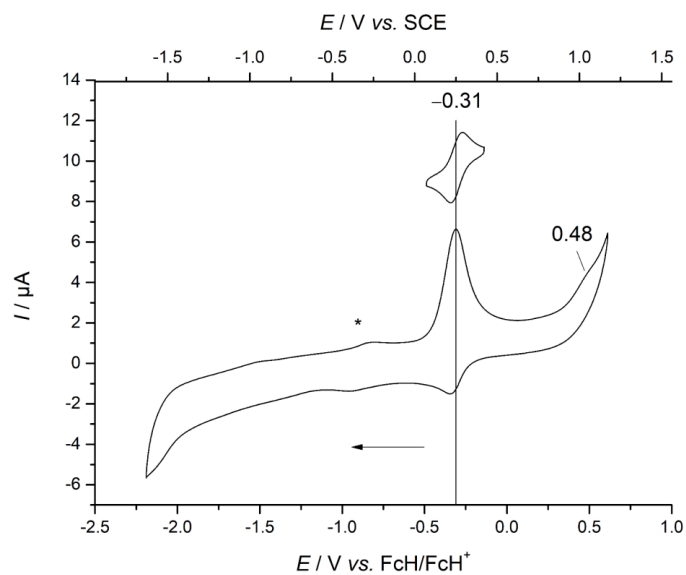


Figure S9: Cyclic voltammogram of **1** in THF (0.05 mM). The asterisk (*) marks an impurity in the solvent. The arrow denote the scan direction. The redox events are labeled with potentials vs. FcH/FcH⁺.

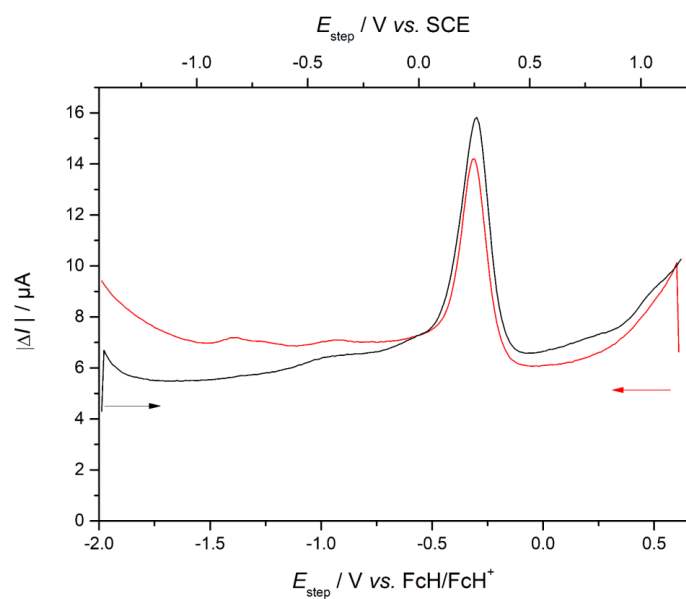


Figure S10: Square-wave voltammogram of **1** in THF (0.05 mM). The arrows denote the scan direction.

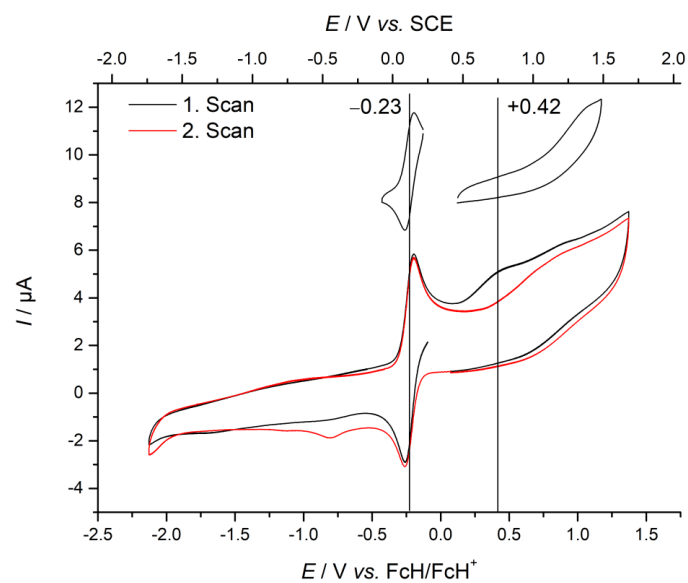


Figure S11: Cyclic voltammogram of **1** in MeCN (0.11 mM). The arrow denote the scan direction. The redox events are labeled with potentials vs. FcH/FcH⁺.

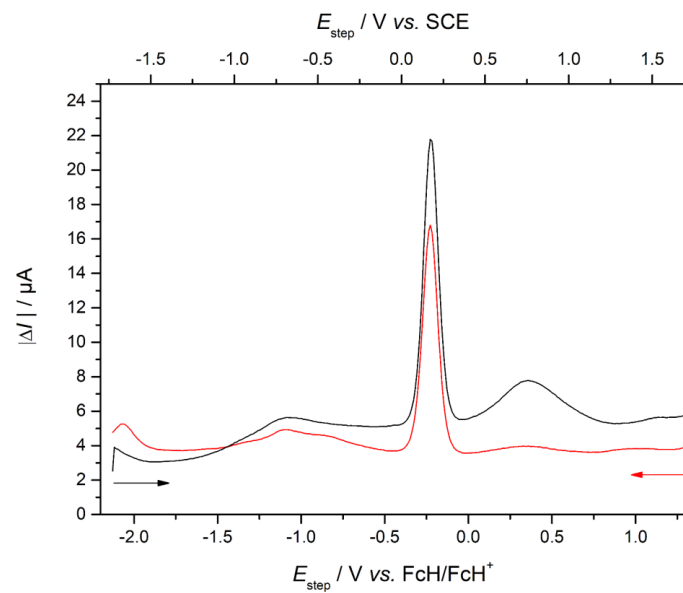


Figure S12: Square-wave voltammogram of **1** in MeCN (0.11 mM). The arrows denote the scan direction.

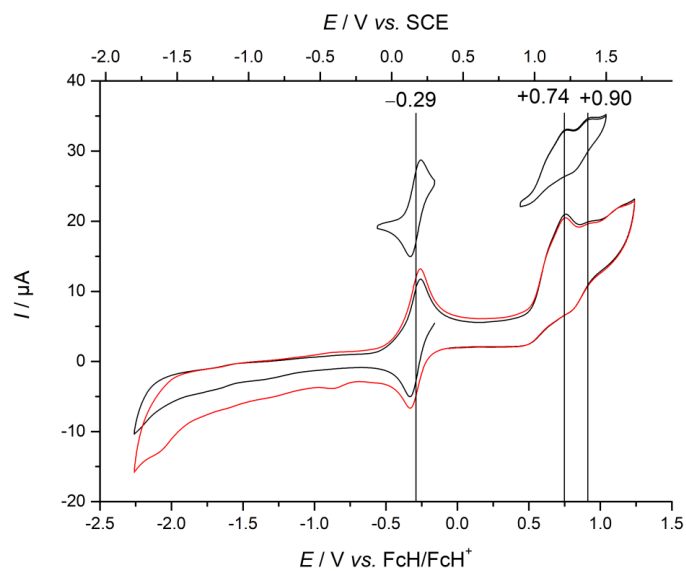


Figure S13: Cyclic voltammogram of **1** in DCM (0.27 mM). The arrow denote the scan direction. The redox events are labeled with potentials vs. FcH/FcH⁺.

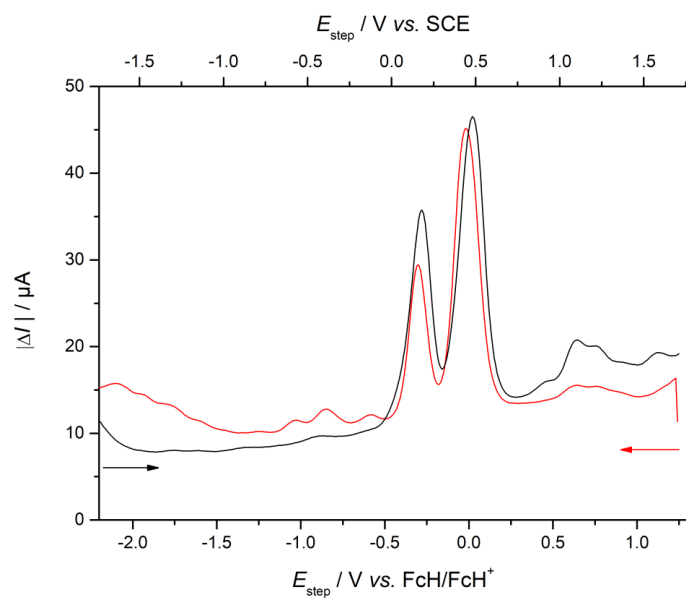


Figure S14: Square-wave voltammogram of **1** in DCM (0.27 mM) with FcH as internal standard. The arrows denote the scan direction.

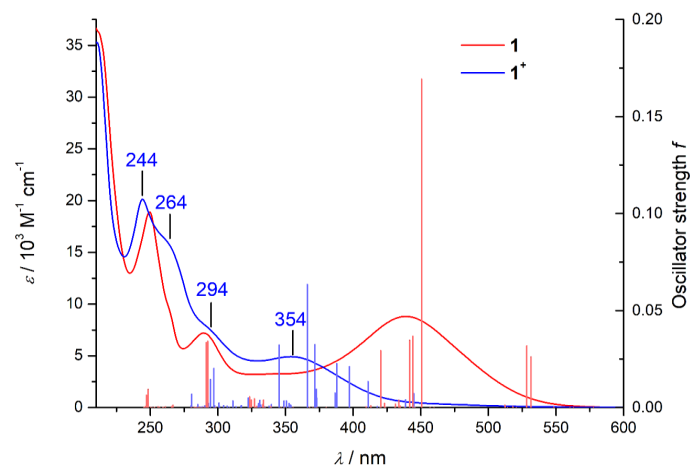


Figure S15: UV/VIS absorption spectra of **1** and **1**⁺ (by oxidizing **1** with 1 eq. of [FcH][PF₆], *c* = 0.114 mM) in MeCN with TD-DFT calculated oscillator strengths for **1** (red sticks) and low-spin **1**⁺ (blue sticks). The spectrum of **1** was corrected for the absorption of ferrocene FcH.

5. Absorption and emission spectroscopy, luminescence lifetimes, TD-DFT

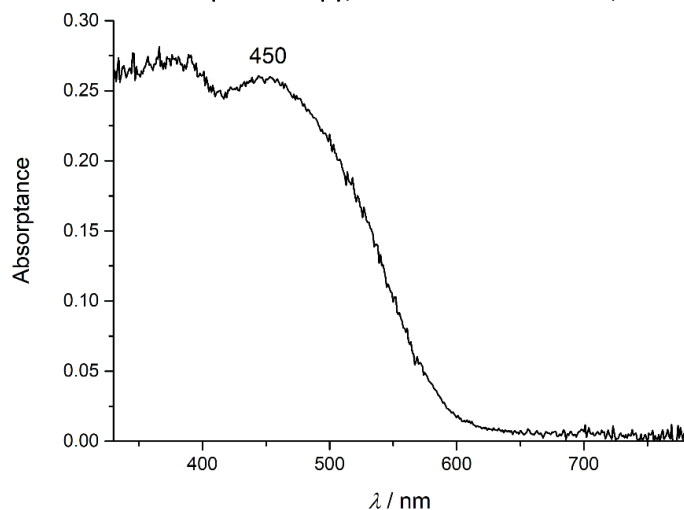


Figure S16: Absorbance spectrum of **1** (0.0055 w% diluted in KBr).

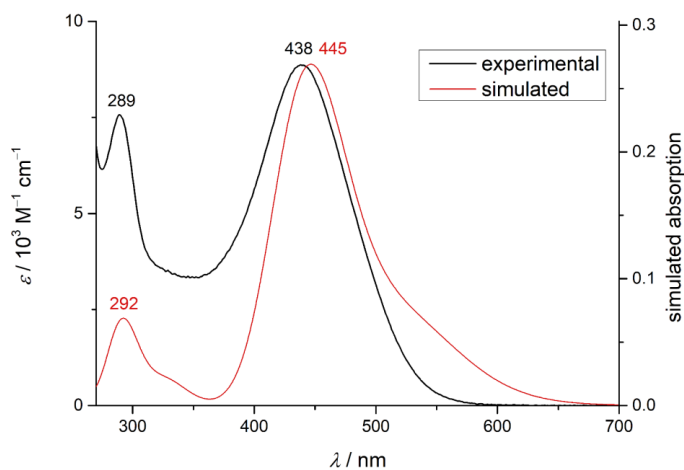


Figure S17: Experimental UV/Vis absorption spectrum (black trace) and simulated spectrum (TDDFT, Gaussian broadening with FWHM of 3500 cm^{-1}) of **1** in MeCN.

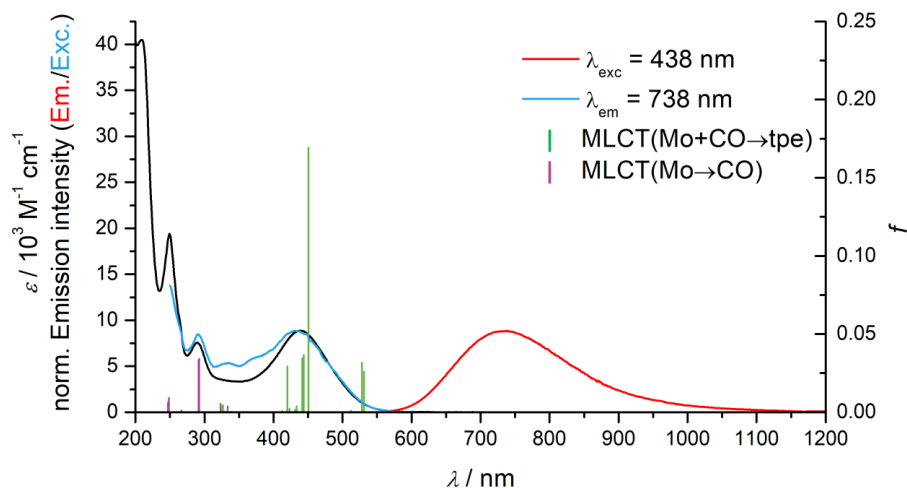


Figure S18: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in MeCN at 293 K with TD-DFT calculated oscillator strengths (green and purple sticks, B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN)). The colors of the sticks indicate the main contribution of the transitions obtained using a charge transfer number analysis with TheoDORE.³¹

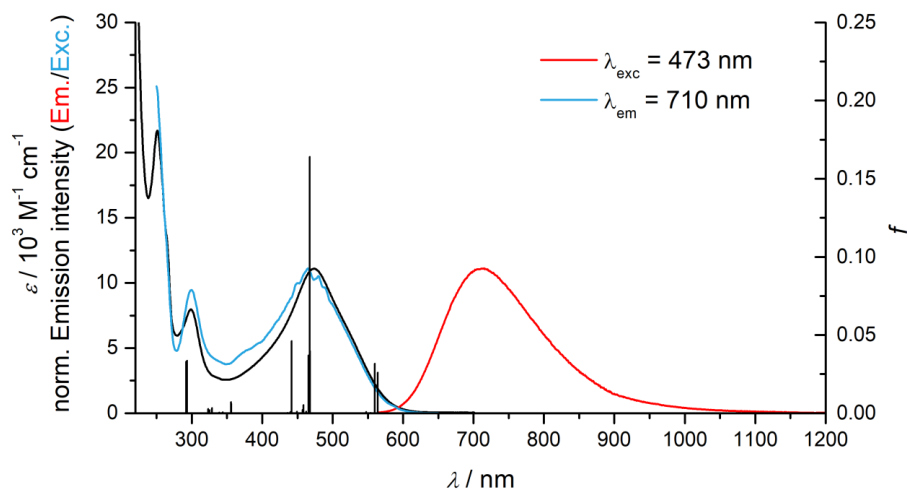


Figure S19: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in THF at 293 K with TD-DFT calculated oscillator strengths (black sticks, B3LYP/D3BJ/ZORA/TZVP/CPCM(THF)).

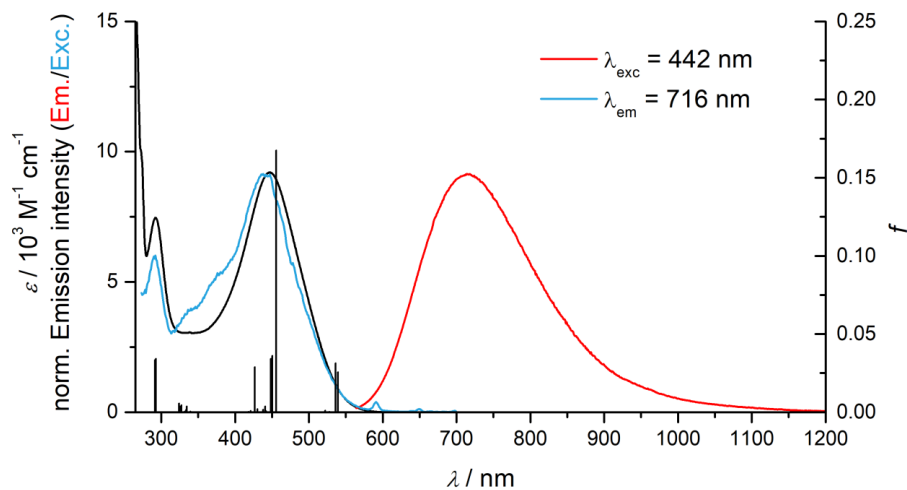


Figure S20: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in DMF at 293 K with TD-DFT calculated oscillator strengths (black sticks, B3LYP/D3BJ/ZORA/TZVP/CPCM(DMF)).

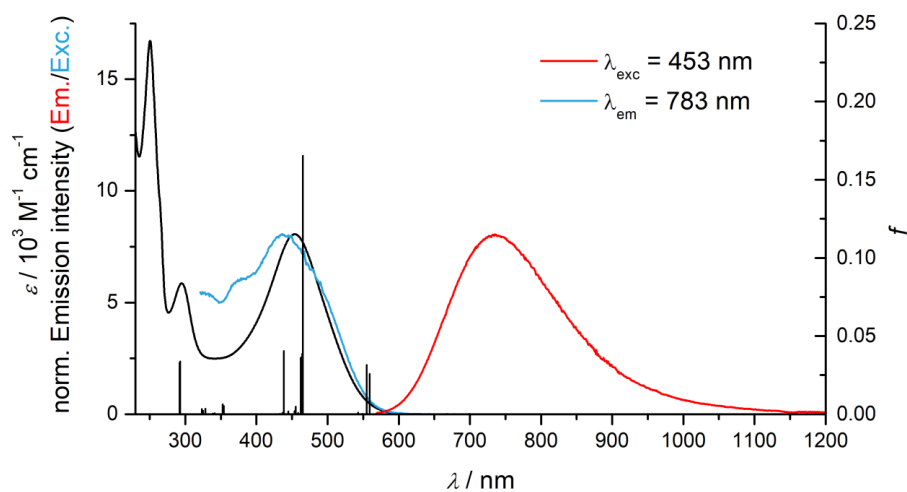


Figure S21: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in DCM at 293 K with TD-DFT calculated oscillator strengths (black sticks, B3LYP/D3BJ/ZORA/TZVP/CPCM(DCM)).

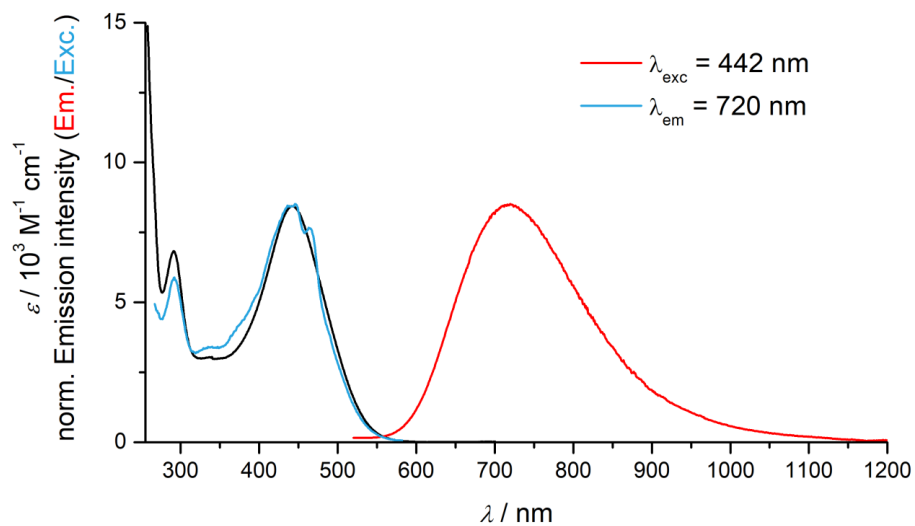


Figure S22: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in DMSO at 293 K.

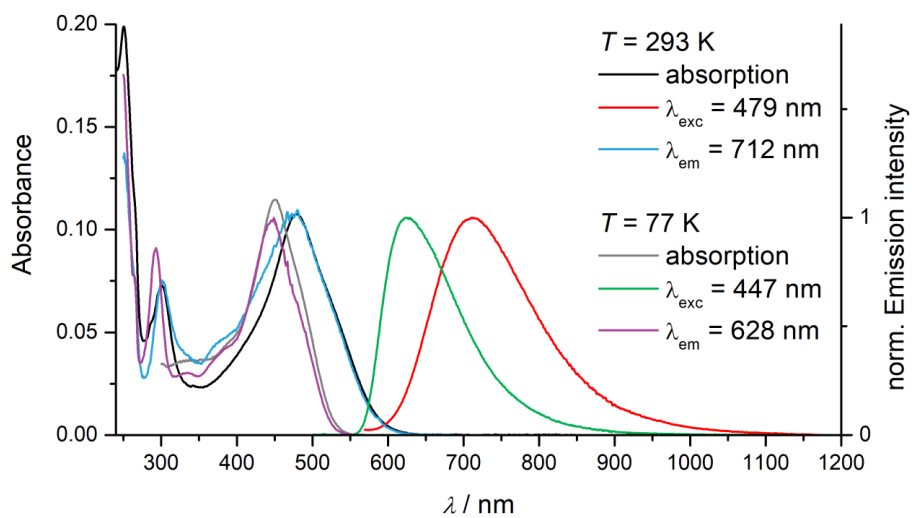


Figure S23: UV/Vis absorption (black and grey traces), normalized emission (red and green traces) and excitation spectra (blue and purple traces) of **1** in 2-MeTHF at 293 and 77 K.

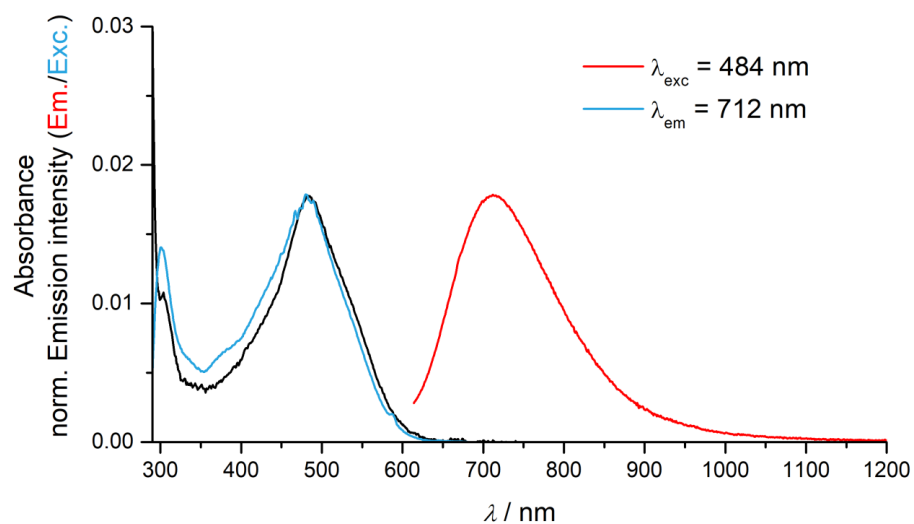


Figure S24: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in 2,5-Me₂THF at 293 K.

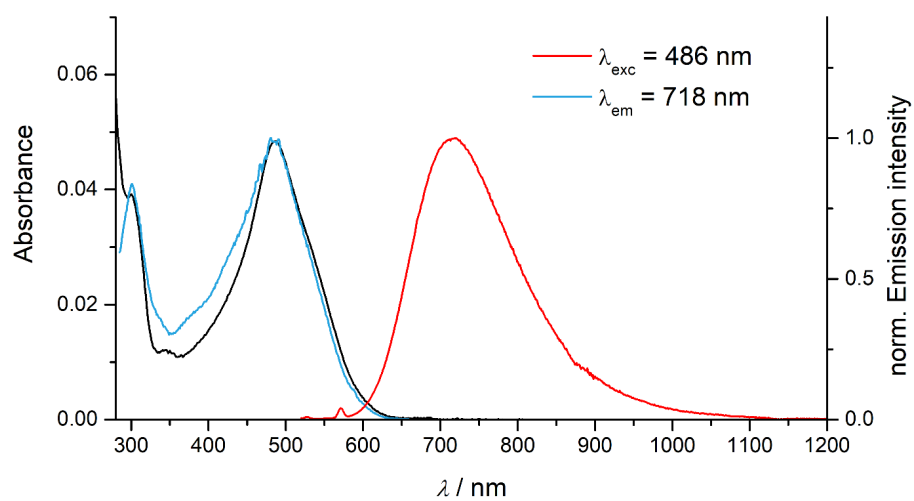


Figure S25: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in benzene at 293 K.

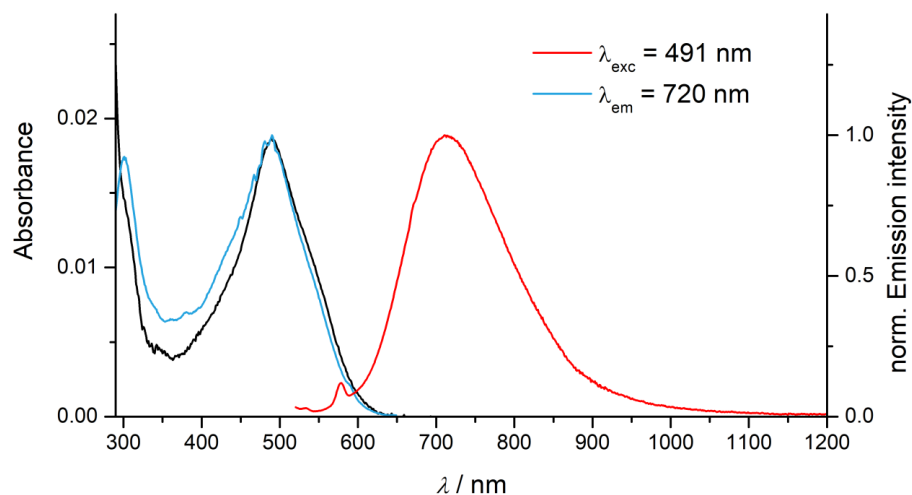


Figure S26: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in toluene at 293 K.

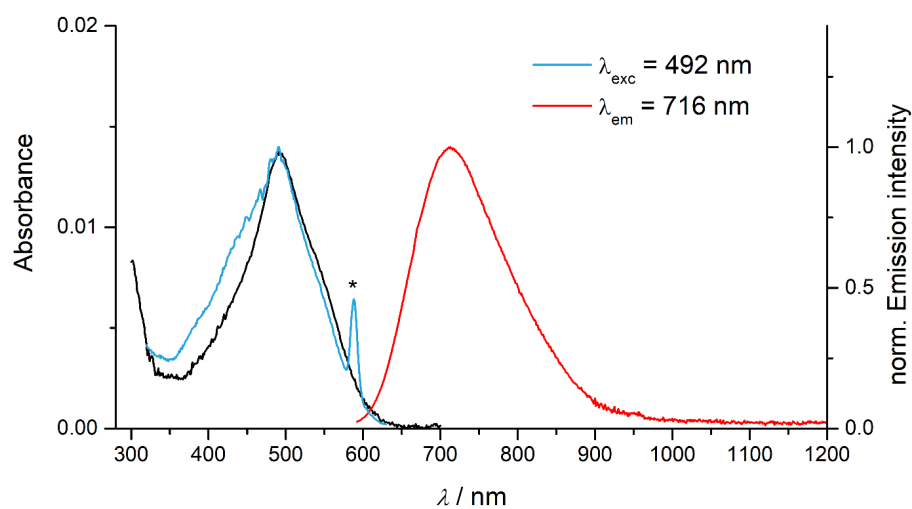


Figure S27: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in xylenes (mixture of isomers) at 293 K. The band marked with an asterisk is caused by Raman scattering.

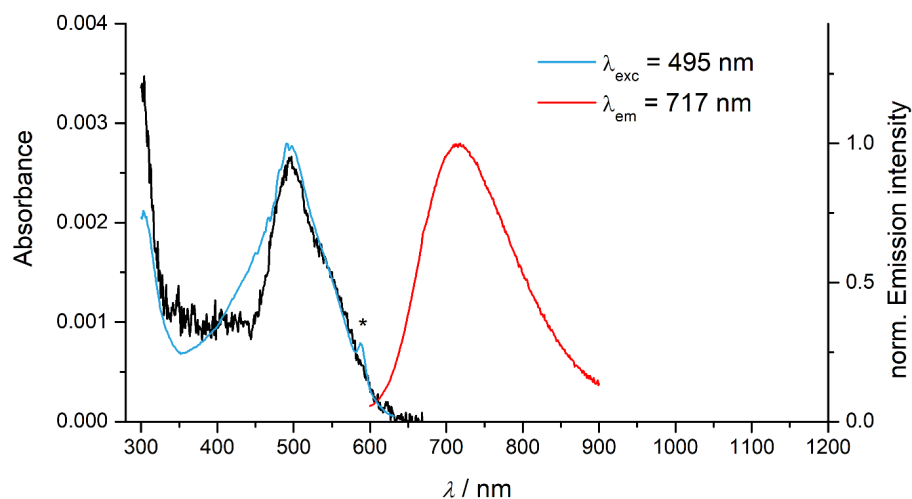


Figure S28: UV/Vis absorption (black line), normalized emission (red line) and excitation spectra (blue line) of **1** in mesitylene at 293 K. The band marked with an asterisk is caused by Raman scattering.

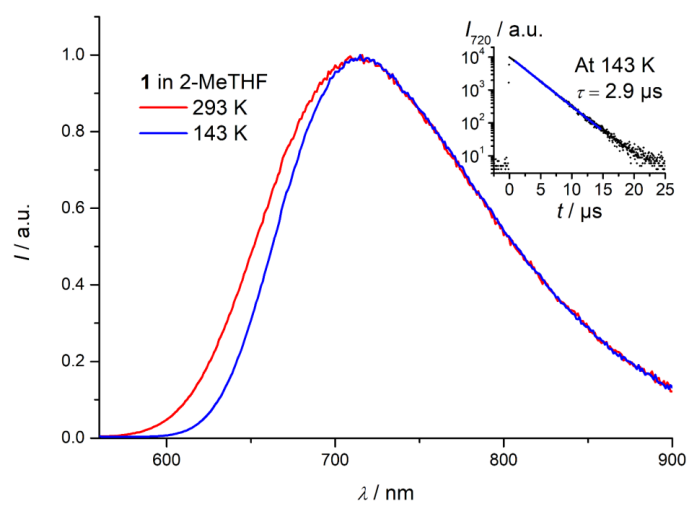


Figure S29: Normalized luminescence spectra of **1** in 2-MeTHF at 293 K (red) and 143 K (blue), $\lambda_{\text{exc}} = 474$ nm. Inset: Luminescence decay at 720 nm after pulsed excitation at 450 nm with monoexponential fit.

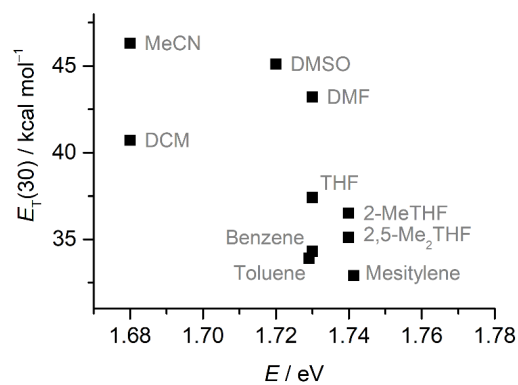


Figure S30: Empirical solvent parameter $E_T(30)^{39}$ plotted against the energy of the emission band maximum of **1** in various solvents.

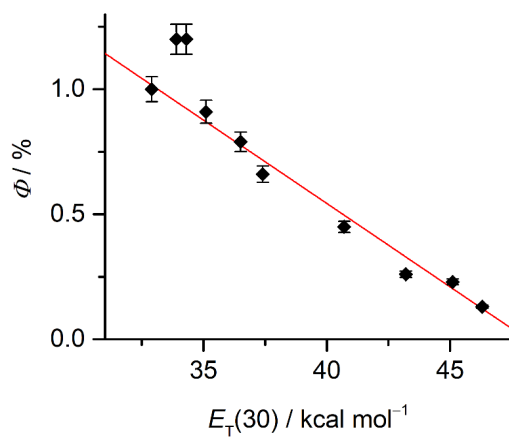


Figure S31: Emission quantum yield Φ of **1** in solution at room temperature plotted against the empiric solvent polarity parameter $E_T(30)^{39}$ with linear fit (red line). Estimated relative error: $\pm 5\%$.

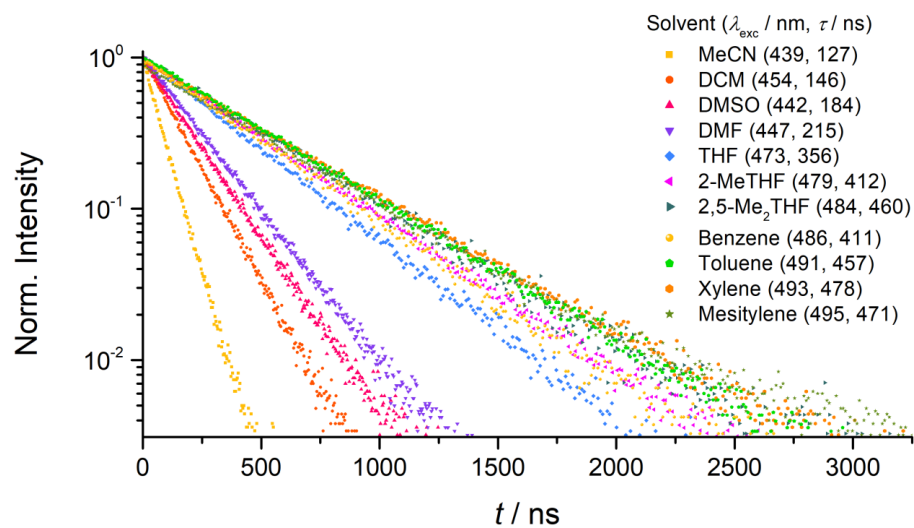


Figure S32: Luminescence decay traces of **1** in various solvents recorded via TCSCP.

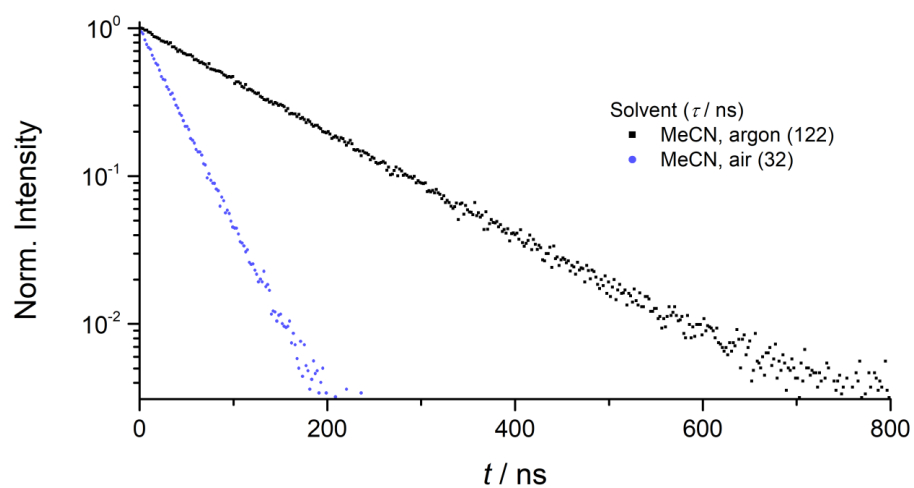


Figure S33: Luminescence decay traces of **1** in deaerated MeCN and after opening the cuvette to air recorded via TCSCP.

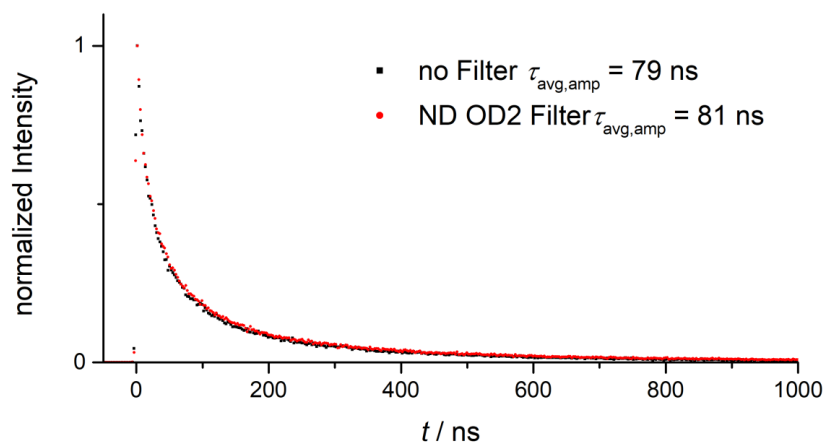


Figure S34: Luminescence decay traces of **1** in the solid state recorded via TCSCP at 420 nm excitation with high laser power (no filter) and reduced laser power (ND OD2 filter, excitation intensity reduced by a factor of 67).

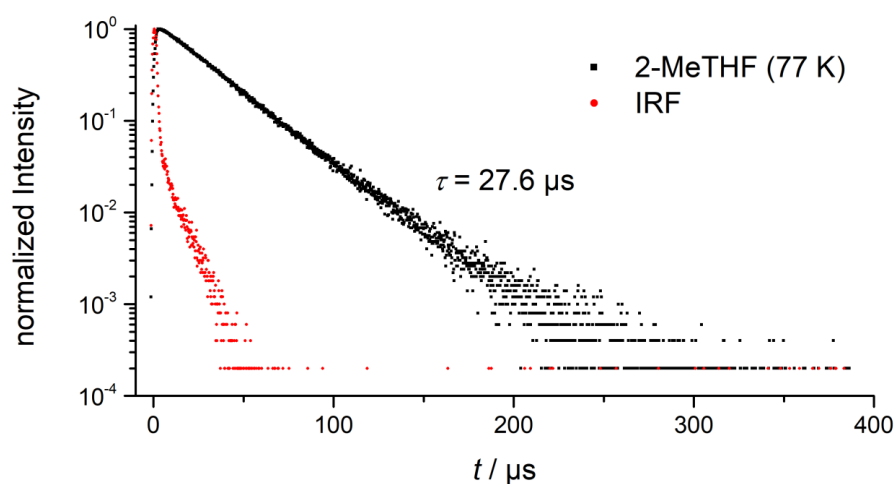


Figure S35: Luminescence decay trace of **1** in 2-MeTHF at 77 K with 447 nm excitation recorded via MCS (black) with instrument response function (IRF, red).

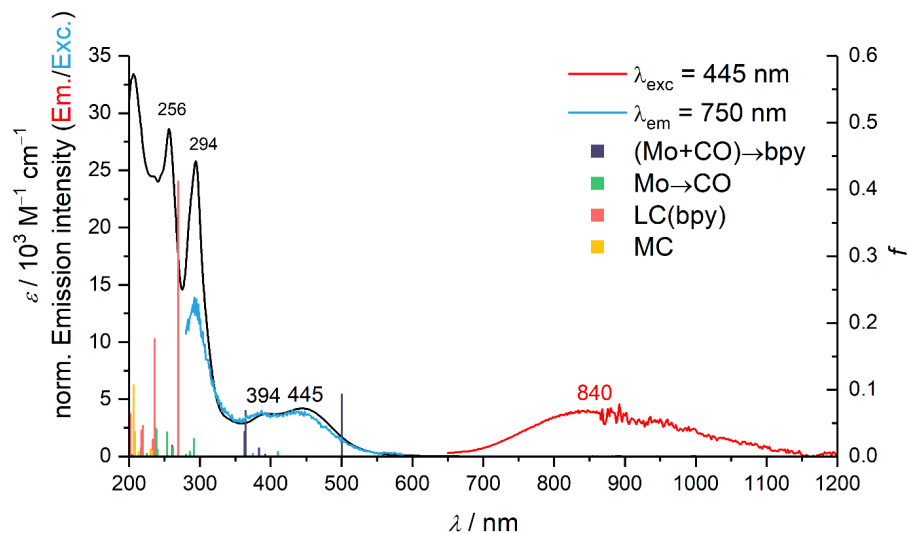


Figure S36: UV/Vis absorption (black line), emission (red line) and excitation spectra (blue line) of **2** in MeCN at 293 K with TD-DFT calculated oscillator strengths (blue, green, red and yellow sticks, B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN)). The colors of the sticks indicate the main contribution of the transitions obtained using a charge transfer number analysis with TheoDORE.³¹

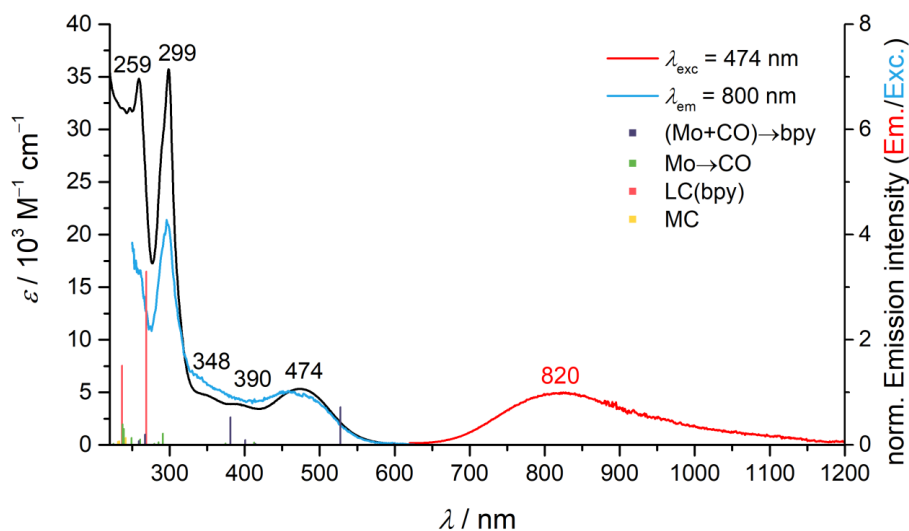


Figure S37: UV/Vis absorption (black line), emission (red line) and excitation spectra (blue line) of **2** in THF at 293 K with TD-DFT calculated oscillator strengths (blue, green, red and yellow sticks, B3LYP/D3BJ/ZORA/TZVP/CPCM(THF)). The colors of the sticks indicate the main contribution of the transitions obtained using a charge transfer number analysis with TheoDORE.³¹

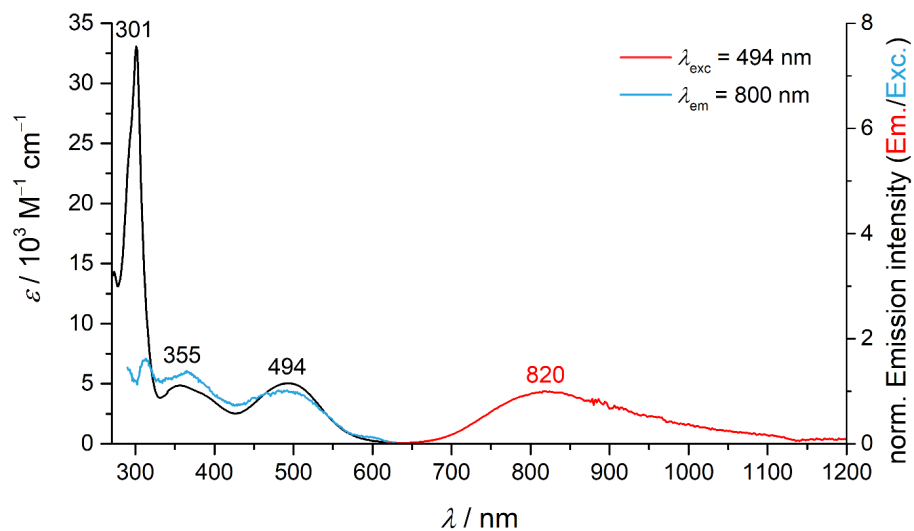


Figure S38: UV/Vis absorption (black line), emission (red line) and excitation spectra (blue line) of **2** in benzene at 293 K.

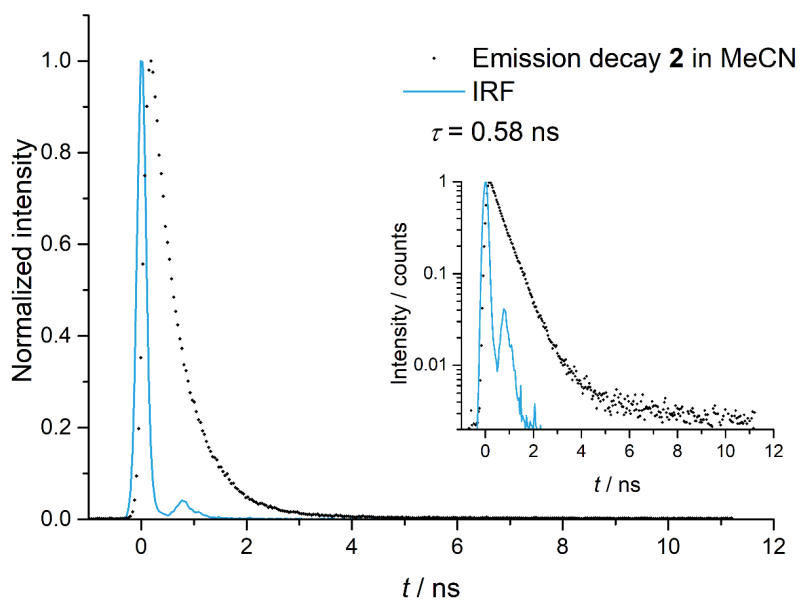


Figure S39: Luminescence decay trace of **2** in MeCN (293 K, $\lambda_{\text{exc}} = 454$ nm, $\lambda_{\text{em}} = 800$ nm) recorded via TCSPC with instrument response function (IRF). Inset: Same data with logarithmic y-axis.

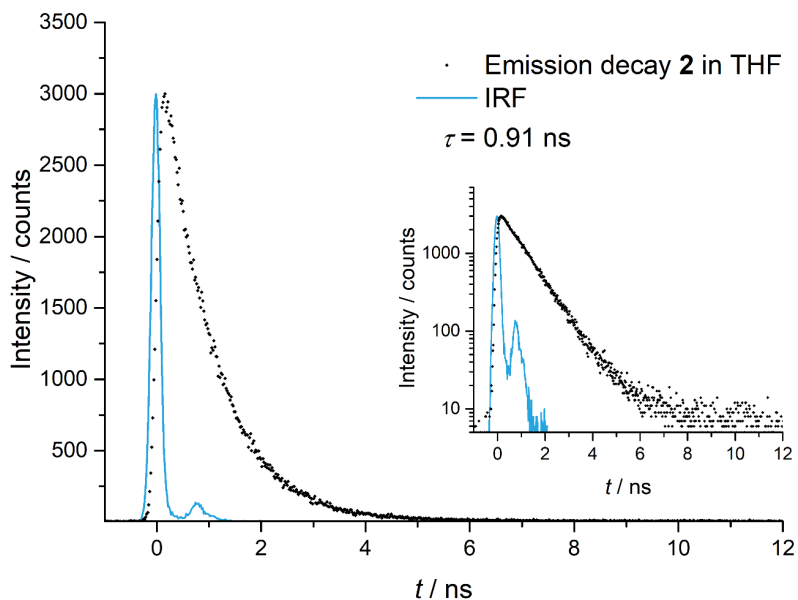


Figure S40: Luminescence decay trace of **2** in THF (293 K, $\lambda_{\text{exc}} = 474$ nm, $\lambda_{\text{em}} = 750$ nm) recorded via TCSPC with instrument response function (IRF). Inset: Same data with logarithmic y-axis.

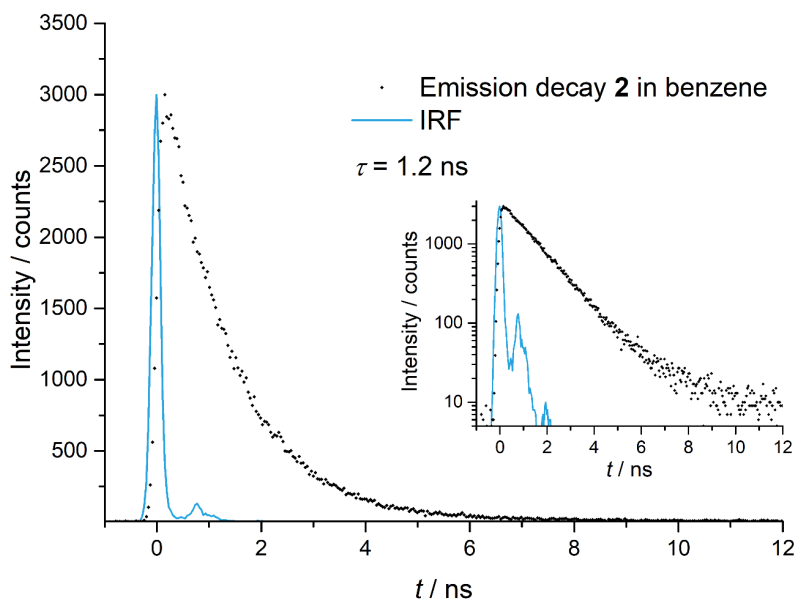


Figure S41: Luminescence decay trace of **2** in benzene at 293 K with 474 nm excitation recorded via TCSPC with instrument response function (IRF). Inset: Same data with logarithmic y-axis.

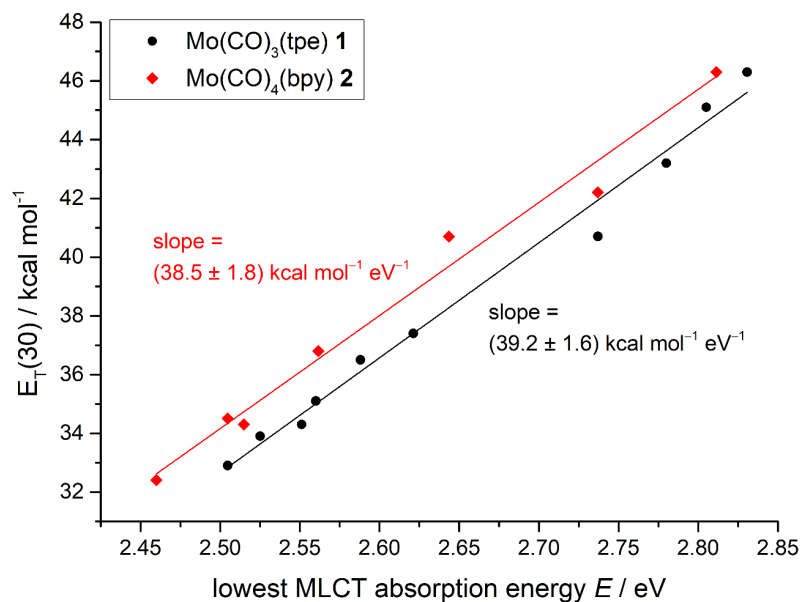


Figure S42: Empirical solvent polarity parameter $E_T(30)$ ³⁹ plotted against energy of the lowest energy MLCT absorption bands of 2 (red diamonds, data from⁴⁰) and 1 (black circles) with linear fits.

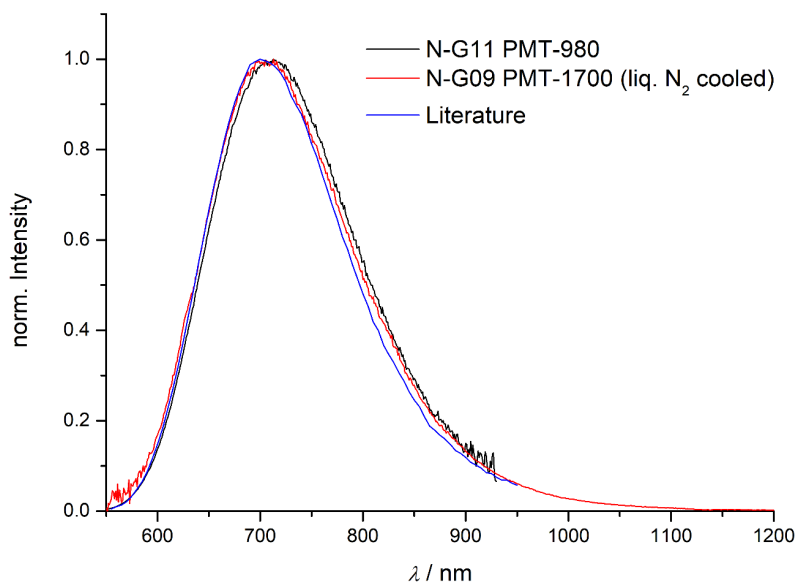


Figure S43: Emission spectra of 4-dimethylamino-4'-nitro-stilbene (4,4'-DMANS) in *o*-dichlorobenzene (1 mM, $\lambda_{\text{exc}} = 520 \text{ nm}$) measured with different photomultipliers as detectors (black and red traces) in comparison with a literature spectrum (blue trace).¹²

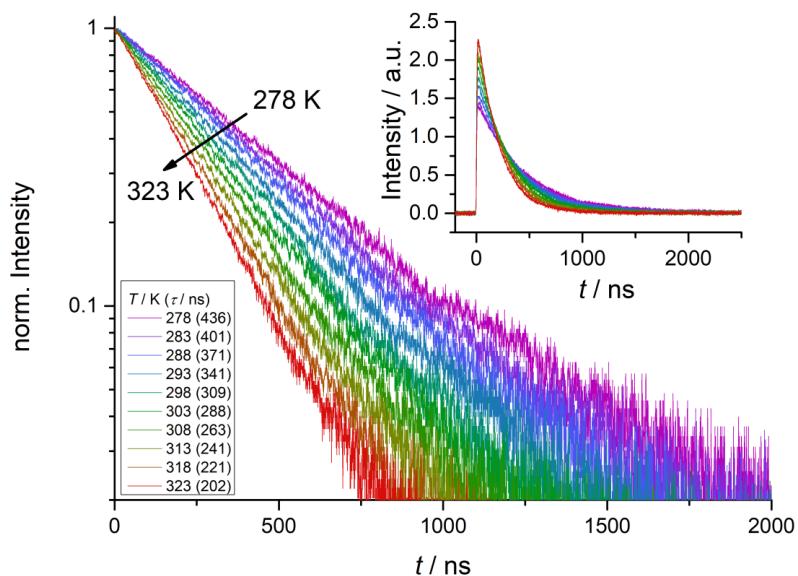


Figure S44: Normalized temperature-dependent luminescence decays of **1** in THF with lifetimes τ ($\lambda_{\text{exc}} = 532$ nm, $\lambda_{\text{em}} = 675$ nm). Inset: Non-normalized data in linear scale.

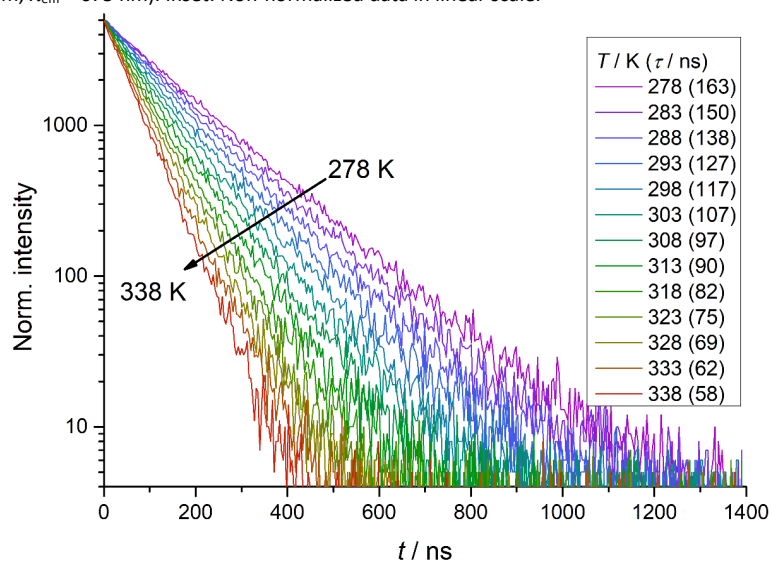


Figure S45: Normalized temperature -dependent luminescence decays of **1** in MeCN with lifetimes τ ($\lambda_{\text{exc}} = 438$ nm, $\lambda_{\text{em}} = 734$ nm).

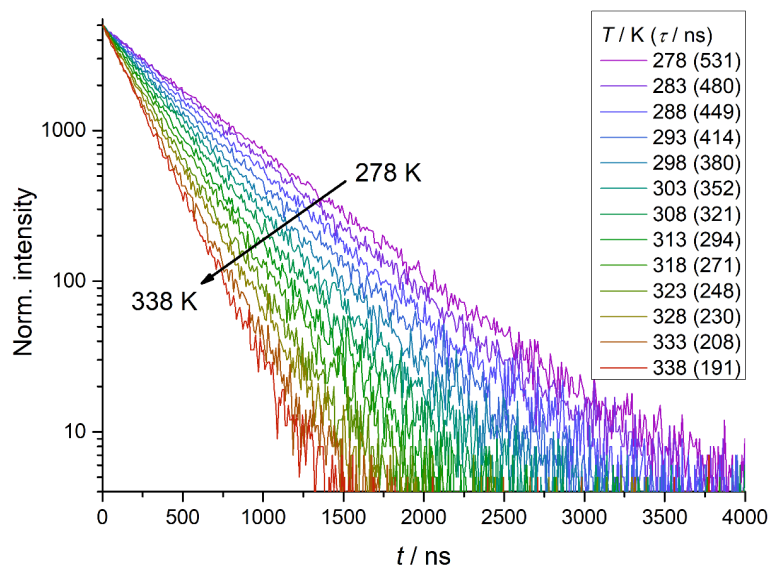


Figure S46: Normalized temperature-dependent luminescence decays of **1** in benzene with lifetimes τ ($\lambda_{\text{exc}} = 486 \text{ nm}$, $\lambda_{\text{em}} = 718 \text{ nm}$).

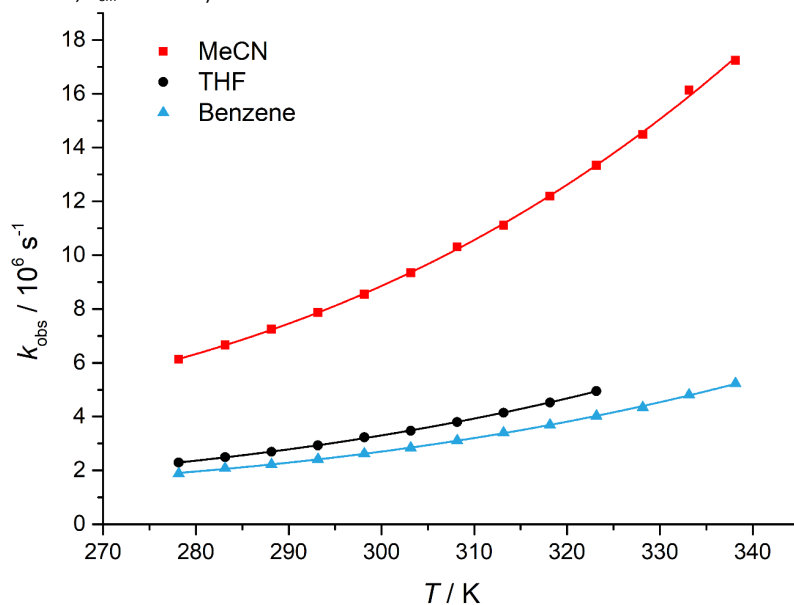


Figure S47: Observed rate constant k_{obs} of **1** in different solvents plotted against temperature with fit curves. A three parameter model was used to fit the observed rate constant $k_{\text{obs}} = 1/\tau$ with the following

equation: $k_{\text{obs}} = \frac{k_{\text{MLCT}} + k_{\text{MC}} \exp\left(-\frac{\Delta E}{k_{\text{B}}T}\right)}{1 + \exp\left(-\frac{\Delta E}{k_{\text{B}}T}\right)}$.^{48,79,80} The model assumes thermally equilibrated ³MLCT and ³MC states and further considers the excited state relaxation via the ³MLCT state (radiative and non-radiative, k_{MLCT}) and via the ³MC state (only non-radiative, k_{MC}) as well as the energy barrier for

$^3\text{MLCT} \rightarrow ^3\text{MC}$ conversion ΔE (Table S5).⁴⁸ In the fit equation, T is the temperature and k_B is the Boltzmann constant.

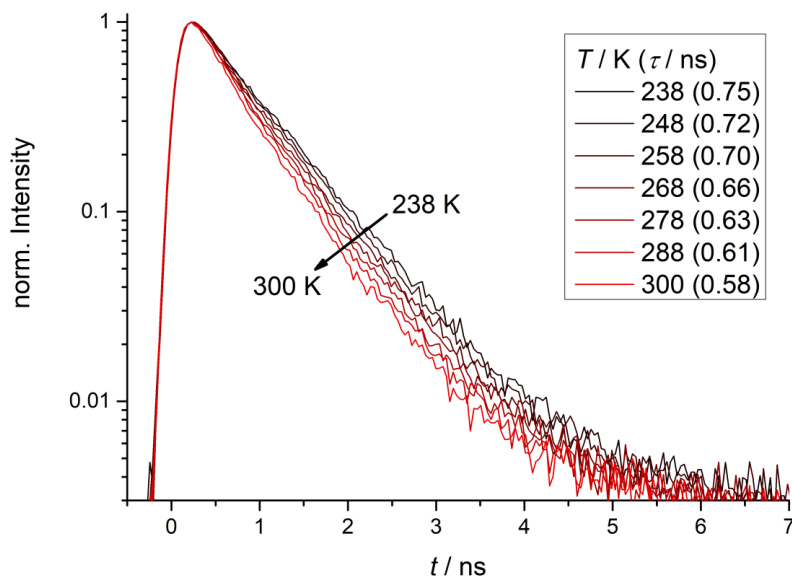


Figure S48: Temperature-dependent luminescence decays of **2** in MeCN with lifetimes τ ($\lambda_{\text{exc}} = 445 \text{ nm}$, $\lambda_{\text{em}} = 800 \text{ nm}$).

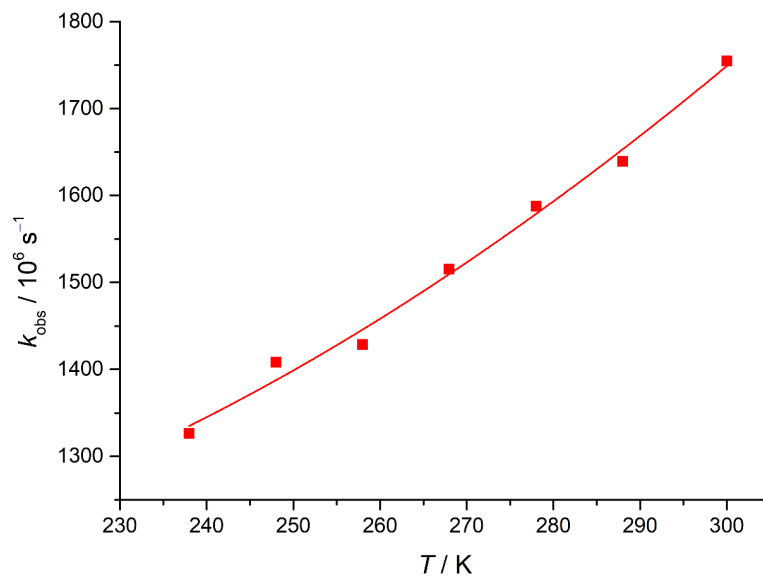


Figure S49: Observed rate constant k_{obs} of **2** in MeCN plotted against temperature with fit curve. A three parameter model was used to fit the observed rate constant $k_{\text{obs}} = 1/\tau$ with the following equation:

$$k_{\text{obs}} = \frac{k_{\text{MLCT}} + k_{\text{MC}} \exp\left(-\frac{\Delta E}{k_{\text{B}}T}\right)}{1 + \exp\left(-\frac{\Delta E}{k_{\text{B}}T}\right)},^{48,79,80}$$

The model assumes thermally equilibrated $^3\text{MLCT}$ and ^3MC states and further considers the excited state relaxation via the $^3\text{MLCT}$ state (radiative and non-radiative, k_{MLCT}) and via the ^3MC state (only non-radiative, k_{MC}) as well as the energy barrier for $^3\text{MLCT} \rightarrow ^3\text{MC}$ conversion ΔE (Table S5).⁴⁸ In the fit equation, T is the temperature and k_{B} is the Boltzmann constant.

Table S5: Fit parameters for temperature dependent emission lifetimes data for **1** (Figure S47) and **2** (Figure S49). Radiative and non-radiative rates of the $^3\text{MLCT}$ state k_{MLCT} , non-radiative relaxation rate of the ^3MC state k_{MC} and energy barrier ΔE for the $^3\text{MLCT} \rightarrow ^3\text{MC}$ conversion.¹⁴

Complex (Solvent)	$k_{\text{MLCT}} / 10^6 \text{ s}^{-1}$	$k_{\text{MC}} / 10^9 \text{ s}^{-1}$	$\Delta E / \text{cm}^{-1}$
1 (MeCN)	3.0±0.3	1.7±0.4	1660±60
1 (THF)	1.1±0.1	5.2±1.4	1620±60
1 (Benzene)	1.0±0.1	5.6±1.1	1690±50
2 (MeCN)	1100±200	32±30	800±250

6. Transient absorption spectroscopy

Calibration of transient absorption spectra using a standard

To calibrate the ns-TA spectrum of **1** in THF ($A_{532} = 0.054$, $c = 10 \mu\text{M}$), we performed measurements under identical conditions using an isoabsorptive solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ($A_{532} = 0.054$, $c = 68 \mu\text{M}$) at the excitation wavelength 532 nm in water with its known difference absorption coefficient $\Delta\epsilon(455 \text{ nm}) = -10100 \text{ M}^{-1} \text{ cm}^{-1}$.^{41–43} The extinction coefficient of **1** in THF at 532 nm ($\epsilon = 5270 \text{ M}^{-1} \text{ cm}^{-1}$) is larger than for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ($\epsilon = 800 \text{ M}^{-1} \text{ cm}^{-1}$). This means that a larger fraction of the sample of **1** compared to $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ is excited with each laser pulse. This leads to saturation effects in the TA signal for **1**, *i.e.* the measured TA signal is underestimated. One solution to the problem is using a lower laser intensity. However, this introduces large errors due to low signal to noise ratios.

Therefore, we opted to do record ns-TA decays of **1** and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ at different laser intensities to find the region where the TA signal is linearly dependent on the excitation power (16–108 mJ/pulse) for the calibration. For each excitation power we averaged 7–21 kinetic traces of the TA signal at 455 nm (Figure S50). The kinetic traces were fitted using a monoexponential decay function yielding the amplitudes A_{fit} . A_{fit} was plotted against the pulse energy I (Figure S51). In the absence of any external effects like saturation at high pulse energies and noisy signals at low pulse energies, a linear relationship is expected. The linear regimes in the plots were fitted with a linear fit with a fixed offset of 0 (as no signal is expected at $I = 0 \text{ mJ}$) yielding the fit functions $A_{\text{fit,Mo}}(I)$ for **1** and $A_{\text{fit,Ru}}(I)$ for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. The difference extinction coefficient of **1** at 455 nm $\Delta\epsilon(455 \text{ nm})$ can now be calculated using $\Delta\epsilon(\text{Mo}, 455 \text{ nm}) = \Delta\epsilon(\text{Ru}, 455 \text{ nm}) \cdot A_{\text{fit,Mo}}(I) / A_{\text{fit,Ru}}(I) = -6500 \text{ M}^{-1} \text{ cm}^{-1}$ (Figure S51).

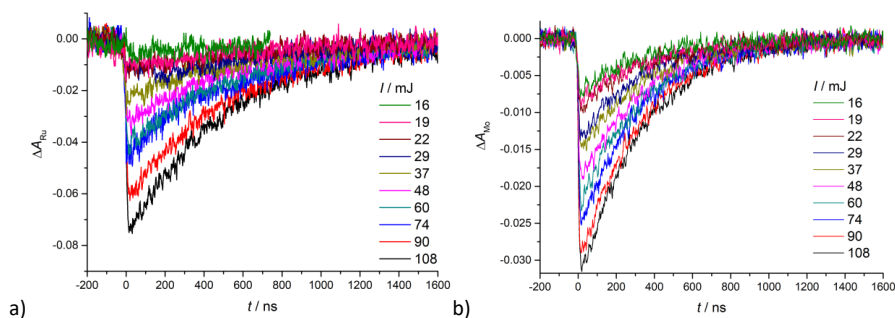


Figure S50: Averaged kinetic traces of the transient absorption signal of a) $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in water and b) **1** in THF at 455 nm with $\lambda_{\text{exc}} = 532 \text{ nm}$ at different laser pulse energies I recorded for the calibration of the TA spectrum of **1**.

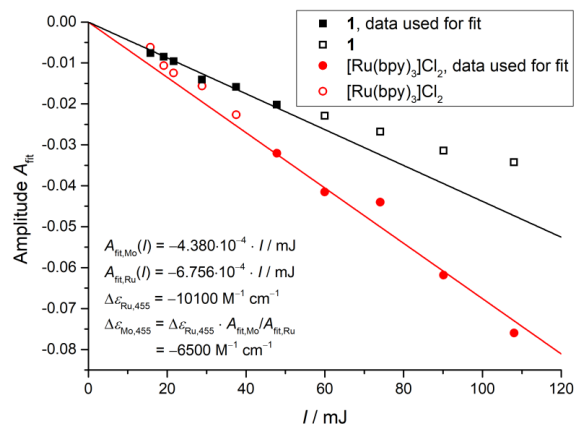


Figure S51: Plot of the amplitudes A_{fit} of the monoexponentially fitted kinetic traces of the transient absorption signal of **1** in THF (black squares) and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in water (red circles) at different laser intensities I ($\lambda_{\text{exc}} = 532 \text{ nm}$). Linear fits (solid lines) of the respective linear regimes of the data (filled squares and filled circles) with a fixed offset of 0 are shown yielding the fit functions $A_{\text{fit},\text{Mo}}(I)$ for **1** and $A_{\text{fit},\text{Ru}}(I)$ for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. For **1** the data at low powers was used for the fit as non-linearity due to the saturation of the transient absorption signal can be observed at high laser powers. For $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ the values at high laser powers were used, as noise distorts the signals at low laser powers and no saturation effects were observed at high laser powers. The fit equations can be used to calculate the difference absorption coefficient of **1** in THF $\Delta\epsilon(\text{Mo}, 455 \text{ nm})$.

Table S6: Absorption band maxima λ_{max} and extinction coefficients ϵ of **1** in the $^3\text{MLCT}$ state in THF with assignments drawn from a TDDFT calculation (B3LYP/D3BJ/TZVP/CPCM(THF), TheoDORE analysis³¹, $\text{py}^\bullet$ = pyridine centered radical anion, py_2 = unreduced part of the tpe ligand).

$\lambda_{\text{max}} / \text{nm}$	$\epsilon / 10^3 \text{ M}^{-1} \text{ cm}^{-1}$	Assignment
700	1.5	$\text{LC}(\text{py}^\bullet) + \text{LL}'\text{CT}(\text{py}^\bullet \rightarrow \text{CO})$
470	2.8	$\text{LMCT}(\text{py}^\bullet \rightarrow \text{Mo}^{\text{I}})$
386	7.3	$\text{MLCT}(\text{Mo}^{\text{I}} \rightarrow \text{py}_2)$
277	14.2	$\text{MLCT}(\text{Mo}^{\text{I}} \rightarrow \text{CO})$

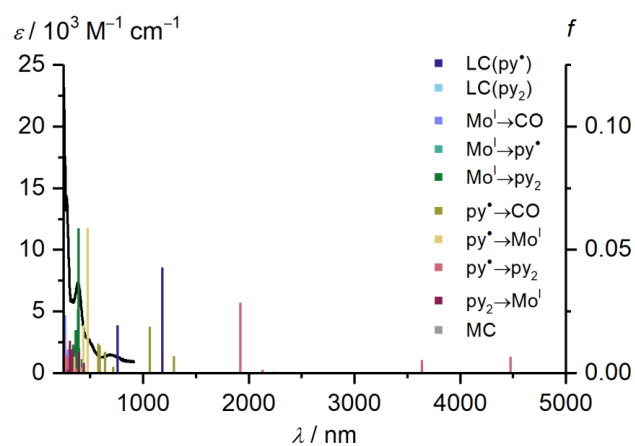


Figure S52: Absorption spectrum of the $^3\text{MLCT}$ state of **1** in THF (see main text for details). The sticks represent oscillator strengths f of the DFT-optimized $^3\text{MLCT}$ state calculated using TDDFT (B3LYP/D3BJ/ZORA/TZVP/CPCM(THF), simulated spectrum: Figure S53). The colors of the sticks indicate the dominant character of the transition derived from a charge transfer number³¹ analysis (py^* = pyridine centered radical anion, py_2 = unreduced part of the tpe ligand). The oscillator strength of the MC transition at 2192 nm is too low to be visible with this axis scaling.

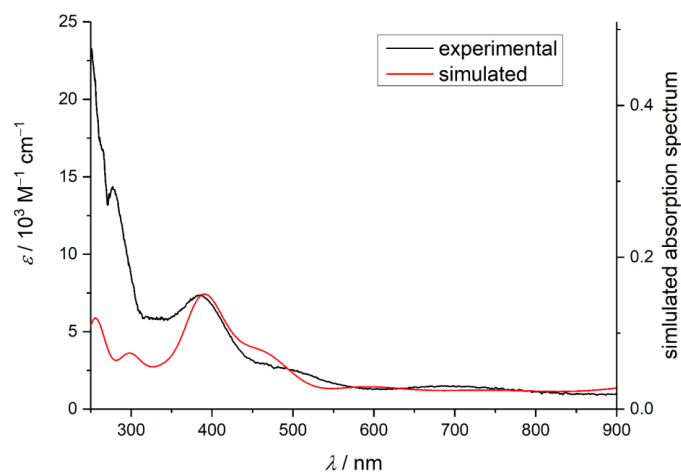


Figure S53: Experimental and simulated (TDDFT, gaussian broadening with $\text{FWHM} = 3500 \text{ cm}^{-1}$) absorption spectra of **1** in the $^3\text{MLCT}$ state in THF.

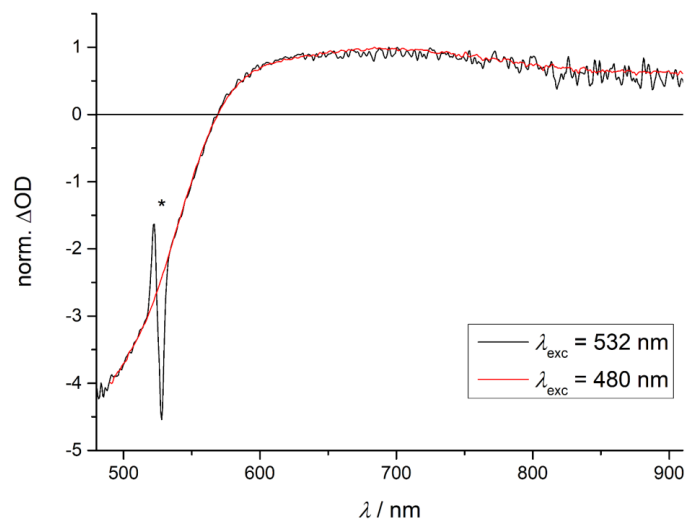


Figure S54: Normalized Vis/NIR-fs-transient absorption spectra of **1** in THF at room temperature (integration time: 7.8 ns) at different excitation wavelengths. The asterisk marks an artifact arising from scattered excitation light.

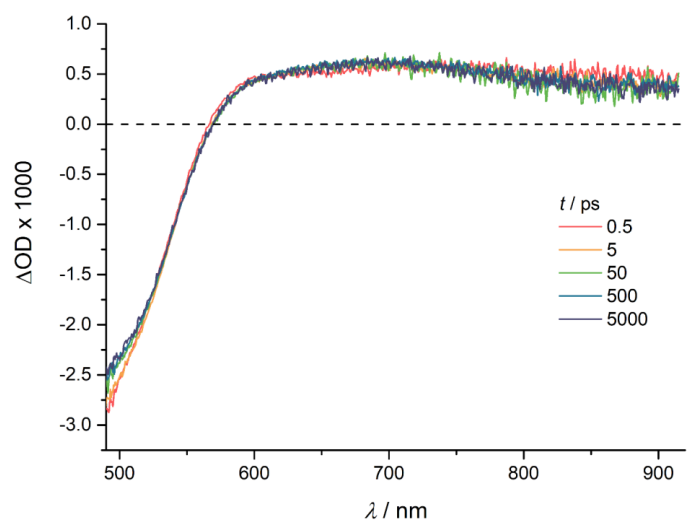


Figure S55: Vis/NIR-fs-transient absorption spectra of **1** in THF at room temperature ($\lambda_{\text{exc}} = 480$ nm) at different delay times t .

7. ns-Step-scan FTIR spectroscopy

Step-scan FTIR spectroscopy of **1** was performed in a KBr pellet at 290 K and 20 K as well as in DMSO solution at 290 K with pulsed laser excitation at 532 nm. For the comparison of experimental spectra with DFT-calculated vibrational frequencies, a scaling factor of 0.985 was applied to the calculated frequencies in order to provide the best match to the experiment.

In a KBr pellet

The difference spectra of **1** in KBr in Figure S56 show strong ground state bleaches that match the steady-state absorption energies and several excited state absorption bands. Excited state lifetimes were obtained from the step-scan data by considering the decay over time of the prominent positive and negative bands in the difference spectra. At 290 K, a global biexponential fit was applied to four bands at 1887, 1908, 1802 and 1773 cm^{-1} (Figure S58 and Table S7). At 20 K, a similar procedure was used for the four bands at 1957, 1886, 1851 and 1748 cm^{-1} , where a global triexponential fit was applied. However, as the band at 1957 cm^{-1} showed rather a biexponential decay, the amplitude A_3 of the third time constant was set to zero for this particular peak. An overview over this global triexponential fit is presented in Figure S59a and the fit curves of the bands including the fit components are plotted separately in Figures S59b–e.

In the difference spectra at 290 K and 20 K (Figure S56), there are two sharp positive bands at ca. 1887 and 1750 cm^{-1} that suggest the presence of an excited state with only slightly shifted vibrational energies. This is clearly visible in the excited state absorptions spectra that were generated by adding a fraction of the ground state spectrum to the difference spectrum (Figure S57). The excited state lifetimes at 290 K show a short-lived component of ca. 1.4 μs and a dominant, long-lived component of 200 μs , which is surprisingly long considering the luminescence lifetimes in the solid state are in the ns-region. It is also unlikely that **1** in an electronically excited state with a shifted electron density features the same vibrational spectrum as the ground state. Taken together, the data suggests that coupling gives rise the observed shifts of the IR absorptions by a few wavenumbers. This could be due to coupling of low energy excitations after local dissipation of the excitation excess energy (e.g. thermally induced shifts of the vibrational bands) or intermolecular coupling of excited **1** with non-excited **1**, assuming that **1** is partially aggregated in KBr. A similar spectral pattern can be found in previously reported step-scan IR spectra of group 6 carbonyl complexes.^{44,45} Further fs-time-resolved IR spectroscopy in a KBr pellet support the assignment of the bands to occur from coupling (see SI Section 8).

Less intense excited state absorptions of **1** in a KBr pellet at ca. 1960 and 1851 cm^{-1} are assigned to the ³MLCT state with the help of DFT calculations (Figure S57). The shorter lifetime component of 11 μs is qualitatively in line with the luminescence lifetime of 29 μs found for **1** in a KBr pellet at 5 K. However, the contributions from coupling prevent a quantitative agreement.

In DMSO solution

In contrast to step-scan spectra of **1** obtained in the KBr pellet, the step-scan spectra of **1** in d_6 -DMSO solution show only the expected ground state bleaches at 1898 and 1774 cm^{-1} as well as excited state absorptions at 1975, 1869 and 1830 cm^{-1} that match the DFT-calculated values (Figure S60 and S62). Excited state lifetimes were obtained from the step-scan data by considering the decay over time of the prominent positive and negative bands in the difference spectra. The step-scan decay curves obtained in deaerated DMSO are very well described by a global monoexponential fit with a lifetime of 150 ns (Figure S61). This value agrees with the luminescence lifetime of 184 ns found for **1** in DMSO at 293 K (Table 3).

The step-scan data and results from DFT calculations are summarized in Table S8.

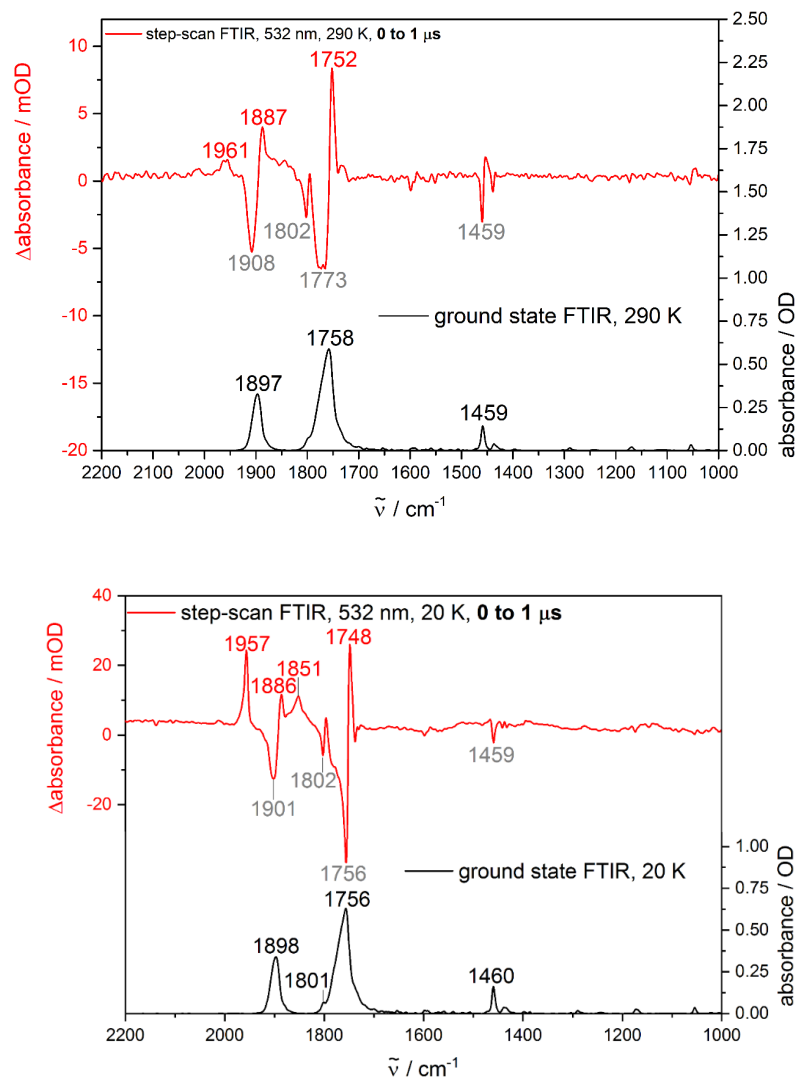


Figure S56: Step-scan FTIR spectrum ($\lambda_{\text{ex}} = 532 \text{ nm}$, 1 μs integration) and ground state FTIR spectrum of **1** in a KBr pellet at 290 K (top) and at 20 K (bottom).

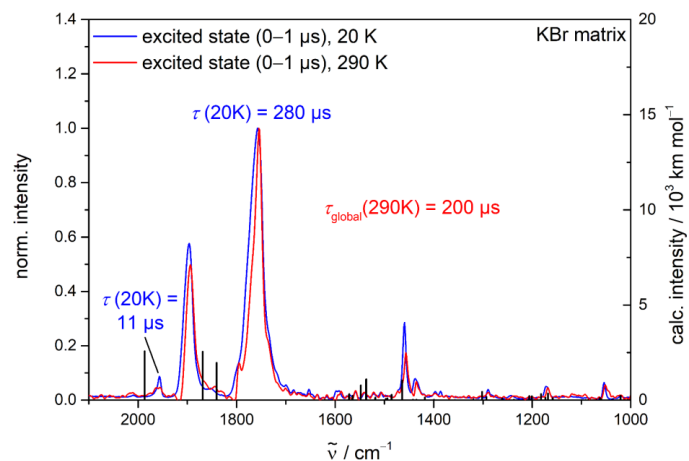


Figure S57: Excited state IR absorption spectra generated from step-scan FTIR ($\lambda_{\text{ex}} = 532$ nm, 1 μs integration) and ground state FTIR spectra of **1** in a KBr pellet at 20 and 290 K with time constants of the main components of the multiexponential fits for the respective bands. A contribution of 50% and 5% of the ground state spectrum was added to the step-scan difference spectrum at 290 and 20 K, respectively. The sticks represent DFT-calculated IR absorptions of **1** in the relaxed $^3\text{MLCT}$ state (energy scaled by 0.985).

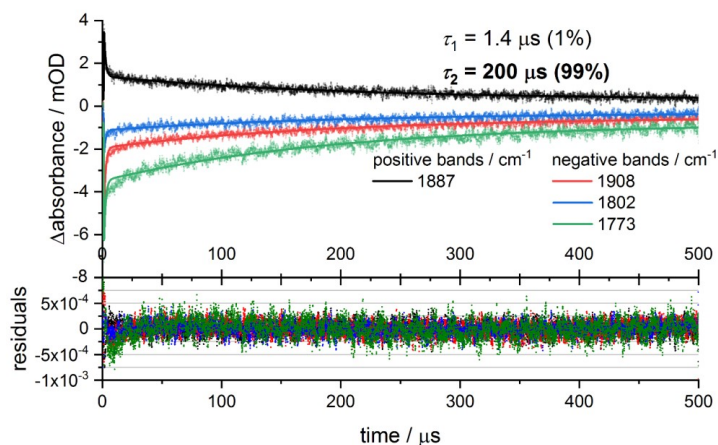


Figure S58: Global biexponential fit and residuals of the ns-step-scan data of **1** (KBr pellet, $\lambda_{\text{ex}} = 532$ nm) at 290 K.

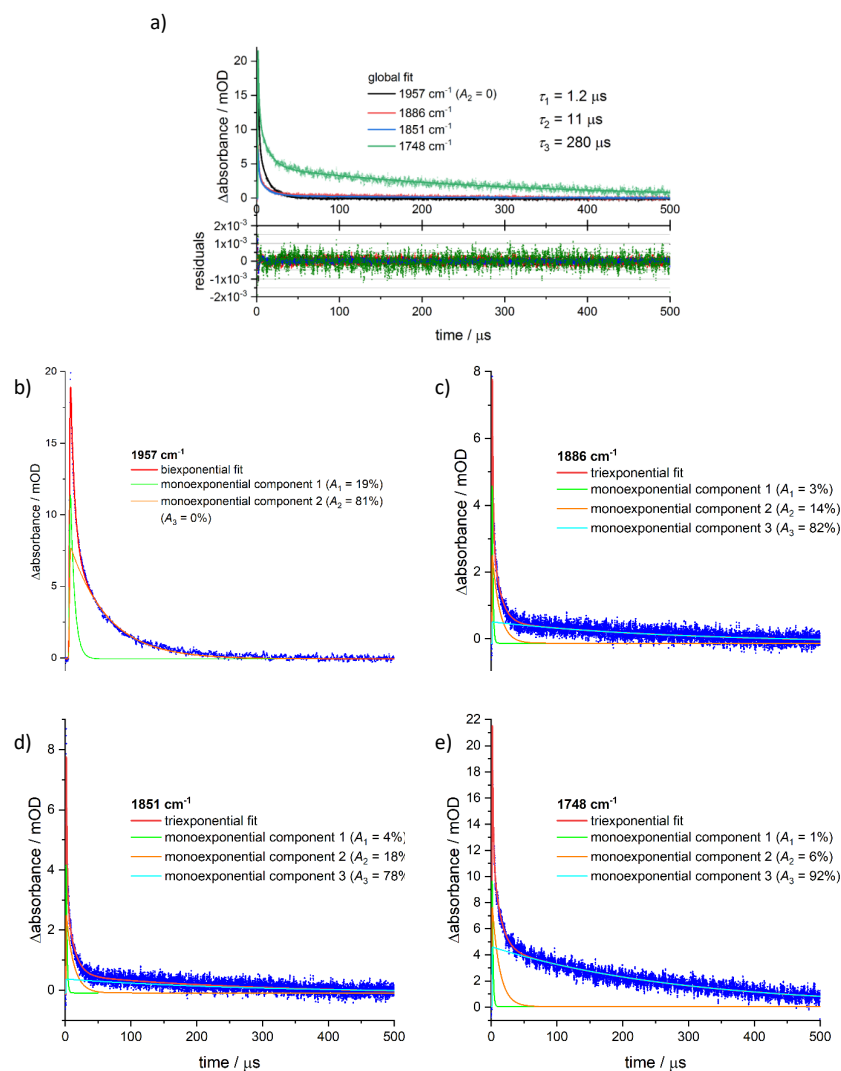


Figure S59: a) Global triexponential fit and residuals of step-scan FTIR data of **1** (KBr pellet, $\lambda_{\text{ex}} = 532 \text{ nm}$) at 20 K. b–e) Plots of the underlying bi- (1957 cm^{-1}) or triexponential (1886, 1851 and 1748 cm^{-1}) fit curves of the four bands, including their monoexponential components.

Table S7: Excited state lifetimes of **1** in KBr obtained by step-scan FTIR spectroscopy ($\lambda_{\text{exc}} = 532 \text{ nm}$) with time constants τ_1 , τ_2 and τ_3 for the multi-exponential fits. The relative contributions for the excited state absorption bands at 20 K are given in Figures S53b–e.

T / K	$\tau_1 / \mu\text{s}$ (contribution)	$\tau_2 / \mu\text{s}$ (contribution)	$\tau_3 / \mu\text{s}$ (contribution)
290	1.4 (1%)	200 (99%)	–
20	1.2 (1–19%)	11 (6–81%)	280 (0–92%)

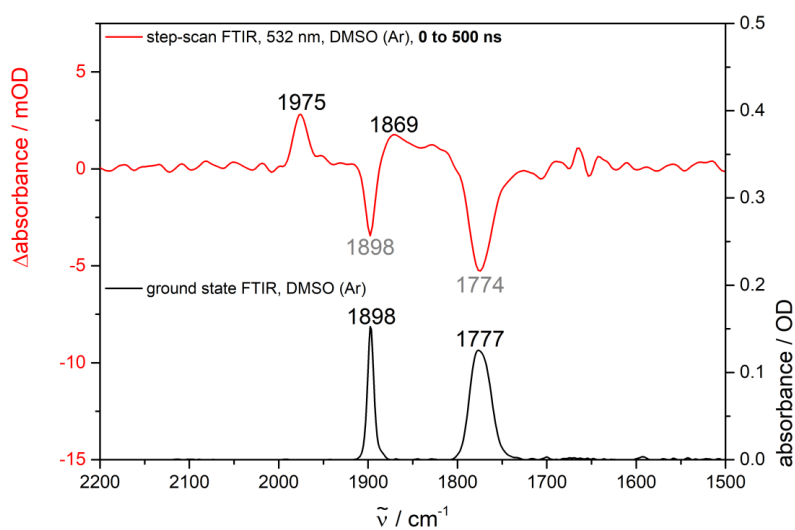


Figure S60: Step-scan FTIR spectrum ($\lambda_{\text{exc}} = 532 \text{ nm}$, 500 ns integration) and ground state FTIR spectrum of **1** in deaerated d_6 -DMSO at 290 K.

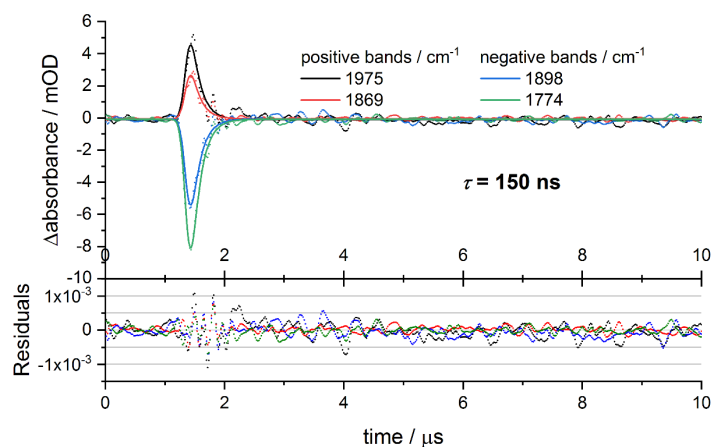


Figure S61: Global monoexponential fit and residuals of the ns-step-scan data of **1** (d_6 -DMSO, $\lambda_{\text{ex}} = 532$ nm) at 290 K.

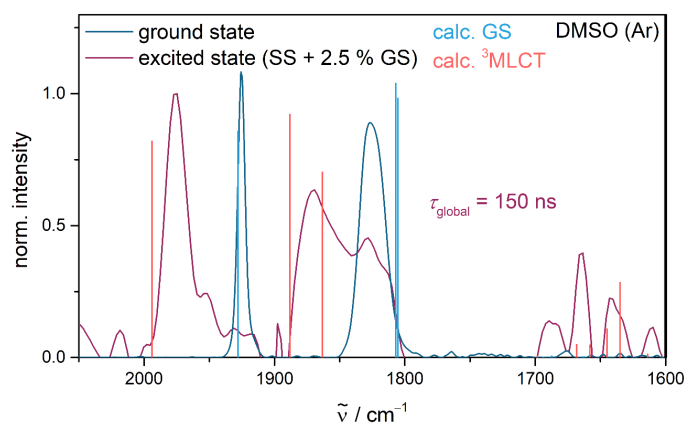


Figure S62: Excited state IR absorption spectrum generated from step-scan FTIR ($\lambda_{\text{ex}} = 532$ nm, 500 ns integration) and ground state FTIR spectra of **1** in d_6 -DMSO at 290 K with the time constant of a global monoexponential fit and DFT calculated IR intensities of the ^1GS and $^3\text{MLCT}$ states (pale blue and pale red sticks, energies scaled by 0.985).

Table S8: Energies of the CO stretching vibrations of **1** in different environments with DFT calculated values.

State	Medium	<i>T</i> / K	ν_1, ν_2 / cm ⁻¹	ν_3 / cm ⁻¹
¹ GS	KBr	290	1758	1897
	KBr	20	1756	1898
	KBr (calcd.) ^a		1769, 1771	1896
	<i>d</i> ₆ -DMSO	290	1775	1897
	DMSO (calcd.) ^b		1751, 1753	1901
³ MLCT	<i>d</i> ₆ -DMSO	290	1829, 1870	1975
	DMSO (calcd.) ^b		1850, 1881	1987

^a The DFT-calculated vibrational frequencies were scaled by a factor of 0.975. ^b The DFT-calculated vibrational frequencies were scaled by a factor of 0.985.

8. Fs-VIS-pump-IR-probe spectroscopy

Fs-VIS-pump-IR-probe spectra, which probe the photophysical response analogously to ns-step-scan FTIR spectroscopy, yet, with higher time-resolution, support the interpretation of the ns-step-scan FTIR data in Section 7. The transient spectral signatures of the C-O vibrations of **1** in DMSO (Figure S63) are consistent with those shown in Figure S60. The fs-VIS-pump-IR-probe spectra demonstrate that these transient signals evolve nearly instantaneously after excitation (*e.g.* at $t_w = 1$ ps) and are hardly altered within 350 ps after photoexcitation, consistent the transient signals arising from the long-lived excited state with little effects of vibrational cooling on this timescale.

Fs-VIS-pump-IR-probe spectroscopy on **1** in a rotating KBr pellet yielded difference spectra (Figure S64) that are similar to the step-scan FTIR results (Figure S56). However, in the fs-VIS-pump-IR-probe experiment the excited state absorptions assigned to the $^3\text{MLCT}$ state (1955, 1853, 1835 cm^{-1}) are much stronger, relative to the sharp positive bands close to the ground state bleaches, as compared to the step-scan FTIR results. This further underpins the assignment of the latter bands originating from coupling, as these intensities depend both on the sample preparation and the time-resolution of the transient spectroscopy. The signals in Figure S64 decay biexponentially ($\tau_1 = 14$ ps, $\tau_2 = 385$ ps, Figure S65). However, it is difficult to assign these time constants to specific relaxation processes.

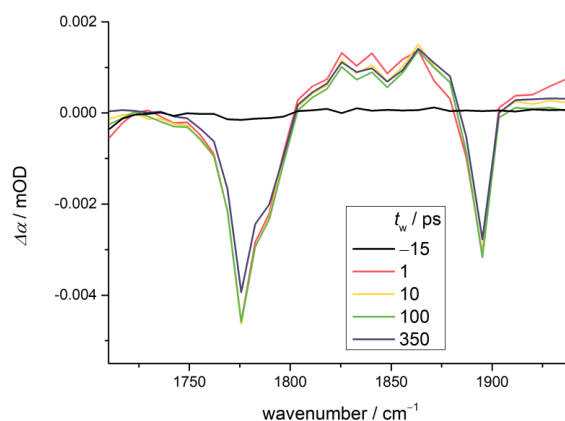


Figure S63: Fs-VIS-pump-IR-probe spectra of **1** (DMSO, room temperature, $\lambda_{\text{exc}} = 400$ nm) at different time delays t_w .

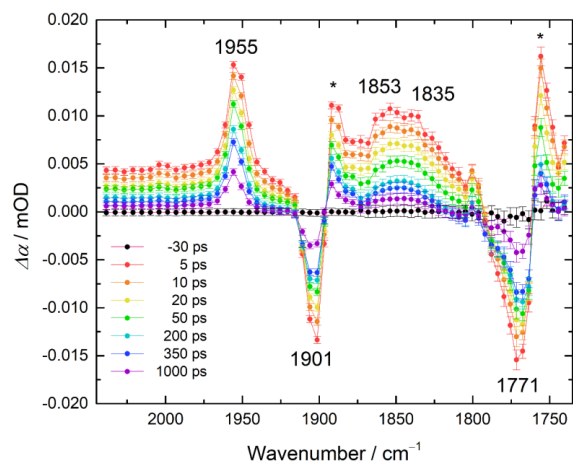


Figure S64: Fs-VIS-pump-IR-probe spectra of **1** (KBr pellet, room temperature, $\lambda_{\text{exc}} = 400$ nm). Spectral contributions ascribed to coupling are marked with an asterisk.

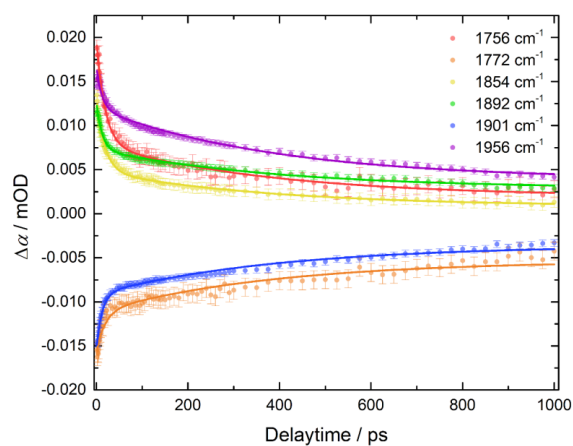


Figure S65: Decay traces obtained from fs-VIS-pump-IR-probe spectra of **1** (KBr pellet, room temperature, $\lambda_{\text{exc}} = 400$ nm) with a global exponential fit ($\tau_1 = 14$ ps, $\tau_2 = 385$ ps, solid traces).

9. Stability in the dark and under irradiation

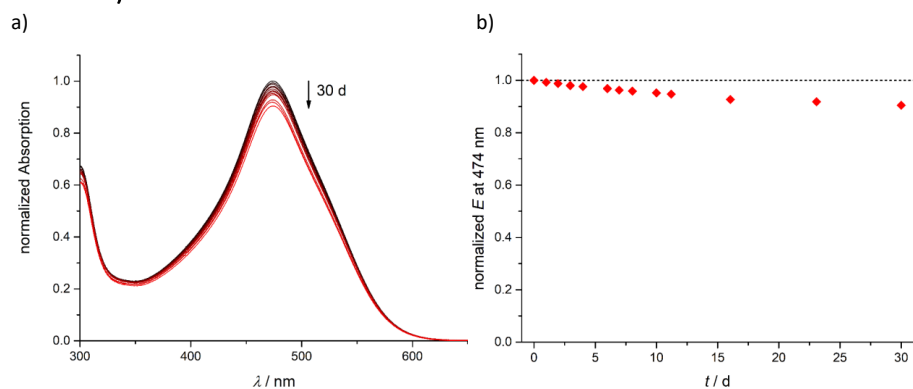


Figure S66: a) Normalized UV/Vis absorption spectra of **1** in deaerated stabilized THF after storing the solution in the dark at room temperature for 30 d in total. b) Normalized extinction of **1** in THF under Argon at 474 nm after storing the solution in the dark for time periods t .

Table S9: Details of the photodecomposition quantum yield Φ_{degr} experiments with green laser irradiation ($\lambda_{\text{exc}} = 514 \text{ nm}$, $P = 827 \text{ mW}$).

	Time Δt / s $t(I/I_0 = 0.8) - t(I/I_0 = 0.9)$	Absorbed Photons N_{abs} in Δt / mmol	Initial concentration / μM	Decomposed molecules / mmol	$\Phi_{\text{degr}} / \%$
$[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ (MeCN)	150	149	129	0.0321	0.022
1 (MeCN)	5990 ^a	6364	86	0.0093	0.00015
2 (MeCN)	720	692	150	0.0375	0.0054
1 (THF)	209	204	23	0.0057	0.0028
2 (THF)	221	219	51	0.0128	0.0059

^a Time $\Delta t = t(I/I_0 = 0.913) - t(I/I_0 = 0.957)$ was used because the luminescence intensity did not decay to $0.8 I_0$ during the duration of the experiment.

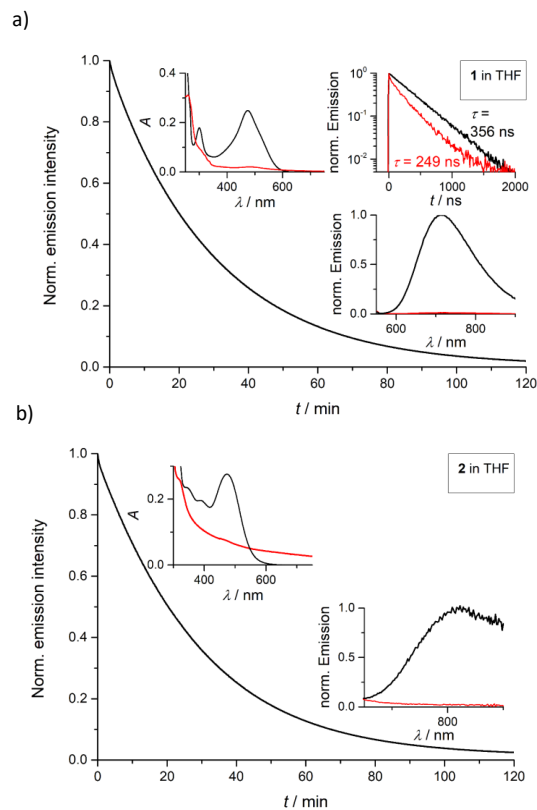


Figure S67: Photostability experiments in deaerated THF of a) **1** and b) **2** with $\text{OD}_{514} = 0.165$ under continuous-wave irradiation with a green laser (514 nm, 0.827 W). Main plots: Normalized decay of the luminescence intensity at a) 720 nm and b) 750 nm vs. irradiation time. Left insets: UV-Vis absorption spectra before (black) and after irradiation (red). Top right insets: Emission decay trace with lifetimes τ before (black) and after irradiation (red). Bottom right inset: Emission spectra before (black) and after irradiation (red).

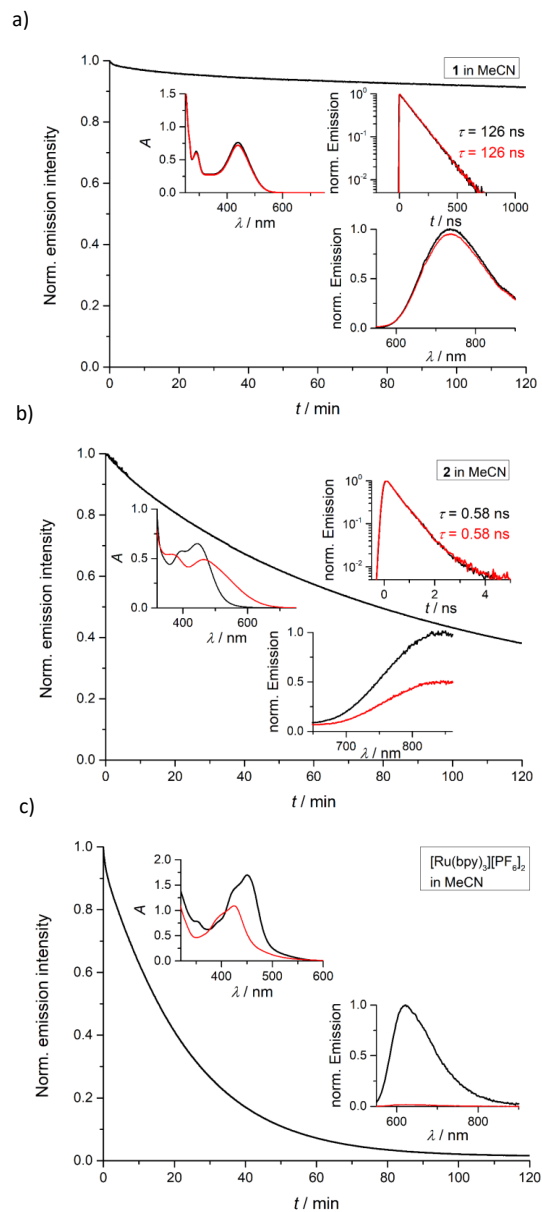
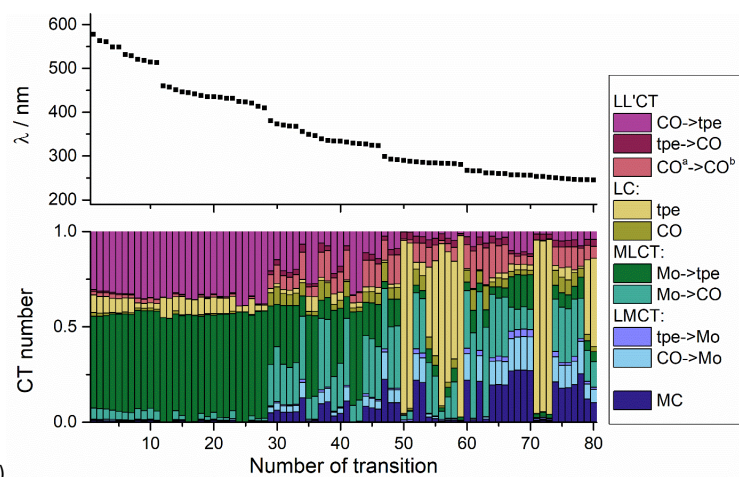


Figure S68: Photostability experiments in deaerated MeCN of a) **1**, b) **2** and c) $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ with $\text{OD}_{514} = 0.165$ under continuous-wave irradiation with a green laser (514 nm, 0.827 W). Main plots: Normalized decay of the luminescence intensity at a) 730 nm, b) 750 nm and c) 620 nm vs. irradiation time. Left insets: UV-Vis absorption spectra before (black) and after irradiation (red). Top right insets: Emission decay trace with lifetimes τ before (black) and after irradiation (red). Bottom right inset: Emission spectra before (black) and after irradiation (red).

10. Quantum chemical calculations

a)



b)

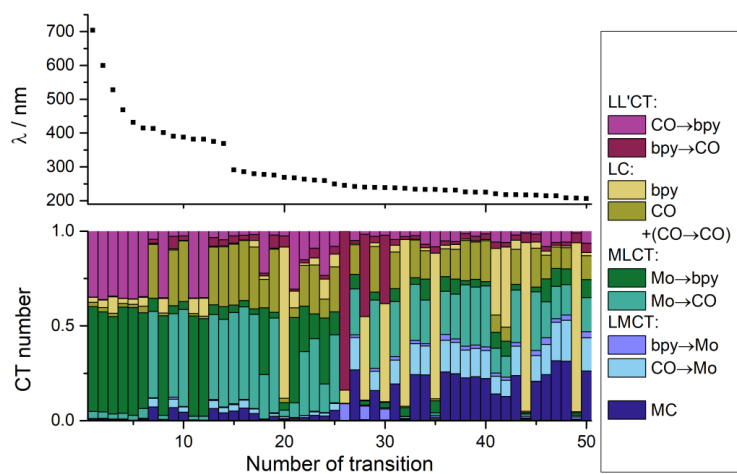


Figure S69: Wavelengths of the TD-DFT calculated electronic transitions (B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN)) and charge transfer number analysis showing the contributions to the electronic transitions, calculated using TheoDOR of a) **1** and b) **2**.³¹

Figure S70: Difference electron densities of TD-DFT calculated electronic transitions of **1** in the ^1GS (B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN), orange: positive, purple: negative; isosurface value = 0.005 a.u.) with transition wavelength in nm and oscillator strengths (in brackets).

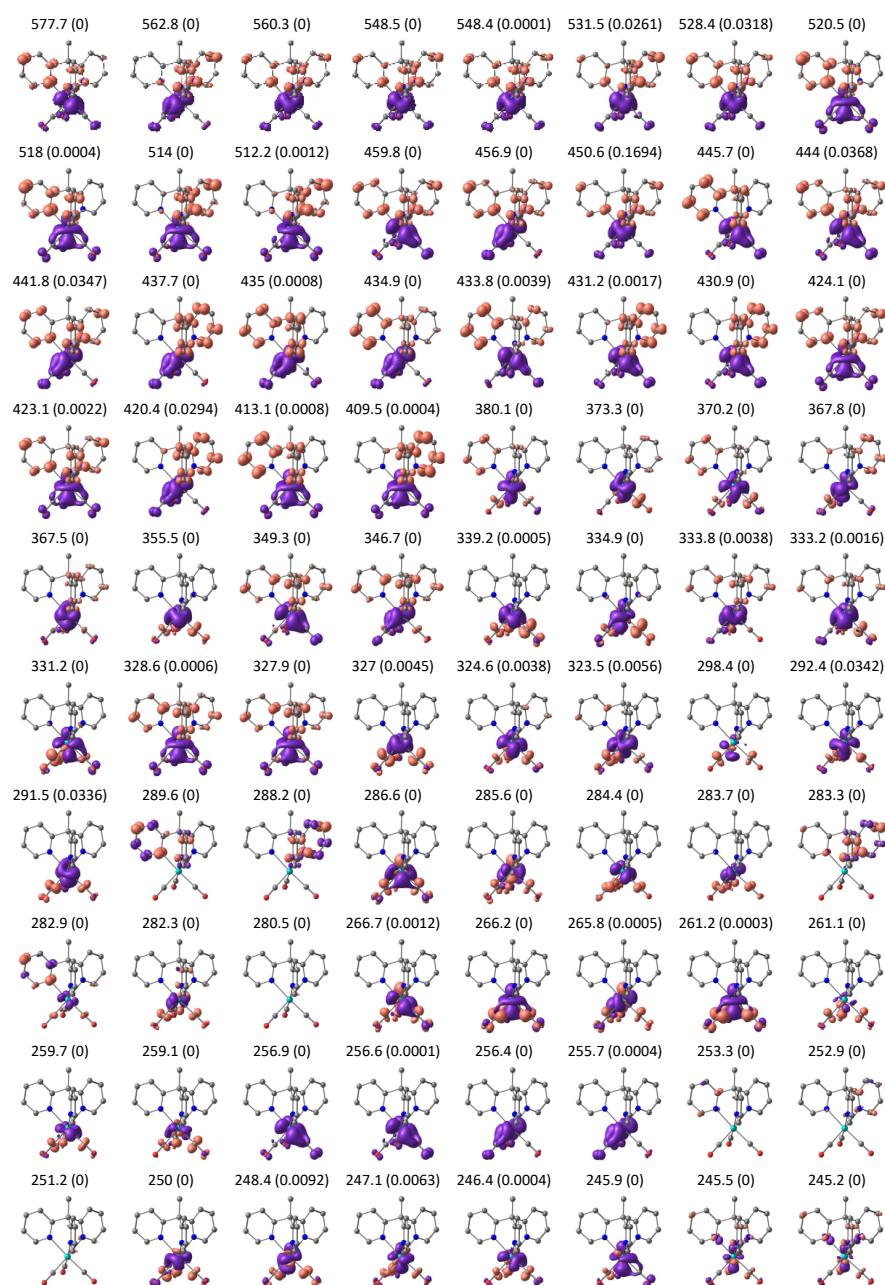
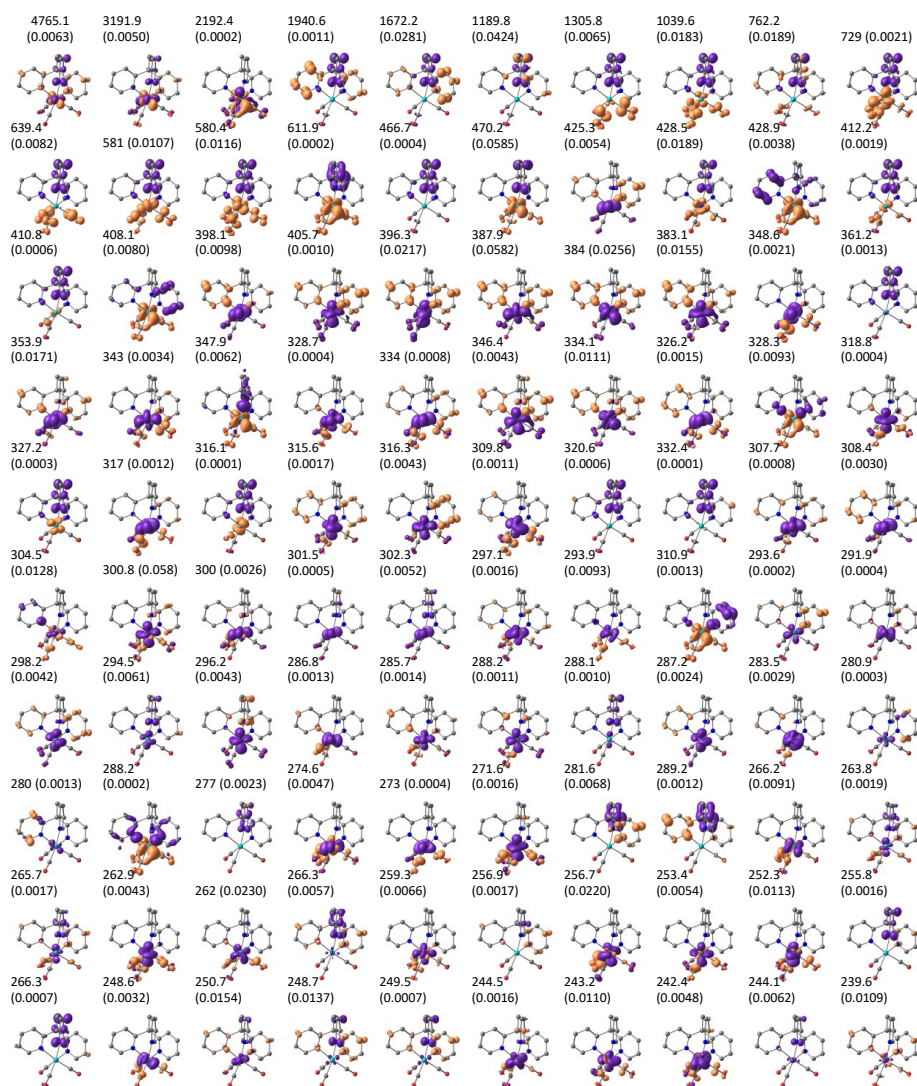


Figure S71: Difference electron densities of TD-DFT calculated electronic transitions of **1** in the $^3\text{MLCT}$ state (B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN), orange: positive, purple: negative; isosurface value = 0.005 a.u.) with transition wavelength in nm and oscillator strengths (in brackets).



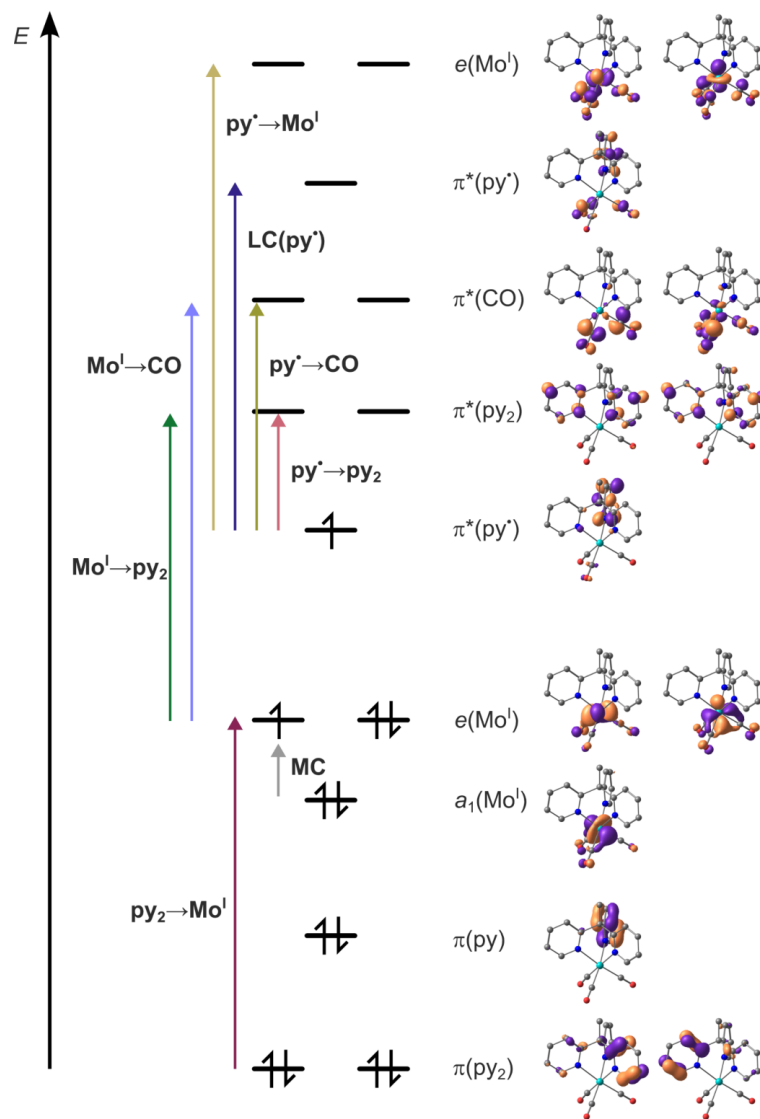


Figure S72: Schematic molecular orbital diagram of **1** in the ³MLCT state with exemplary orbital pictures obtained from DFT calculations (B3LYP/D3BJ/ZORA/TZVP/CPCM(MeCN), isosurface value = 0.07 a.u.) and electronic transitions.

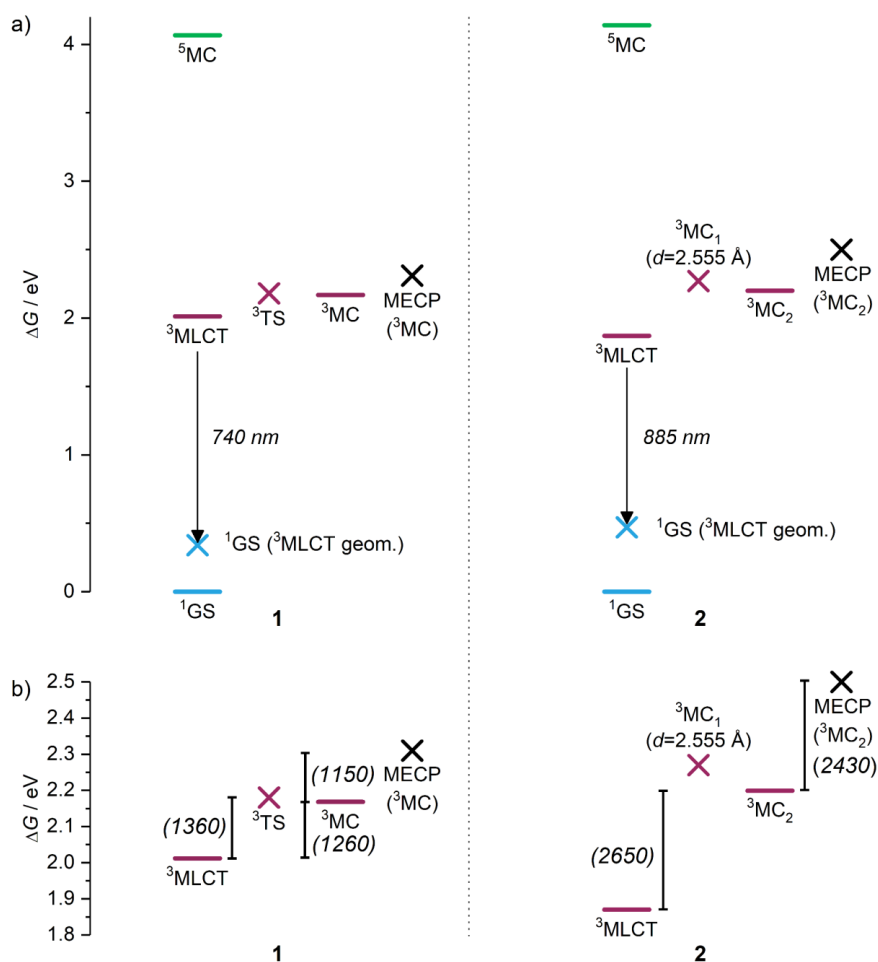


Figure S73: a) DFT-calculated energies (B3LYP/D3BJ/TZVP/CPCM(MeCN)) of different electronic states of **1** and **2** (in their respective relaxed geometries, if not stated otherwise) relative to the respective ^1GS . The $^3\text{MC}_1$ geometry was obtained in a geometry optimization where one $\text{Mo}-\text{CO}^{\text{transCO}}$ bond length was constrained to 2.555 Å and does not correspond to an optimized minimum. b) Zoom to the triplet states with energy differences in cm^{-1} (in brackets). $^3\text{TS} = ^3\text{MLCT}-^3\text{MC}$ transition state, MECP = minimum energy crossing point with ^1GS potential energy surface.

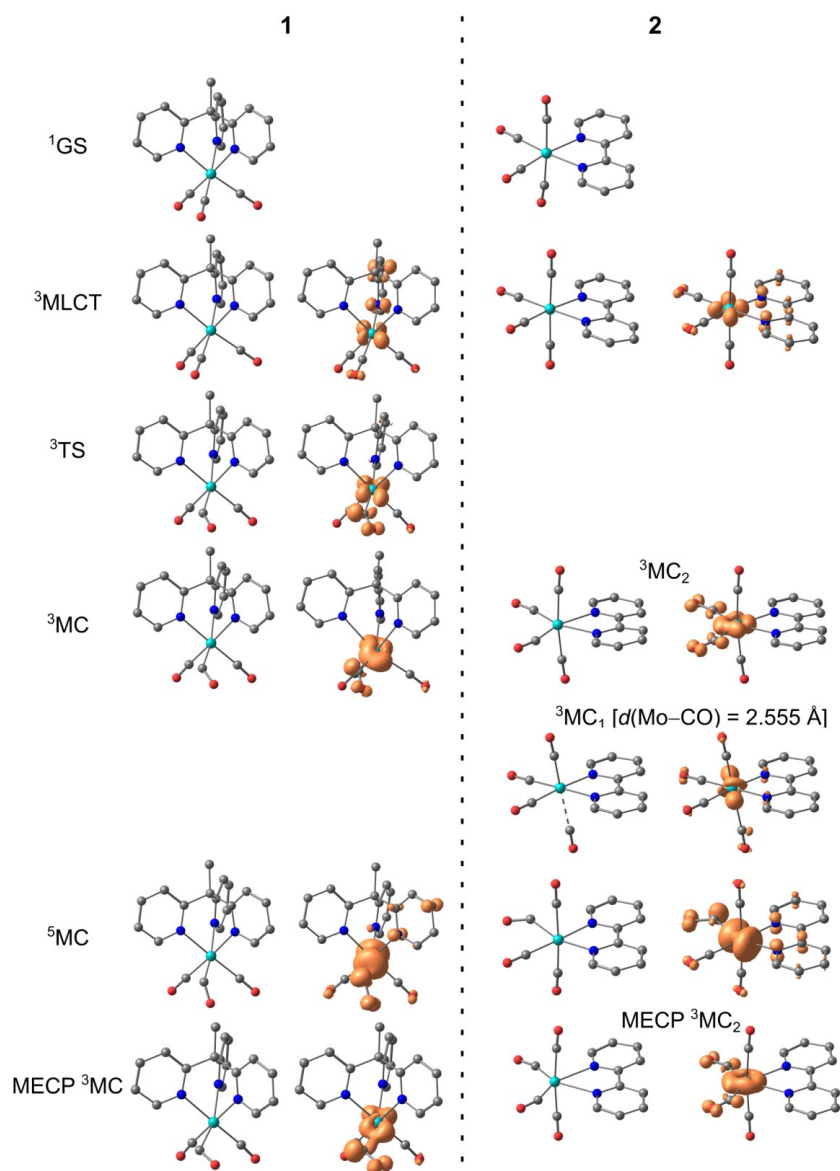


Figure S74: DFT-optimized geometries and spin-densities (isosurface value = 0.02 a.u.) for ground and excited states of **1** and **2**. MECP = minimum energy crossing point with ^1GS . TS = transition state between $^3\text{MLCT}$ and ^3MC . The $^3\text{MC}_1$ geometry of **2** does not correspond to an optimized minimum but was obtained from a relaxed surface scan where one $\text{Mo-CO}^{\text{transCO}}$ bond length (dashed bond) was constrained to 2.555 Å.

Table S10: DFT-calculated energies of ground and excited states of **1** and **2** (CPCM(MeCN)) relative to their respective ground state energies (ΔG) in eV, Mo–CO bond lengths and Mo–C–O bond angles (bold values for significantly elongated or bent bonds). In **2** CO¹ and CO² are *trans* to the bpy ligand. The ³MC₁ geometry was obtained in an geometry optimization where $d(\text{Mo}–\text{CO}^4)$ was constrained to 2.555 Å and does not correspond to an optimized minimum. MECP = minimum energy crossing point, TS = transition state.

1									
Electronic state (Geometry)	$\Delta G/\text{eV}$	$\Delta d/\text{\AA}$				angle / deg			
		CO ¹	CO ²	CO ³	CO ⁴	CO ¹	CO ²	CO ³	CO ⁴
¹ GS	0	1.958	1.957	1.954		180	178	179	
¹ GS (³ MLCT)	0.34								
³ MLCT	2.01	2.041	1.993	2.004		176	176	179	
³ MC	2.17	2.143	1.959	1.980		135	177	176	
TS ³ MLCT– ³ MC	2.18	2.131	1.973	1.982		146	177	176	
MECP ¹ GS– ³ MC	2.31	2.165	1.959	1.992		122	176	174	
⁵ MC	4.06	2.274	2.045	2.031		129	179	178	
2									
¹ GS	0	1.974	1.973	2.046	2.050	179	178	177	175
¹ GS (³ MLCT)	0.47								
³ MLCT	1.87	2.069	2.061	2.056	2.061	179	178	178	180
³ MC ₁	2.27	2.018	2.041	1.979	(2.555)	178	178	178	176
³ MC ₂	2.20	2.021	2.021	2.041	2.044	166	165	178	177
MECP ¹ GS– ³ MC ₂	2.50	2.027	2.027	2.042	2.034	160	157	176	177
⁵ MC	4.14	2.345	2.055	2.102	2.100	128	179	179	178

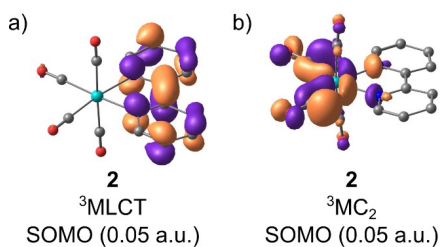


Figure S75: Highest singly occupied molecular orbital (SOMO) of **2** in the optimized a) ³MLCT and b) ³MC₂ state.

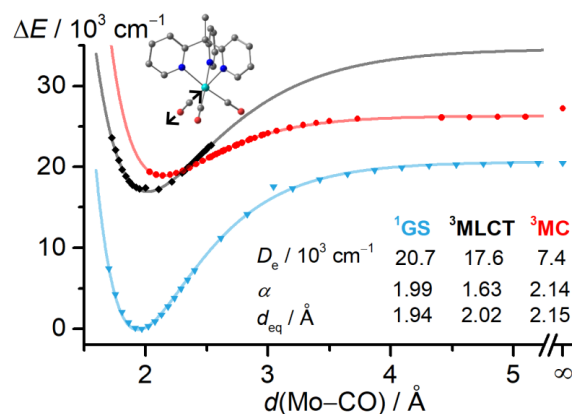


Figure S76: DFT-calculated potential energy curves of the ¹GS (blue triangles), ³MLCT (black diamonds) and ³MC states (red circles) in **1** along one Mo–CO bond with energies ΔE relative to the fully relaxed ¹GS and Morse potential fits⁴⁶ (solid lines, equation: $\Delta E = \Delta E_0 + D_e \left(1 - \exp\left(-\alpha(d - d_{eq})\right)\right)^2$, ΔE_0 = energy offset, D_e = dissociation energy, α = stiffness of the potential, d_{eq} = equilibrium bond length). The point at infinite distance corresponds to the sum of the energies of separately optimized Mo(CO)₃(bpy) and CO.

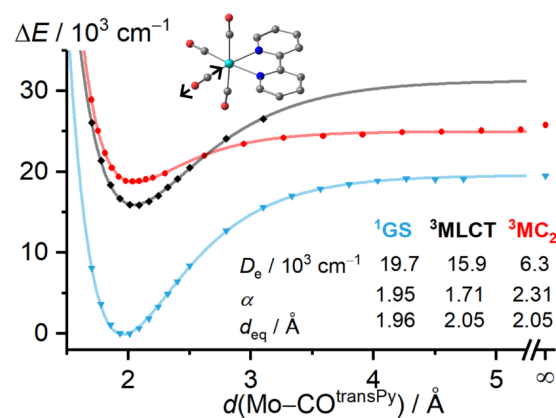


Figure S77: DFT-calculated potential energy curves of the ¹GS (blue triangles), ³MLCT (black diamonds) and ³MC₁ states (red circles) in **2** along one Mo–CO bond trans to a pyridyl moiety with energies ΔE relative to the fully relaxed ¹GS and Morse potential fits⁴⁶ (solid lines, equation: $\Delta E = \Delta E_0 + D_e \left(1 - \exp\left(-\alpha(d - d_{eq})\right)\right)^2$, ΔE_0 = energy offset, D_e = dissociation energy, α = stiffness of the potential, d_{eq} = equilibrium bond length). The point at infinite distance corresponds to the sum of the energies of separately optimized Mo(CO)₃(bpy) and CO.

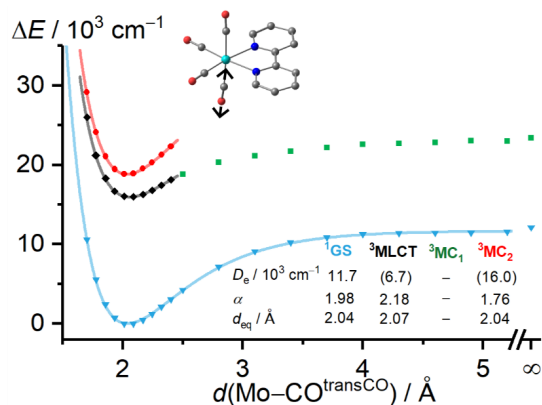


Figure S78: DFT-calculated potential energy curves of the ¹GS (blue triangles), ³MLCT (black diamonds), ³MC₁ (green squares) and ³MC₂ states (red circles) in **2** along one Mo–CO bond *trans* to another CO ligand with energies ΔE relative to the fully relaxed ¹GS and Morse potential fits⁴⁶ (solid lines, equation: $\Delta E = \Delta E_0 + D_e \left(1 - \exp\left(-\alpha(d - d_{eq})\right)\right)^2$, ΔE_0 = energy offset, D_e = dissociation energy, α = stiffness of the potential, d_{eq} = equilibrium bond length). Fit parameters in brackets are not meaningful because of the lack of data points in the region of long Mo–CO bonds. The point at infinite distance corresponds to the sum of the energies of separately optimized Mo(CO)₃(bpy) and CO.

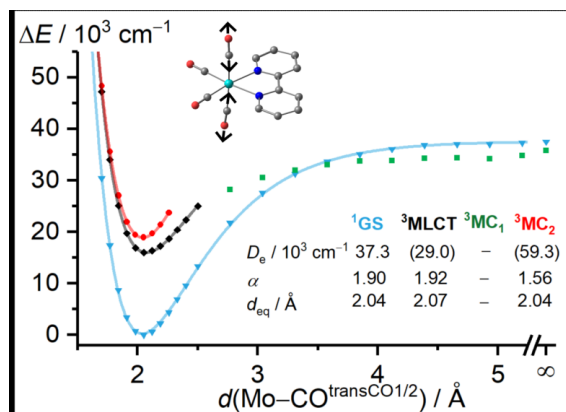


Figure S79: DFT-calculated potential energy curves of the ¹GS (blue triangles), ³MLCT (black diamonds), ³MC₁ (green squares) and ³MC₂ states (red circles) in **2** along the two Mo–CO bond *trans* to each other with energies ΔE relative to the fully relaxed ¹GS and Morse potential fits⁴⁶ (solid lines, equation: $\Delta E = \Delta E_0 + D_e \left(1 - \exp\left(-\alpha(d - d_{eq})\right)\right)^2$, ΔE_0 = energy offset, D_e = dissociation energy, α = stiffness of the potential, d_{eq} = equilibrium bond length). Fit parameters in brackets are not meaningful because of the lack of data points in the region of long Mo–CO bonds. The point at infinite distance corresponds to the sum of the energies of separately optimized Mo(CO)₂(bpy) and 2x CO. Note the different y-axis scaling compared to Figures S76–S78.

Table S11: Energy barriers in 10^3 cm^{-1} for the dissociation of CO *trans* to a pyridyl moiety or a CO ligand in the ^1GS and on the triplet potential energy surface ($^3\text{MLCT}/^3\text{MC}$). The energy barriers were calculated as $E(\infty) - E(\text{min})$ where $E(\infty)$ is the sum of the energies of the dissociated molecules (for example $\text{Mo}(\text{CO})_2(\text{tpe})$ and CO for **1**, see Figures S76–S79) and $E(\text{min})$ is the energy of the complexes at the minimum of the lowest-energy potential energy well in a given multiplicity obtained by DFT (CPCM(MeCN)). For the triplet manifold $E(\text{min})$ corresponds to the energy of the respective optimized $^3\text{MLCT}$ states.

Electronic state	1 <i>trans</i> -Py	2 <i>trans</i> -Py	2 <i>trans</i> -CO	2 <i>trans</i> -CO ¹ and <i>trans</i> -CO ²
^1GS	20.7	19.5	12.1	37.5
$^3\text{MLCT}/^3\text{MC}$	10.3	9.9	7.4	19.8

11. Photon upconversion with DPA

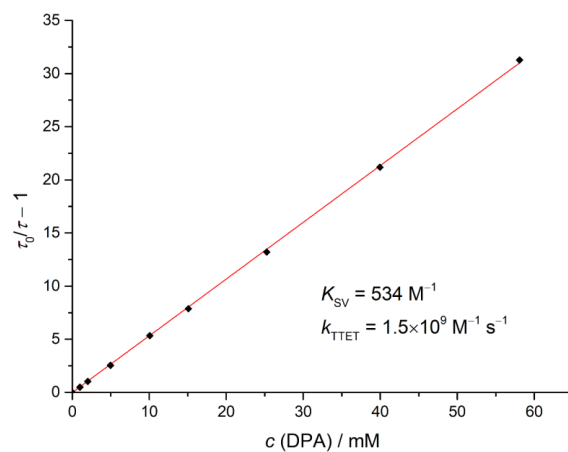


Figure S80: Stern-Volmer plot of the luminescence lifetime quenching of photoexcited **1** with DPA in THF ($\lambda_{\text{exc}} = 525 \text{ nm}$, $\lambda_{\text{em}} = 720 \text{ nm}$) with Stern-Volmer constant K_{SV} and triplet-triplet energy transfer rate constant k_{TTET} .

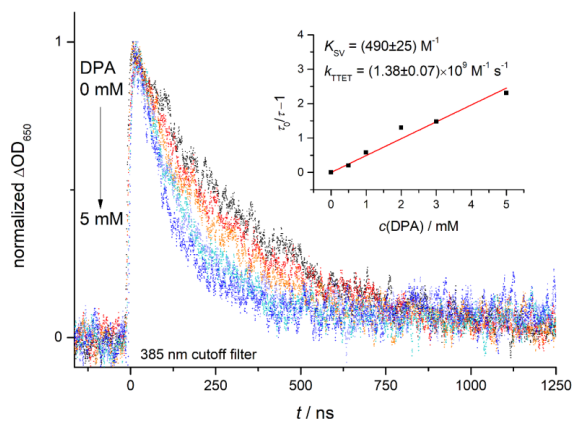


Figure S81: Decays of the transient absorption at 650 nm of **1** in THF with DPA at different concentrations ($\lambda_{\text{exc}} = 532 \text{ nm}$). Inset: Stern-Volmer plot for quenching of **1** with DPA in THF based on TA data at 650 nm with Stern-Volmer constant K_{SV} and triplet-triplet energy transfer rate constant k_{TTET} .

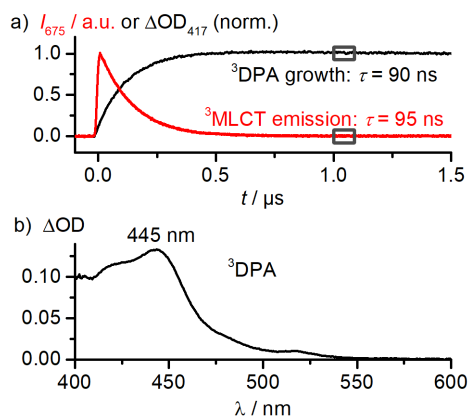


Figure S82: a) $^3\text{MLCT}$ luminescence decay of **1** and ^3DPA growth after pulsed excitation ($\lambda_{\text{exc}} = 532 \text{ nm}$, pulse energy = 8 mJ) of **1** with DPA (3 mM) in THF at room temperature. b) Transient absorption spectrum of ^3DPA measured after complete decay of the $^3\text{MLCT}$ state of **1** (time delay marked with boxes in top figure).

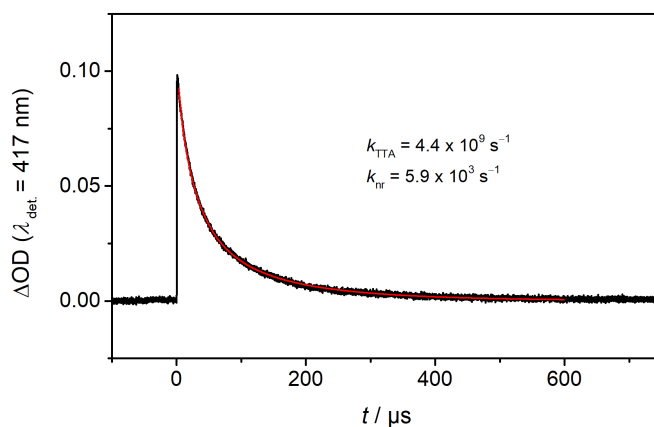


Figure S83: Decay of the ^3DPA transient absorption signal at 417 nm measured after pulsed excitation of **1** at 532 nm with 3 mM DPA in THF with fit considering the mixed first and second order decay of ^3DPA with the time constant of TTA (k_{TTA}) and of the unquenched deactivation of ^3DPA (k_{nr}).⁴⁷ The initial concentration of ^3DPA for the fit was determined from the ^3DPA absorption spectrum in Figure S82 and the previously reported extinction coefficient at 445 nm.⁴⁸

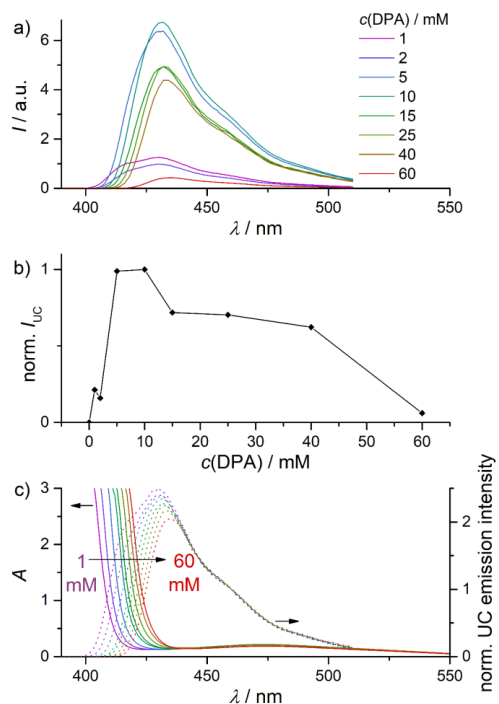


Figure S84: Optimization studies with **1** in THF (Xe-lamp at 525 nm) to find the ideal DPA concentration for more detailed UC experiments. a) UC emission spectra, b) integrated UC emission and c) comparison of absorption and normalized UC emission spectra, at different DPA concentrations.

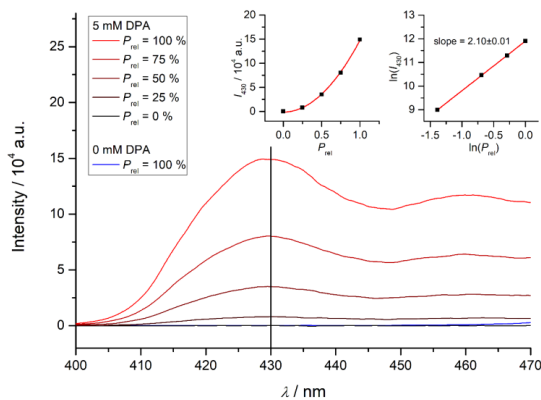


Figure S85: Upconverted emission spectra of **1** with 5 mM DPA (quenching efficiency = 73 %) in THF at different excitation power settings of a green LED (525 nm) and control experiment with no DPA and 100 % excitation power (blue trace). Left inset: Plot of the upconverted emission intensity at 430 nm against relative excitation power P_{rel} fitted with a power function and an exponent of 2.1. Right inset: Doubly logarithmic plot of the upconverted emission intensity at 430 nm against relative excitation power P_{rel} with linear fit.

12. Catalysis

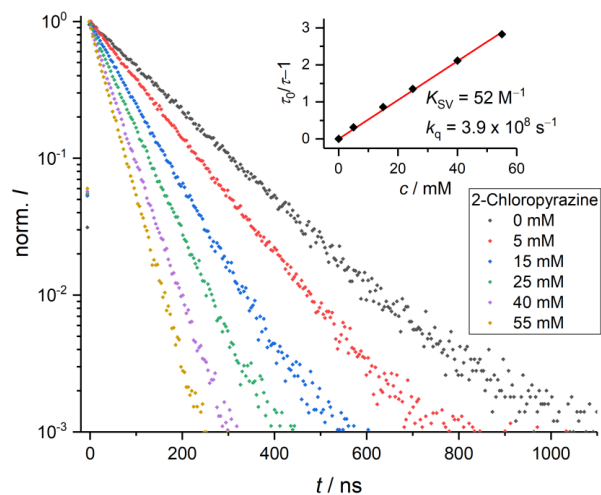


Figure S86: Stern-Volmer quenching experiments of **1** in d_3 -MeCN with chloropyrazine. Luminescence decay curves at 720 nm after pulsed excitation at 438 nm. Inset: Stern-Volmer plot with linear fit, Stern-Volmer constant K_{SV} and quenching constant k_q .

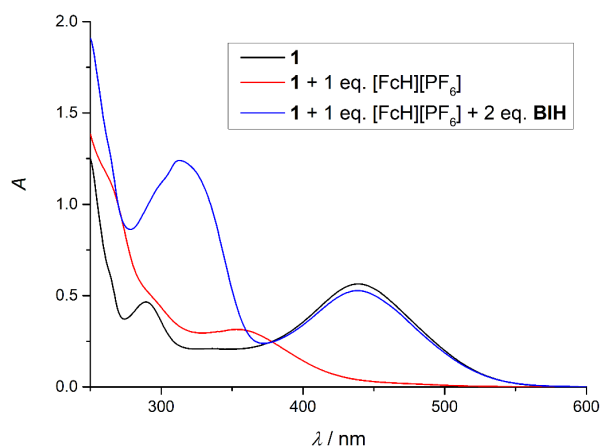


Figure S87: Regeneration of **1** (63 μM) after chemical oxidation with $[\text{Fch}][\text{PF}_6]$ by BIH. The absorbance was corrected for dilution.

General procedure

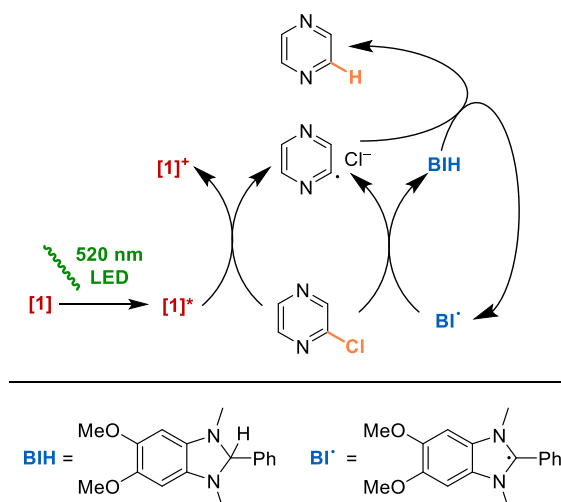
A stock solution of **1** in d_3 -MeCN was prepared in an argon-filled glovebox. Chloropyrazine (2.72 μL), BIH (8.66 mg) and mesitylene (10.3 μL , internal standard) were added to 3.5 mL of the stock solution of **1** (87 μM). 0.5 mL of the solution are used to measure a ^1H NMR spectrum (400 MHz, D1 = 60 s, Figure S88) and the remaining 3.0 mL are filled in an air-tight cuvette equipped with a stirring bar. The solution was irradiated using focused green light of an LED ($\lambda_{\text{max}} = 522 \text{ nm}$, Prismatix UHP-T-520-DI, 2.2

W, focus spot diameter ca. 0.8 cm, Figure S89) under stirring in a temperature controlled Peltier-holder (Agilent Cary dual-cell holder) at 20.0°C. Conversion and yield were determined from ^1H -NMR spectra recorded before and after the irradiation using the integrated resonances of chloropyrazine (8.65 ppm (1H), 8.54 ppm (1H), 8.40 ppm (1H)), pyrazine (8.59 ppm, 4H) and mesitylene (6.80 ppm).

Table S12: Results and conditions of the photocatalysis experiments for the dehalogenation of 2-chloropyrazine with **1** in MeCN at 20.0°C with excitation wavelength λ_{exc} and turn-over number TON.

Entry	1 / μM	2-Chloropyrazine / mM	BIH / mM	λ_{exc} / nm	t / h	Conversion (Yield) / %
1 ^a	87	8.7	8.7	520	24	82 (80)
2 ^a	–	8.7	8.7	520	24	traces
3 ^a	87	8.7	–	520	24	0 (0)
4 ^b	87	8.7	8.7	–	24	0 (0)

a Reaction performed in an air-tight cuvette (3 mL). *b* Reaction performed in an NMR tube (0.5 mL).



Scheme S1: Alternative radical chain mechanism for the dehalogenation of chloropyrazine using **1** in green light driven photoredox catalysis.

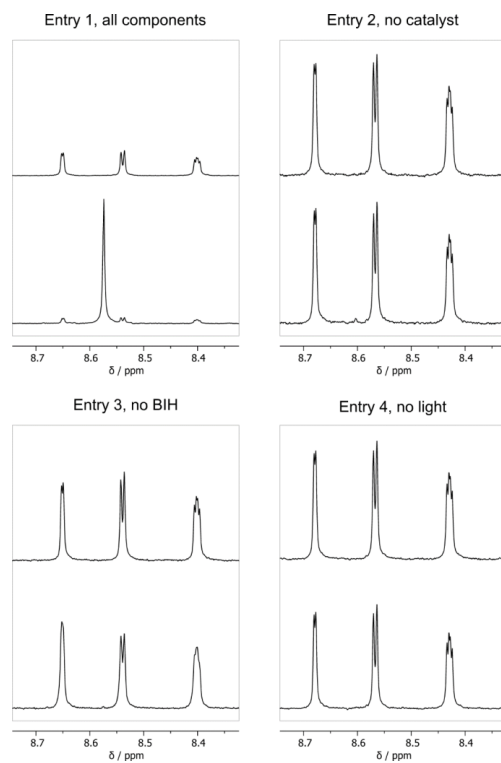


Figure S88: ^1H NMR spectra (400 MHz) of catalysis experiments (Table S12) with **1** in CD_3CN with spectra before (top) and after irradiation (bottom).

13. Emission spectra of excitation sources

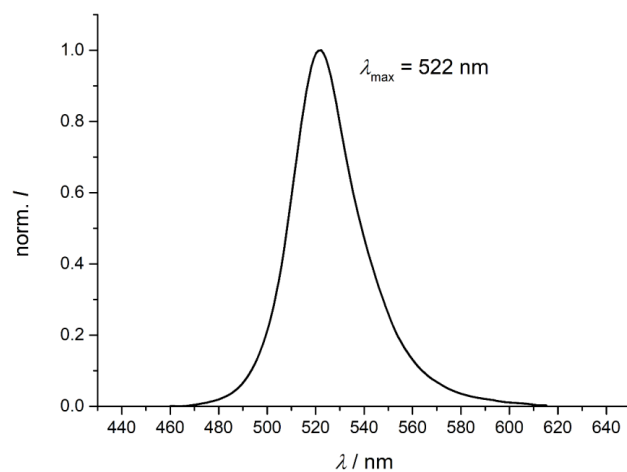


Figure S89: Emission spectrum of the green LED used in the photocatalysis experiments.

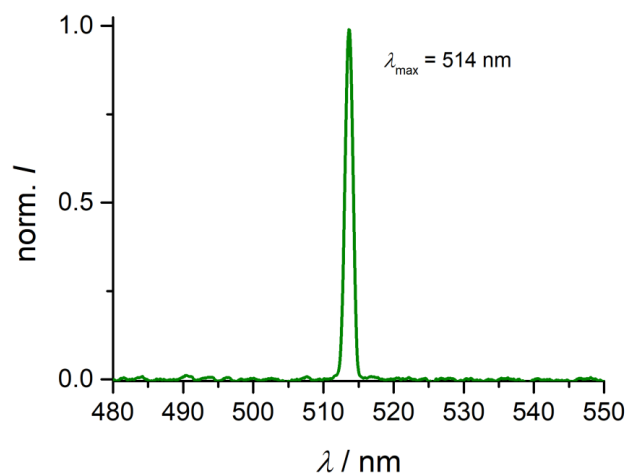


Figure S90: Emission spectrum of the green cw-laser used for photostability and upconversion experiments.

13. DFT-optimized structures

1 (¹GS, CPCM(MeCN))

42	1.912377000	1.560776000	7.437414000
6	2.950041000	-0.087810000	7.240048000
6	3.602615000	2.544275000	7.515465000
6	2.053629000	1.377878000	9.377787000
7	0.625729000	3.401017000	7.512247000
7	-0.089829000	0.570209000	7.330913000
7	1.504487000	1.816836000	5.246963000
6	1.108816000	2.075109000	2.514505000
1	0.937397000	2.181164000	1.450959000
6	-0.858436000	2.377381000	5.799759000
6	-1.514255000	-1.179958000	8.144747000
1	-1.617660000	-2.076657000	8.739496000
6	-2.382372000	0.522774000	6.708742000
1	-3.215725000	0.950237000	6.178963000
6	-2.589094000	-0.617677000	7.469292000
1	-3.574762000	-1.061417000	7.525112000
6	-0.290412000	-0.552299000	8.048557000
1	0.576922000	-0.935676000	8.563997000
6	0.281712000	2.133407000	4.779839000
6	2.367587000	1.761176000	3.009129000
1	3.218210000	1.610792000	2.358761000
6	2.514989000	1.638547000	4.375268000
1	3.468863000	1.388794000	4.815099000
6	0.064557000	2.259004000	3.407604000
1	-0.908306000	2.509046000	3.021471000
6	-2.147868000	2.742043000	5.046754000
1	-2.001045000	3.624801000	4.430078000
1	-2.459231000	1.924748000	4.399466000
1	-2.954610000	2.948858000	5.744731000
6	-0.457255000	3.549760000	6.727989000
6	-1.184780000	4.740627000	6.746271000
1	-2.048903000	4.872697000	6.118021000
6	-0.794165000	5.781418000	7.574199000
1	-1.352966000	6.708251000	7.578213000
6	0.314270000	5.609783000	8.393682000
1	0.658212000	6.386808000	9.062478000
6	0.987973000	4.407767000	8.330750000
1	1.857787000	4.221172000	8.942246000
6	-1.115279000	1.104999000	6.644307000
8	2.135330000	1.281317000	10.544138000
8	3.577735000	-1.072143000	7.123592000
8	4.621248000	3.119798000	7.610606000

1 (¹GS, CPCM(THF))

42	1.910761000	1.561691000	7.436898000
6	2.949183000	-0.089365000	7.237262000
6	3.602523000	2.548254000	7.512490000
6	2.050695000	1.377158000	9.379902000
7	0.625653000	3.400658000	7.512728000
7	-0.089081000	0.570431000	7.331171000
7	1.504754000	1.816836000	5.247598000
6	1.110147000	2.075114000	2.514308000
1	0.939477000	2.181194000	1.450598000
6	-0.857934000	2.377311000	5.800012000
6	-1.513181000	-1.179811000	8.145778000
1	-1.615914000	-2.076253000	8.741038000
6	-2.382099000	0.521987000	6.709687000
1	-3.215773000	0.949028000	6.179955000
6	-2.588624000	-0.618210000	7.470633000
1	-3.574184000	-1.062206000	7.527208000
6	-0.289461000	-0.552215000	8.048928000
1	0.578671000	-0.934664000	8.563727000
6	0.282220000	2.133637000	4.779645000
6	2.368464000	1.760541000	3.009877000
1	3.219441000	1.609460000	2.360127000
6	2.515399000	1.638062000	4.375979000
1	3.468620000	1.387949000	4.817051000
6	0.065795000	2.259429000	3.407154000
1	-0.906844000	2.509927000	3.020537000
6	-2.147496000	2.741661000	5.046968000
1	-2.001002000	3.624414000	4.430112000
1	-2.458853000	1.924282000	4.399655000
1	-2.954425000	2.948584000	5.744825000
6	-0.457197000	3.550214000	6.728214000
6	-1.184072000	4.741632000	6.746316000
1	-2.047882000	4.874267000	6.117632000
6	-0.793468000	5.782212000	7.574457000
1	-1.351643000	6.709476000	7.578541000
6	0.314541000	5.609474000	8.394398000
1	0.658815000	6.385992000	9.063606000
6	0.987720000	4.407285000	8.331700000
1	1.857284000	4.219257000	8.943128000
6	-1.115084000	1.104617000	6.644640000
8	2.126153000	1.278309000	10.544929000
8	3.572965000	-1.073991000	7.118126000
8	4.618469000	3.126002000	7.602121000

1 (¹GS, CPCM(DMF))

42	1.912380000	1.560781000	7.437503000
6	2.950066000	-0.087793000	7.240163000
6	3.602639000	2.544248000	7.515456000
6	2.053638000	1.377878000	9.377880000
7	0.625761000	3.400988000	7.512167000
7	-0.089789000	0.570282000	7.330914000
7	1.504432000	1.816784000	5.247079000
6	1.108810000	2.075228000	2.514554000
1	0.937423000	2.181357000	1.451013000
6	-0.858491000	2.377390000	5.799774000
6	-1.514168000	-1.179986000	8.144698000
1	-1.617544000	-2.076716000	8.739407000
6	-2.382350000	0.522723000	6.708730000
1	-3.215695000	0.950158000	6.178918000
6	-2.589049000	-0.617749000	7.469254000
1	-3.574697000	-1.061530000	7.525061000
6	-0.290367000	-0.552275000	8.048529000
1	0.576975000	-0.935644000	8.563960000
6	0.281695000	2.133442000	4.779888000
6	2.367551000	1.761175000	3.009215000
1	3.218160000	1.610758000	2.358837000
6	2.514911000	1.638467000	4.375332000
1	3.468776000	1.388616000	4.815133000
6	0.064565000	2.259132000	3.407666000
1	-0.908290000	2.509239000	3.021553000
6	-2.147924000	2.742039000	5.046772000
1	-2.001120000	3.624835000	4.430150000
1	-2.459263000	1.924748000	4.399470000
1	-2.954671000	2.948805000	5.744762000
6	-0.457283000	3.549778000	6.727996000
6	-1.184824000	4.740622000	6.746299000
1	-2.049017000	4.872613000	6.118127000
6	-0.794151000	5.781464000	7.574131000
1	-1.352957000	6.708291000	7.578175000
6	0.314387000	5.609841000	8.393504000
1	0.658386000	6.386909000	9.062220000
6	0.988052000	4.407829000	8.330581000
1	1.857904000	4.221271000	8.942036000
6	-1.115290000	1.104997000	6.644325000
8	2.134827000	1.280990000	10.544243000
8	3.577813000	-1.072096000	7.123723000
8	4.621320000	3.119736000	7.610463000

1 (¹GS, CPCM(DMSO))

42	1.912361000	1.560772000	7.437471000
6	2.950045000	-0.087804000	7.240109000
6	3.602610000	2.544259000	7.515480000
6	2.053626000	1.377875000	9.377849000
7	0.625738000	3.400990000	7.512204000
7	-0.089811000	0.570242000	7.330914000
7	1.504449000	1.816811000	5.247041000
6	1.108813000	2.075188000	2.514538000
1	0.937415000	2.181285000	1.450994000
6	-0.858476000	2.377383000	5.799773000
6	-1.514191000	-1.179997000	8.144720000
1	-1.617567000	-2.076718000	8.739441000
6	-2.382367000	0.522720000	6.708748000
1	-3.215721000	0.950153000	6.178952000
6	-2.589064000	-0.617748000	7.469281000
1	-3.574716000	-1.061521000	7.525097000
6	-0.290379000	-0.552299000	8.048534000
1	0.576968000	-0.935666000	8.563959000
6	0.281698000	2.133431000	4.779873000
6	2.367565000	1.761186000	3.009189000
1	3.218182000	1.610781000	2.358818000
6	2.514938000	1.638509000	4.375315000
1	3.468806000	1.388698000	4.815132000
6	0.064561000	2.259084000	3.407644000
1	-0.908299000	2.509157000	3.021518000
6	-2.147899000	2.742068000	5.046767000
1	-2.001068000	3.624853000	4.430135000
1	-2.459258000	1.924788000	4.399460000
1	-2.954644000	2.948863000	5.744749000
6	-0.457279000	3.549767000	6.727998000
6	-1.184802000	4.740626000	6.746277000
1	-2.048962000	4.872653000	6.118067000
6	-0.794144000	5.781453000	7.574137000
1	-1.352937000	6.708290000	7.578156000
6	0.314352000	5.609822000	8.393555000
1	0.658342000	6.386878000	9.062289000
6	0.988020000	4.407801000	8.330641000
1	1.857861000	4.221227000	8.942107000
6	-1.115297000	1.104986000	6.644325000
8	2.135038000	1.281133000	10.544197000
8	3.577762000	-1.072112000	7.123657000
8	4.621261000	3.119764000	7.610550000

1 (¹GS, CPCM(KBr))

42	1.909899000	1.561117000	7.436729000
6	2.948717000	-0.091024000	7.236153000
6	3.601826000	2.549791000	7.507722000
6	2.048691000	1.378960000	9.381400000
7	0.626284000	3.400080000	7.512809000
7	-0.089238000	0.570331000	7.332304000
7	1.505049000	1.815450000	5.248008000
6	1.111767000	2.076357000	2.514421000
1	0.941790000	2.183667000	1.450699000
6	-0.857283000	2.376820000	5.800302000
6	-1.513651000	-1.179587000	8.147183000
1	-1.616418000	-2.075528000	8.743194000
6	-2.381992000	0.520809000	6.709367000
1	-3.215519000	0.947156000	6.178771000
6	-2.588875000	-0.618953000	7.470859000
1	-3.574341000	-1.063264000	7.527074000
6	-0.290017000	-0.551888000	8.050639000
1	0.578125000	-0.933419000	8.566111000
6	0.282859000	2.133386000	4.779640000
6	2.369523000	1.760226000	3.010510000
1	3.220785000	1.608946000	2.361170000
6	2.515844000	1.636548000	4.376517000
1	3.468524000	1.385411000	4.818216000
6	0.067252000	2.260630000	3.407060000
1	-0.904968000	2.512432000	3.020103000
6	-2.146755000	2.741347000	5.047074000
1	-2.000325000	3.624469000	4.430666000
1	-2.457875000	1.924318000	4.399124000
1	-2.954031000	2.947852000	5.744724000
6	-0.456911000	3.549906000	6.728647000
6	-1.183872000	4.741362000	6.747415000
1	-2.047916000	4.874292000	6.119035000
6	-0.793276000	5.781703000	7.575845000
1	-1.351597000	6.708909000	7.580610000
6	0.315097000	5.608604000	8.395262000
1	0.659598000	6.384816000	9.064712000
6	0.988447000	4.406575000	8.331990000
1	1.858323000	4.217978000	8.942827000
6	-1.115090000	1.103917000	6.644830000
8	2.119588000	1.282803000	10.545928000
8	3.570667000	-1.075173000	7.113339000
8	4.614828000	3.131500000	7.590668000

1 (³MLCT, CPCM(MeCN))

42	1.870503000	1.563409000	7.440183000
6	3.058645000	-0.066319000	7.126059000
6	3.611356000	2.517254000	7.613091000
6	2.026666000	1.446135000	9.434613000
7	0.646711000	3.337352000	7.518423000
7	-0.117240000	0.540483000	7.310446000
7	1.492742000	1.814356000	5.246972000
6	1.107558000	2.084460000	2.512039000
1	0.938638000	2.188889000	1.447978000
6	-0.883603000	2.357728000	5.789353000
6	-1.549806000	-1.190010000	8.153791000
1	-1.654403000	-2.090705000	8.742125000
6	-2.424896000	0.539665000	6.750491000
1	-3.263443000	0.986869000	6.245545000
6	-2.632631000	-0.602027000	7.509286000
1	-3.624243000	-1.028730000	7.588376000
6	-0.321087000	-0.578705000	8.037305000
1	0.546428000	-0.978294000	8.543814000
6	0.259725000	2.118551000	4.775278000
6	2.371128000	1.787795000	3.011800000
1	3.226150000	1.648325000	2.364938000
6	2.514746000	1.669399000	4.376808000
1	3.477174000	1.447473000	4.813693000
6	0.058337000	2.255860000	3.402315000
1	-0.915235000	2.498770000	3.013017000
6	-2.170199000	2.714308000	5.027820000
1	-2.019376000	3.589642000	4.402257000
1	-2.483199000	1.889279000	4.389845000
1	-2.976051000	2.935386000	5.721915000
6	-0.472774000	3.524034000	6.708569000
6	-1.158520000	4.719446000	6.717836000
1	-2.017076000	4.853036000	6.079168000
6	-0.766281000	5.790282000	7.539196000
1	-1.308179000	6.725355000	7.525343000
6	0.349195000	5.585720000	8.385041000
1	0.700551000	6.359190000	9.056742000
6	1.004141000	4.391153000	8.348707000
1	1.863607000	4.209093000	8.976681000
6	-1.149291000	1.096058000	6.641290000
8	2.126156000	1.389282000	10.584858000
8	3.795681000	-0.938125000	6.948324000
8	4.645228000	3.018512000	7.768332000

1 (³MLCT, CPCM(KBr))

42	1.874114000	1.528823000	7.442021000
6	3.091145000	-0.053122000	7.058787000
6	3.611424000	2.491347000	7.627239000
6	2.009492000	1.398620000	9.445601000
7	0.629800000	3.307970000	7.527725000
7	-0.115186000	0.507154000	7.312071000
7	1.506444000	1.808785000	5.262609000
6	1.133062000	2.105740000	2.523698000
1	0.968729000	2.214930000	1.459545000
6	-0.881312000	2.325791000	5.792504000
6	-1.563481000	-1.183316000	8.209687000
1	-1.673074000	-2.074144000	8.812150000
6	-2.435232000	0.546213000	6.804244000
1	-3.275993000	1.005569000	6.314026000
6	-2.649761000	-0.581325000	7.582535000
1	-3.647737000	-0.986327000	7.690752000
6	-0.325801000	-0.599556000	8.057206000
1	0.545306000	-1.009825000	8.549206000
6	0.268363000	2.100222000	4.783449000
6	2.401908000	1.832039000	3.031747000
1	3.264847000	1.717353000	2.390477000
6	2.538488000	1.701713000	4.394172000
1	3.502671000	1.497259000	4.834914000
6	0.076508000	2.250203000	3.410879000
1	-0.898681000	2.480718000	3.017574000
6	-2.167338000	2.677048000	5.027616000
1	-2.015179000	3.544914000	4.392330000
1	-2.481868000	1.844777000	4.399501000
1	-2.972141000	2.910017000	5.718990000
6	-0.472864000	3.495366000	6.705478000
6	-1.145664000	4.702594000	6.692430000
1	-1.991926000	4.842450000	6.038824000
6	-0.753315000	5.767651000	7.510308000
1	-1.282296000	6.709841000	7.480666000
6	0.343935000	5.558994000	8.375716000
1	0.692074000	6.332723000	9.047973000
6	0.987321000	4.356583000	8.352668000
1	1.837791000	4.169855000	8.991558000
6	-1.151285000	1.074729000	6.657962000
8	2.083620000	1.336523000	10.595683000
8	3.843891000	-0.893011000	6.806703000
8	4.640493000	2.998259000	7.783364000

1 (³MLCT, CPCM(DMSO))

42	1.870503000	1.563409000	7.440183000
6	3.058645000	-0.066319000	7.126059000
6	3.611356000	2.517254000	7.613091000
6	2.026666000	1.446135000	9.434613000
7	0.646711000	3.337352000	7.518423000
7	-0.117240000	0.540483000	7.310446000
7	1.492742000	1.814356000	5.246972000
6	1.107558000	2.084460000	2.512039000
1	0.938638000	2.188889000	1.447978000
6	-0.883603000	2.357728000	5.789353000
6	-1.549806000	-1.190010000	8.153791000
1	-1.654403000	-2.090705000	8.742125000
6	-2.424896000	0.539665000	6.750491000
1	-3.263443000	0.986869000	6.245545000
6	-2.632631000	-0.602027000	7.509286000
1	-3.624243000	-1.028730000	7.588376000
6	-0.321087000	-0.578705000	8.037305000
1	0.546428000	-0.978294000	8.543814000
6	0.259725000	2.118551000	4.775278000
6	2.371128000	1.787795000	3.011800000
1	3.226150000	1.648325000	2.364938000
6	2.514746000	1.669399000	4.376808000
1	3.477174000	1.447473000	4.813693000
6	0.058337000	2.255860000	3.402315000
1	-0.915235000	2.498770000	3.013017000
6	-2.170199000	2.714308000	5.027820000
1	-2.019376000	3.589642000	4.402257000
1	-2.483199000	1.889279000	4.389845000
1	-2.976051000	2.935386000	5.721915000
6	-0.472774000	3.524034000	6.708569000
6	-1.158520000	4.719446000	6.717836000
1	-2.017076000	4.853036000	6.079168000
6	-0.766281000	5.790282000	7.539196000
1	-1.308179000	6.725355000	7.525343000
6	0.349195000	5.585720000	8.385041000
1	0.700551000	6.359190000	9.056742000
6	1.004141000	4.391153000	8.348707000
1	1.863607000	4.209093000	8.976681000
6	-1.149291000	1.096058000	6.641290000
8	2.126156000	1.389282000	10.584858000
8	3.795681000	-0.938125000	6.948324000
8	4.645228000	3.018512000	7.768332000

1 (³MLCT, CPCM(THF))

42	1.870497000	1.540481000	7.432579000
6	3.090252000	-0.043911000	7.059309000
6	3.606764000	2.503293000	7.618371000
6	2.009853000	1.412242000	9.433895000
7	0.631525000	3.317348000	7.519791000
7	-0.119428000	0.519658000	7.300693000
7	1.502719000	1.817596000	5.249281000
6	1.127153000	2.100001000	2.511967000
1	0.961751000	2.204448000	1.447443000
6	-0.882603000	2.339845000	5.781741000
6	-1.570560000	-1.169095000	8.196995000
1	-1.681937000	-2.059631000	8.799556000
6	-2.439100000	0.560771000	6.789630000
1	-3.278684000	1.020554000	6.297769000
6	-2.655525000	-0.566134000	7.568236000
1	-3.654028000	-0.970114000	7.675351000
6	-0.331940000	-0.586951000	8.045767000
1	0.538003000	-0.998465000	8.538751000
6	0.265988000	2.108698000	4.772116000
6	2.395012000	1.825839000	3.018293000
1	3.256568000	1.705855000	2.376207000
6	2.532875000	1.701421000	4.382037000
1	3.496740000	1.495104000	4.822648000
6	0.071378000	2.250414000	3.398618000
1	-0.904003000	2.479488000	3.005060000
6	-2.167057000	2.694335000	5.015830000
1	-2.012502000	3.563090000	4.382137000
1	-2.482305000	1.863564000	4.386300000
1	-2.972418000	2.926957000	5.706526000
6	-0.474379000	3.507130000	6.698725000
6	-1.151113000	4.710753000	6.693972000
1	-1.998876000	4.850735000	6.042279000
6	-0.761647000	5.774953000	7.517709000
1	-1.293798000	6.715466000	7.493401000
6	0.337083000	5.563740000	8.382045000
1	0.682880000	6.334629000	9.059040000
6	0.984563000	4.364148000	8.352831000
1	1.834897000	4.176541000	8.991665000
6	-1.154489000	1.088182000	6.645486000
8	2.089856000	1.351488000	10.584056000
8	3.846888000	-0.884417000	6.820349000
8	4.636678000	3.009586000	7.775205000

1 (³MC, CPCM(MeCN))

42	1.910767000	1.579253000	7.458590000
6	2.888682000	-0.270616000	6.998006000
6	3.673570000	2.434469000	7.472103000
6	2.256585000	1.565770000	9.408595000
7	0.694632000	3.481484000	7.417665000
7	-0.113323000	0.640925000	7.391711000
7	1.493920000	1.786646000	5.258343000
6	1.139793000	2.081811000	2.530354000
1	0.986048000	2.206824000	1.466268000
6	-0.853640000	2.398962000	5.795419000
6	-1.510747000	-1.160301000	8.131954000
1	-1.621048000	-2.043932000	8.745020000
6	-2.334894000	0.452030000	6.569905000
1	-3.135198000	0.815514000	5.948888000
6	-2.540242000	-0.690872000	7.327747000
1	-3.493151000	-1.202368000	7.288430000
6	-0.319956000	-0.463254000	8.134040000
1	0.516825000	-0.789201000	8.734890000
6	0.291062000	2.157797000	4.784147000
6	2.372419000	1.691298000	3.032049000
1	3.216599000	1.495911000	2.385156000
6	2.504300000	1.557587000	4.400556000
1	3.435416000	1.248053000	4.850853000
6	0.094015000	2.315092000	3.413562000
1	-0.861555000	2.616602000	3.020720000
6	-2.134201000	2.771945000	5.031722000
1	-1.993451000	3.694051000	4.472713000
1	-2.408916000	1.987325000	4.331179000
1	-2.965989000	2.915707000	5.716235000
6	-0.472723000	3.559176000	6.747541000
6	-1.306884000	4.663118000	6.915308000
1	-2.248351000	4.729521000	6.397667000
6	-0.930061000	5.701045000	7.755837000
1	-1.580016000	6.556836000	7.883938000
6	0.289401000	5.623932000	8.415364000
1	0.636396000	6.411614000	9.069716000
6	1.066175000	4.500789000	8.216743000
1	2.020214000	4.386691000	8.709171000
6	-1.107932000	1.113354000	6.618385000
8	2.539811000	1.592033000	10.539852000
8	3.125076000	-1.281169000	7.595035000
8	4.731866000	2.930696000	7.531211000

1 (³MLCT–³MC transition state, CPCM(MeCN))

42	1.687140000	-0.522478000	1.050804000
6	2.706298000	-2.354623000	0.668021000
6	3.423261000	0.411996000	1.133387000
6	1.997453000	-0.554096000	3.008116000
7	0.519284000	1.356650000	0.985293000
7	-0.303615000	-1.494047000	0.949015000
7	1.292242000	-0.336036000	-1.156614000
6	0.975642000	0.059049000	-3.881823000
1	0.839067000	0.232090000	-4.941597000
6	-1.054070000	0.282643000	-0.627226000
6	-1.705038000	-3.285246000	1.708591000
1	-1.810126000	-4.175613000	2.312181000
6	-2.549550000	-1.637919000	0.193810000
1	-3.363923000	-1.254083000	-0.395701000
6	-2.754141000	-2.780841000	0.952006000
1	-3.719873000	-3.269357000	0.945278000
6	-0.505308000	-2.606734000	1.682027000
1	0.341563000	-2.950524000	2.257870000
6	0.094461000	0.058290000	-1.636233000
6	2.195125000	-0.371558000	-3.377687000
1	3.044306000	-0.560986000	-4.020407000
6	2.310650000	-0.548054000	-2.013356000
1	3.236431000	-0.876090000	-1.562877000
6	-0.078170000	0.272768000	-3.000587000
1	-1.022610000	0.609058000	-3.392864000
6	-2.339345000	0.647926000	-1.387289000
1	-2.206476000	1.569127000	-1.948677000
1	-2.609703000	-0.140963000	-2.086317000
1	-3.168529000	0.790792000	-0.700028000
6	-0.661039000	1.445903000	0.313693000
6	-1.468681000	2.570046000	0.453185000
1	-2.412916000	2.632942000	-0.060440000
6	-1.063158000	3.642491000	1.239004000
1	-1.690467000	4.518987000	1.332060000
6	0.167786000	3.560355000	1.889132000
1	0.547872000	4.370328000	2.496922000
6	0.912409000	2.413996000	1.741375000
1	1.864352000	2.304721000	2.237717000
6	-1.308844000	-1.000427000	0.201561000
8	2.261216000	-0.540307000	4.142862000
8	2.935638000	-3.454358000	1.044229000
8	4.443390000	0.964183000	1.251586000

1 (⁵MC, CPCM(MeCN))

42	1.891861000	1.641618000	7.428057000
6	2.828597000	-0.384029000	6.989977000
6	3.760698000	2.462575000	7.307627000
6	2.181990000	1.442136000	9.428501000
7	0.671774000	3.513935000	7.407083000
7	-0.066498000	0.725150000	7.388385000
7	1.509325000	1.810253000	5.249610000
6	1.140910000	1.970798000	2.508934000
1	0.983313000	2.048537000	1.441069000
6	-0.849161000	2.452260000	5.759480000
6	-1.486870000	-1.080088000	8.153126000
1	-1.596169000	-1.951827000	8.785578000
6	-2.313358000	0.514389000	6.555198000
1	-3.109440000	0.879850000	5.926726000
6	-2.538246000	-0.633919000	7.323396000
1	-3.488017000	-1.148768000	7.284206000
6	-0.308580000	-0.390155000	8.163615000
1	0.511552000	-0.706557000	8.792203000
6	0.301058000	2.175965000	4.764647000
6	2.372866000	1.584245000	3.023464000
1	3.212231000	1.346785000	2.384788000
6	2.507645000	1.514090000	4.392702000
1	3.442010000	1.212877000	4.841812000
6	0.105710000	2.258109000	3.386027000
1	-0.848214000	2.552563000	2.984231000
6	-2.113065000	2.834611000	4.974686000
1	-1.953115000	3.754244000	4.414673000
1	-2.388576000	2.049020000	4.276127000
1	-2.952683000	2.986860000	5.646787000
6	-0.500212000	3.593765000	6.733196000
6	-1.359223000	4.663548000	6.969264000
1	-2.302570000	4.732609000	6.454481000
6	-1.004322000	5.669015000	7.860736000
1	-1.670071000	6.505417000	8.027534000
6	0.217924000	5.582912000	8.526929000
1	0.544308000	6.344027000	9.222102000
6	1.015606000	4.489572000	8.280018000
1	1.966178000	4.366405000	8.781992000
6	-1.102297000	1.180180000	6.588058000
8	2.383622000	1.333912000	10.555570000
8	3.527706000	-1.036932000	7.682036000
8	4.825098000	2.902192000	7.247956000

1 (MECP ¹GS-³MC, CPCM(MeCN))

42	1.891842000	1.529218000	7.493186000
6	2.920481000	-0.269924000	6.867707000
6	3.653718000	2.376124000	7.621917000
6	2.259846000	1.507705000	9.450575000
7	0.652994000	3.464249000	7.441186000
7	-0.095228000	0.558918000	7.349561000
7	1.486802000	1.816592000	5.288107000
6	1.141561000	2.154768000	2.564614000
1	0.990012000	2.295774000	1.501917000
6	-0.880332000	2.363876000	5.821800000
6	-1.475088000	-1.248655000	8.101018000
1	-1.562373000	-2.160653000	8.674283000
6	-2.368598000	0.458866000	6.682330000
1	-3.204752000	0.869920000	6.144144000
6	-2.552214000	-0.703708000	7.416272000
1	-3.524914000	-1.177418000	7.444462000
6	-0.270662000	-0.579488000	8.046635000
1	0.602843000	-0.953497000	8.561347000
6	0.271889000	2.142197000	4.811174000
6	2.392671000	1.838231000	3.071431000
1	3.255930000	1.718807000	2.431305000
6	2.516489000	1.671396000	4.437602000
1	3.456266000	1.394376000	4.889624000
6	0.075603000	2.302861000	3.441524000
1	-0.891935000	2.557322000	3.044891000
6	-2.169831000	2.713140000	5.061348000
1	-2.037292000	3.614667000	4.468900000
1	-2.451843000	1.903954000	4.391085000
1	-2.990973000	2.882184000	5.752483000
6	-0.490792000	3.550480000	6.739809000
6	-1.273045000	4.701191000	6.811784000
1	-2.197967000	4.780276000	6.267113000
6	-0.853121000	5.778369000	7.581157000
1	-1.453132000	6.678374000	7.621014000
6	0.337004000	5.683016000	8.285543000
1	0.711011000	6.496863000	8.891065000
6	1.052518000	4.503672000	8.192180000
1	1.982425000	4.372426000	8.724377000
6	-1.120704000	1.080622000	6.653452000
8	2.579066000	1.544961000	10.568967000
8	2.872306000	-1.298864000	7.528333000
8	4.712812000	2.848960000	7.775368000

Mo(CO)₂(tpe) (¹GS, CPCM(MeCN))

42	1.892069000	1.682523000	7.429123000
6	2.934577000	0.069604000	7.282973000
6	2.061676000	1.425576000	9.330209000
7	0.610388000	3.493199000	7.517334000
7	0.059892000	0.636307000	7.398167000
7	1.559561000	1.908468000	5.255325000
6	1.179378000	2.146478000	2.524686000
1	1.015488000	2.243108000	1.459134000
6	-0.810617000	2.386206000	5.810371000
6	-1.328682000	-1.141045000	8.248602000
1	-1.402450000	-2.026332000	8.865446000
6	-2.243096000	0.495270000	6.776606000
1	-3.086062000	0.885254000	6.233211000
6	-2.427673000	-0.628323000	7.565096000
1	-3.401275000	-1.095228000	7.635018000
6	-0.123774000	-0.489779000	8.137983000
1	0.751283000	-0.841986000	8.659297000
6	0.328315000	2.179331000	4.781091000
6	2.447290000	1.884670000	3.030326000
1	3.308308000	1.768564000	2.386626000
6	2.587025000	1.765011000	4.397223000
1	3.544145000	1.543920000	4.849866000
6	0.117481000	2.289405000	3.407103000
1	-0.862227000	2.496271000	3.011192000
6	-2.119203000	2.677101000	5.058160000
1	-2.010458000	3.550245000	4.420135000
1	-2.398642000	1.834153000	4.429279000
1	-2.931064000	2.869163000	5.754419000
6	-0.465764000	3.596637000	6.713501000
6	-1.224681000	4.766563000	6.701636000
1	-2.084415000	4.864291000	6.060320000
6	-0.872525000	5.830681000	7.519496000
1	-1.454628000	6.742980000	7.499065000
6	0.227293000	5.702742000	8.360478000
1	0.535658000	6.499835000	9.023161000
6	0.932729000	4.516834000	8.331004000
1	1.794396000	4.355805000	8.964694000
6	-0.997868000	1.121005000	6.687967000
8	2.110821000	1.177941000	10.490580000
8	3.518070000	-0.961858000	7.219633000

Mo(CO)₂(tpe) (³MC, CPCM(MeCN))

42	1.854104000	1.513054000	7.446853000
6	3.774917000	0.969045000	7.430305000
6	1.945994000	1.399402000	9.363230000
7	0.632619000	3.347310000	7.555684000
7	-0.141749000	0.583460000	7.405686000
7	1.472311000	1.731208000	5.257555000
6	1.074267000	2.056760000	2.524192000
1	0.905283000	2.195466000	1.464158000
6	-0.867342000	2.371677000	5.824344000
6	-1.562381000	-1.214502000	8.116835000
1	-1.679550000	-2.114238000	8.704531000
6	-2.384398000	0.461916000	6.624186000
1	-3.193051000	0.863590000	6.038413000
6	-2.603677000	-0.693251000	7.358358000
1	-3.571782000	-1.176598000	7.333231000
6	-0.360124000	-0.540772000	8.121786000
1	0.478157000	-0.888115000	8.707177000
6	0.260874000	2.110237000	4.795587000
6	2.314516000	1.660142000	3.007829000
1	3.152030000	1.471549000	2.350218000
6	2.465604000	1.509721000	4.370146000
1	3.409324000	1.202651000	4.795005000
6	0.046003000	2.276566000	3.427998000
1	-0.914328000	2.586594000	3.053755000
6	-2.155552000	2.766766000	5.083755000
1	-2.002595000	3.662643000	4.488592000
1	-2.474316000	1.971534000	4.413652000
1	-2.958302000	2.961562000	5.790635000
6	-0.437226000	3.531081000	6.754260000
6	-1.114120000	4.750887000	6.755769000
1	-1.969831000	4.909696000	6.121701000
6	-0.689480000	5.783959000	7.576607000
1	-1.211281000	6.731991000	7.567600000
6	0.402286000	5.574760000	8.411961000
1	0.766203000	6.343332000	9.079932000
6	1.023293000	4.344842000	8.378017000
1	1.870478000	4.121215000	9.009468000
6	-1.139360000	1.091928000	6.652179000
8	1.945769000	1.350289000	10.548040000
8	4.907149000	0.641230000	7.516305000

2 (¹GS, CPCM(MeCN))

42	-2.453722000	1.731020000	5.948522000
8	-5.140594000	0.121031000	6.155244000
8	-3.742561000	3.798647000	3.971819000
8	-1.648979000	-0.155868000	3.499512000
8	-3.608755000	3.352107000	8.450872000
7	-0.438792000	2.698130000	5.985563000
7	-1.159586000	0.479282000	7.272576000
6	-4.141841000	0.714243000	6.069580000
6	-3.292405000	3.019952000	4.711855000
6	-1.906817000	0.549135000	4.370847000
6	-3.133998000	2.798226000	7.560747000
6	-0.136903000	3.816819000	5.309341000
1	-0.935956000	4.253314000	4.728785000
6	1.118015000	4.397186000	5.338676000
1	1.305890000	5.298797000	4.772811000
6	2.109651000	3.795362000	6.103468000
1	3.103202000	4.220667000	6.155604000
6	1.807478000	2.639673000	6.806585000
1	2.566271000	2.160931000	7.406269000
6	0.523331000	2.103581000	6.729445000
6	0.126544000	0.870550000	7.436449000
6	1.004835000	0.133470000	8.228900000
1	2.029191000	0.449538000	8.352382000
6	0.556827000	-1.013663000	8.864113000
1	1.231943000	-1.592496000	9.479984000
6	-0.764741000	-1.405631000	8.692425000
1	-1.160979000	-2.293242000	9.164794000
6	-1.584146000	-0.633655000	7.887653000
1	-2.615040000	-0.906547000	7.716842000

2 (¹GS, CPCM(THF))

42	-2.453287000	1.730676000	5.948805000
8	-5.136939000	0.114032000	6.155290000
8	-3.737623000	3.807154000	3.977783000
8	-1.648200000	-0.148785000	3.494149000
8	-3.611154000	3.346966000	8.453179000
7	-0.439215000	2.697410000	5.986792000
7	-1.158769000	0.479089000	7.271372000
6	-4.141726000	0.710454000	6.068501000
6	-3.291785000	3.024577000	4.714463000
6	-1.907666000	0.553503000	4.366929000
6	-3.136852000	2.794720000	7.562185000
6	-0.137617000	3.815627000	5.309422000
1	-0.937846000	4.251436000	4.729933000
6	1.117564000	4.395352000	5.336247000
1	1.304864000	5.296354000	4.769175000
6	2.110410000	3.793859000	6.099895000
1	3.104316000	4.218752000	6.149738000
6	1.808527000	2.639119000	6.804395000
1	2.568131000	2.160488000	7.403214000
6	0.523945000	2.103218000	6.729813000
6	0.127043000	0.870855000	7.437534000
6	1.003963000	0.134686000	8.232734000
1	2.027864000	0.451542000	8.358491000
6	0.555529000	-1.012122000	8.867902000
1	1.229426000	-1.590110000	9.485984000
6	-0.765494000	-1.404928000	8.693153000
1	-1.162316000	-2.292432000	9.165288000
6	-1.583622000	-0.633975000	7.886271000
1	-2.614110000	-0.906961000	7.713030000

2 (³MLCT, CPCM(MeCN))

42	-2.427804000	1.688399000	5.938762000
8	-5.216552000	0.132040000	6.293350000
8	-3.754633000	3.793399000	3.918719000
8	-1.622307000	0.013668000	3.336250000
8	-3.147621000	3.411962000	8.540739000
7	-0.466398000	2.653586000	5.922664000
7	-1.187172000	0.436287000	7.228710000
6	-4.218473000	0.673985000	6.155333000
6	-3.299861000	3.043434000	4.653593000
6	-1.888211000	0.597889000	4.282019000
6	-2.887048000	2.795918000	7.615522000
6	-0.141136000	3.761636000	5.226535000
1	-0.913779000	4.166287000	4.586510000
6	1.082954000	4.379653000	5.303578000
1	1.276394000	5.269338000	4.722010000
6	2.060947000	3.821006000	6.162895000
1	3.032888000	4.286890000	6.264362000
6	1.763641000	2.685799000	6.867741000
1	2.502385000	2.248814000	7.524290000
6	0.490107000	2.072435000	6.750508000
6	0.113750000	0.882464000	7.428864000
6	0.971334000	0.136698000	8.279380000
1	1.984612000	0.474967000	8.441091000
6	0.527060000	-1.001254000	8.896726000
1	1.189386000	-1.564131000	9.542154000
6	-0.801288000	-1.438718000	8.674726000
1	-1.192165000	-2.334013000	9.135908000
6	-1.598170000	-0.690425000	7.841698000
1	-2.615473000	-0.997449000	7.637024000

2 (³MLCT, CPCM(THF))

42	-2.428630000	1.688716000	5.939291000
8	-5.218155000	0.135178000	6.296122000
8	-3.753149000	3.793171000	3.918040000
8	-1.619150000	0.017554000	3.334350000
8	-3.144376000	3.408894000	8.545825000
7	-0.467323000	2.653424000	5.922330000
7	-1.187908000	0.435975000	7.228634000
6	-4.219685000	0.676440000	6.157070000
6	-3.299433000	3.043216000	4.653787000
6	-1.886458000	0.600261000	4.280272000
6	-2.885399000	2.794395000	7.619491000
6	-0.140666000	3.759771000	5.224079000
1	-0.912590000	4.162770000	4.582138000
6	1.083188000	4.377838000	5.301119000
1	1.277632000	5.265997000	4.717632000
6	2.059893000	3.821092000	6.162973000
1	3.031637000	4.287200000	6.264944000
6	1.761646000	2.687252000	6.869237000
1	2.499627000	2.251513000	7.527386000
6	0.488620000	2.073260000	6.751596000
6	0.112601000	0.883175000	7.429669000
6	0.970062000	0.137717000	8.280389000
1	1.982904000	0.476788000	8.443008000
6	0.526869000	-1.000934000	8.896778000
1	1.189399000	-1.563482000	9.542227000
6	-0.800755000	-1.439730000	8.673581000
1	-1.190773000	-2.335796000	9.133886000
6	-1.597703000	-0.691601000	7.840789000
1	-2.614557000	-0.999489000	7.635016000

2 (³MC₂, CPCM(MeCN))

42	-2.435310000	1.731317000	5.949846000
8	-4.925818000	-0.220831000	6.046779000
8	-3.781255000	3.987800000	4.189535000
8	-1.281307000	0.263111000	3.362573000
8	-3.133236000	3.207707000	8.694058000
7	-0.270011000	2.681119000	6.084873000
7	-0.982805000	0.429532000	7.299971000
6	-3.927992000	0.380584000	6.123520000
6	-3.125656000	3.271892000	4.839479000
6	-1.726982000	0.784509000	4.286652000
6	-2.916773000	2.679240000	7.695382000
6	0.045135000	3.774743000	5.382498000
1	-0.763722000	4.227690000	4.825524000
6	1.323636000	4.304192000	5.347443000
1	1.525182000	5.190000000	4.761519000
6	2.323163000	3.666843000	6.072034000
1	3.338081000	4.042707000	6.063660000
6	2.002760000	2.536797000	6.807822000
1	2.767667000	2.024297000	7.371170000
6	0.690133000	2.065165000	6.800381000
6	0.268626000	0.863859000	7.545965000
6	1.100304000	0.206723000	8.452982000
1	2.090590000	0.581155000	8.664055000
6	0.639658000	-0.931210000	9.096355000
1	1.271626000	-1.449782000	9.805325000
6	-0.641342000	-1.389719000	8.815327000
1	-1.042461000	-2.277152000	9.284553000
6	-1.415454000	-0.675640000	7.916118000
1	-2.421893000	-0.988674000	7.674156000

2 ($^3\text{MC}_1$ with $d(\text{Mo}-\text{CO}^{\text{transCO}})$ constrained to 2.555 Å, CPCM(MeCN))

42	-2.490211824	1.881383344	6.210421019
8	-5.229766675	0.290454808	6.319176998
8	-4.085011820	3.778899186	4.203285581
8	-0.994023478	0.175592653	3.314605418
8	-3.761678700	3.224167968	8.737352452
7	-0.536405810	2.837963828	6.180189123
7	-1.264492320	0.623258085	7.469372325
6	-4.223724523	0.849827440	6.255966247
6	-3.488136926	3.092941006	4.905964704
6	-1.438691121	0.657243435	4.228843255
6	-3.273174543	2.736165471	7.814773194
6	-0.210674459	3.940592999	5.469187630
1	-1.020591880	4.398761011	4.918012482
6	1.051229126	4.476659077	5.432203432
1	1.247974582	5.360135311	4.842352307
6	2.070127639	3.839859347	6.182974183
1	3.077102202	4.237919174	6.185409457
6	1.770351903	2.719001607	6.909151951
1	2.541048294	2.227825106	7.485431266
6	0.456872586	2.188164329	6.906430921
6	0.069235964	1.005307125	7.594752936
6	0.933006166	0.230984811	8.409077875
1	1.967555626	0.523649463	8.517016804
6	0.469964961	-0.883857242	9.055905514
1	1.137580270	-1.472460567	9.671945092
6	-0.888043034	-1.257798757	8.913474282
1	-1.292551944	-2.131991106	9.402796018
6	-1.696487755	-0.476583910	8.126975600
1	-2.739510930	-0.725903654	7.986726166

2 (MECP ¹GS-³MC₂, CPCM(MeCN))

42	-2.562393000	1.719804000	5.878206000
8	-4.966324000	-0.191852000	6.574199000
8	-3.570785000	3.926125000	3.893051000
8	-1.392089000	0.036365000	3.435672000
8	-3.318508000	3.670354000	8.277715000
7	-0.250719000	2.651363000	6.065136000
7	-0.988746000	0.443292000	7.346842000
6	-3.940974000	0.354956000	6.465290000
6	-2.932284000	3.249824000	4.600577000
6	-1.848901000	0.607867000	4.321739000
6	-3.056458000	2.939259000	7.429431000
6	0.053680000	3.782494000	5.424137000
1	-0.742778000	4.223580000	4.839846000
6	1.302284000	4.379596000	5.489683000
1	1.492509000	5.297475000	4.951061000
6	2.284978000	3.769221000	6.258487000
1	3.273804000	4.201426000	6.342522000
6	1.978069000	2.595152000	6.927524000
1	2.728397000	2.109146000	7.532321000
6	0.695521000	2.056401000	6.810418000
6	0.293654000	0.813688000	7.500679000
6	1.181395000	0.065472000	8.277312000
1	2.211995000	0.367153000	8.386011000
6	0.730032000	-1.077021000	8.917766000
1	1.407415000	-1.666483000	9.521870000
6	-0.599627000	-1.447671000	8.766276000
1	-1.003275000	-2.327806000	9.247349000
6	-1.414026000	-0.660131000	7.967536000
1	-2.451303000	-0.921075000	7.810902000

2 (⁵MC, CPCM(MeCN))

42	-2.362029000	1.845079000	5.923081000
8	-5.232251000	0.417403000	5.833392000
8	-4.196752000	3.691233000	4.061504000
8	-1.463533000	0.038680000	3.389744000
8	-3.576837000	3.297563000	8.549153000
7	-0.390884000	2.713973000	5.981269000
7	-1.173020000	0.498876000	7.238156000
6	-4.121410000	0.317575000	6.192525000
6	-3.525713000	3.040499000	4.722706000
6	-1.786432000	0.671405000	4.276375000
6	-3.121975000	2.798547000	7.633044000
6	-0.045230000	3.823133000	5.283619000
1	-0.830781000	4.266369000	4.684431000
6	1.207644000	4.371506000	5.319684000
1	1.430873000	5.257450000	4.743545000
6	2.188716000	3.746668000	6.138796000
1	3.185947000	4.162391000	6.206359000
6	1.865198000	2.620424000	6.846329000
1	2.608603000	2.143479000	7.468828000
6	0.564664000	2.065420000	6.768532000
6	0.145985000	0.884189000	7.432866000
6	0.985578000	0.105174000	8.271237000
1	2.012912000	0.403296000	8.422343000
6	0.499257000	-1.014096000	8.892516000
1	1.142203000	-1.604388000	9.533218000
6	-0.846089000	-1.389647000	8.683981000
1	-1.272752000	-2.265584000	9.151405000
6	-1.620757000	-0.606835000	7.857936000
1	-2.653378000	-0.861544000	7.659503000

Mo(CO)₃(bpy), *trans*-py vacancy (¹GS, CPCM(MeCN))

42	-2.381003000	1.632280000	5.917731000
8	-3.723516000	3.802050000	4.137550000
8	-1.646023000	0.450611000	3.058362000
8	-3.385864000	3.550148000	8.252542000
7	-0.475714000	2.611803000	5.970435000
7	-1.123317000	0.368667000	7.237979000
6	-3.256931000	2.949747000	4.805948000
6	-1.885347000	0.788079000	4.140859000
6	-3.013072000	2.789757000	7.462444000
6	-0.180293000	3.735424000	5.286476000
1	-0.982653000	4.152720000	4.699062000
6	1.065117000	4.331449000	5.320287000
1	1.238974000	5.231111000	4.746648000
6	2.069775000	3.755746000	6.091051000
1	3.057292000	4.195085000	6.139745000
6	1.777541000	2.604296000	6.801933000
1	2.539947000	2.137957000	7.407335000
6	0.503195000	2.043651000	6.732972000
6	0.133229000	0.819725000	7.459364000
6	0.987186000	0.155948000	8.340593000
1	1.984555000	0.525154000	8.524791000
6	0.542292000	-0.981836000	8.994436000
1	1.194002000	-1.501312000	9.684277000
6	-0.749132000	-1.440661000	8.753674000
1	-1.137974000	-2.322657000	9.242412000
6	-1.544201000	-0.737047000	7.867675000
1	-2.555674000	-1.053355000	7.646396000

Mo(CO)₃(bpy), *trans*-CO vacancy (¹GS, CPCM(MeCN))

42	-2.697585000	1.943925000	6.598248000
8	-5.513920000	0.669400000	7.084373000
8	-4.161354000	3.852678000	4.609897000
8	-3.629386000	3.957152000	8.730836000
7	-0.623629000	2.715167000	6.295480000
7	-1.325911000	0.602102000	7.763113000
6	-4.444508000	1.103763000	6.893378000
6	-3.612930000	3.122324000	5.341663000
6	-3.260078000	3.187056000	7.924314000
6	-0.340182000	3.802911000	5.562509000
1	-1.184643000	4.308906000	5.119207000
6	0.949617000	4.271445000	5.382908000
1	1.121933000	5.155212000	4.785044000
6	1.995553000	3.587156000	5.988820000
1	3.016269000	3.928353000	5.875864000
6	1.712975000	2.460508000	6.748060000
1	2.513918000	1.922414000	7.231588000
6	0.392509000	2.035463000	6.878063000
6	0.005441000	0.839918000	7.656197000
6	0.938622000	-0.007429000	8.247031000
1	1.995871000	0.185073000	8.144968000
6	0.501973000	-1.112680000	8.963019000
1	1.219618000	-1.777854000	9.424273000
6	-0.862068000	-1.351401000	9.069250000
1	-1.249403000	-2.201017000	9.613835000
6	-1.737886000	-0.473365000	8.452988000
1	-2.806908000	-0.622736000	8.505038000

Mo(CO)₂(bpy), *trans*-CO^{1/2} vacancy (¹GS, CPCM(MeCN))

42	-2.708072000	1.903600000	6.541168000
8	-5.539174000	0.791078000	7.219039000
8	-4.127413000	3.888649000	4.616891000
7	-0.623320000	2.669302000	6.238559000
7	-1.324984000	0.564562000	7.720397000
6	-4.452422000	1.189830000	6.969055000
6	-3.599908000	3.132762000	5.361621000
6	-0.340088000	3.762868000	5.508768000
1	-1.180655000	4.240270000	5.027086000
6	0.942100000	4.263918000	5.373649000
1	1.112544000	5.148890000	4.776675000
6	1.983804000	3.610837000	6.022357000
1	2.998672000	3.977938000	5.943830000
6	1.701672000	2.484891000	6.782720000
1	2.498040000	1.974163000	7.302453000
6	0.389041000	2.025229000	6.870932000
6	0.006067000	0.825344000	7.642172000
6	0.941325000	-0.008191000	8.250072000
1	1.997152000	0.199986000	8.163530000
6	0.511867000	-1.118471000	8.962338000
1	1.232024000	-1.772497000	9.435417000
6	-0.851497000	-1.374203000	9.050192000
1	-1.234833000	-2.227381000	9.592418000
6	-1.730536000	-0.513151000	8.415082000
1	-2.798033000	-0.679987000	8.448395000

Mo(CO)₃(bpy), trans-py vacancy (³MC₁, CPCM(MeCN))

42	-2.333961000	1.830551000	5.871106000
8	-4.294727000	3.521643000	3.999470000
8	-1.504833000	-0.187974000	3.554446000
8	-3.559133000	3.304986000	8.415942000
7	-0.354066000	2.726585000	5.996229000
7	-1.124369000	0.537430000	7.216019000
6	-3.591573000	2.892203000	4.673718000
6	-1.811384000	0.572824000	4.375632000
6	-3.092432000	2.785063000	7.488579000
6	-0.042840000	3.852615000	5.329136000
1	-0.839410000	4.299962000	4.750813000
6	1.216666000	4.416130000	5.374519000
1	1.417290000	5.321161000	4.818648000
6	2.201848000	3.799345000	6.141276000
1	3.197793000	4.217200000	6.201888000
6	1.885040000	2.641610000	6.832317000
1	2.633126000	2.147036000	7.433444000
6	0.597625000	2.115612000	6.743212000
6	0.165543000	0.889397000	7.426298000
6	0.998019000	0.119451000	8.237102000
1	2.026999000	0.405964000	8.393486000
6	0.492383000	-1.017648000	8.846060000
1	1.127780000	-1.624721000	9.477074000
6	-0.836493000	-1.365342000	8.630962000
1	-1.271441000	-2.242983000	9.087380000
6	-1.607995000	-0.564918000	7.807566000
1	-2.643060000	-0.798642000	7.600656000

Mo(CO)₃(bpy), trans-CO vacancy (³MC₂, CPCM(MeCN))

42	-2.613380000	2.102443000	6.684609000
8	-5.329865000	0.497861000	6.849997000
8	-4.294219000	3.906666000	4.667578000
8	-3.908756000	3.414957000	9.194923000
7	-0.592325000	2.781241000	6.302595000
7	-1.334320000	0.692115000	7.710819000
6	-4.326960000	1.070731000	6.775615000
6	-3.661927000	3.251432000	5.376184000
6	-3.406358000	2.933208000	8.268871000
6	-0.266416000	3.837069000	5.509154000
1	-1.099417000	4.368091000	5.071411000
6	1.024381000	4.231275000	5.271685000
1	1.217276000	5.081105000	4.632016000
6	2.076389000	3.519360000	5.880866000
1	3.104862000	3.814705000	5.719232000
6	1.772885000	2.442053000	6.681403000
1	2.564567000	1.879926000	7.154938000
6	0.434171000	2.061400000	6.880174000
6	0.026972000	0.915089000	7.648994000
6	0.917701000	0.051582000	8.309168000
1	1.980628000	0.238733000	8.258958000
6	0.442731000	-1.032566000	9.011071000
1	1.128267000	-1.701756000	9.513628000
6	-0.946447000	-1.257310000	9.061767000
1	-1.363773000	-2.098051000	9.598046000
6	-1.780331000	-0.381642000	8.417102000
1	-2.852428000	-0.515273000	8.439161000

Mo(CO)₂(bpy), *trans*-CO^{1/2} vacancy (³MC₂, CPCM(MeCN))

42	-2.659526000	1.900420000	6.527258000
8	-5.597499000	0.926814000	7.067559000
8	-4.482046000	3.750230000	4.759849000
7	-0.583631000	2.661936000	6.230695000
7	-1.294678000	0.565491000	7.698202000
6	-4.480185000	1.245332000	6.891876000
6	-3.767151000	3.083633000	5.412336000
6	-0.297070000	3.754295000	5.499266000
1	-1.135944000	4.229180000	5.011981000
6	0.986246000	4.255371000	5.371622000
1	1.161564000	5.139451000	4.775048000
6	2.024019000	3.603308000	6.027603000
1	3.039362000	3.970514000	5.954572000
6	1.739432000	2.478400000	6.788164000
1	2.533226000	1.968729000	7.312981000
6	0.426871000	2.019197000	6.871148000
6	0.038050000	0.827987000	7.645174000
6	0.961823000	0.001151000	8.279318000
1	2.018844000	0.212090000	8.216750000
6	0.518886000	-1.105911000	8.987706000
1	1.229895000	-1.755391000	9.480642000
6	-0.845622000	-1.365632000	9.047346000
1	-1.237443000	-2.217454000	9.585423000
6	-1.713232000	-0.510452000	8.389978000
1	-2.780818000	-0.678452000	8.402317000

CO (¹GS, CPCM(MeCN))

8	-3.907998000	3.407877000	9.191220000
6	-3.417512000	2.942488000	8.289884000

References

- (1) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179. DOI: 10.1021/om100106e.
- (2) Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96* (2), 877–910. DOI: 10.1021/cr940053x.
- (3) Bao, D.; Millare, B.; Xia, W.; Steyer, B. G.; Gerasimenko, A. A.; Ferreira, A.; Contreras, A.; Vullev, V. I. Electrochemical oxidation of ferrocene: a strong dependence on the concentration of the supporting electrolyte for nonpolar solvents. *J. Phys. Chem. A* **2009**, *113* (7), 1259–1267. DOI: 10.1021/jp809105f.
- (4) Frantz, R.; Carre', F.; Durand, J.-O.; Lanneau, G. F. New phosphonates containing a π -conjugated ferrocenyl unit. *New J. Chem.* **2001**, *25* (2), 188–190. DOI: 10.1039/B008937K.
- (5) STOE & Cie, X-Area; STOE & Cie, 2002.
- (6) Koziskova, J.; Hahn, F.; Richter, J.; Kožišek, J. Comparison of different absorption corrections on the model structure of tetrakis(μ 2 -acetato)-diaqua-di-copper(II). *Acta Chim. Slov.* **2016**, *9* (2), 136–140. DOI: 10.1515/acs-2016-0023.
- (7) STOE & Cie, X-Area LANA; STOE & Cie GmbH, 2002.
- (8) Sheldrick, G. M. SHELXT - integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015**, *71* (Pt 1), 3–8. DOI: 10.1107/S2053273314026370.
- (9) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015**, *71* (Pt 1), 3–8. DOI: 10.1107/S2053229614024218.
- (10) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. A* **2008**, *64* (Pt 1), 112–122. DOI: 10.1107/S0108767307043930.
- (11) Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44* (Pt 6), 1281–1284. DOI: 10.1107/S0021889811043202.
- (12) Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishi, S.; Tobita, S. Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector. *Phys. Chem. Chem. Phys.* **2009**, *11* (42), 9850–9860. DOI: 10.1039/b912178a.
- (13) Zhang, Y.; Lee, T. S.; Favale, J. M.; Leary, D. C.; Petersen, J. L.; Scholes, G. D.; Castellano, F. N.; Milsmann, C. Delayed fluorescence from a zirconium(IV) photosensitizer with ligand-to-metal charge-transfer excited states. *Nat. Chem.* **2020**, *12* (4), 345–352. DOI: 10.1038/s41557-020-0430-7.
- (14) Bilger, J. B.; Kerzig, C.; Larsen, C. B.; Wenger, O. S. A Photorobust Mo(0) Complex Mimicking Os(2,2'-bipyridine)₃²⁺ and Its Application in Red-to-Blue Upconversion. *J. Am. Chem. Soc.* **2021**, *143* (3), 1651–1663. DOI: 10.1021/jacs.0c12805.
- (15) Montalti, M.; Murov, S. L. *Handbook of photochemistry*, 3rd ed.; CRC/Taylor & Francis, 2006.
- (16) Wang, C.; Reichenauer, F.; Kitzmann, W. R.; Kerzig, C.; Heinze, K.; Resch-Genger, U. Efficient Triplet-Triplet Annihilation Upconversion Sensitized by a Chromium(III) Complex via an Underexplored Energy Transfer Mechanism. *Angew. Chem. Int. Ed.* **2022**, *61* (27), e202202238. DOI: 10.1002/anie.202202238.
- (17) Schmid, L.; Kerzig, C.; Prescimone, A.; Wenger, O. S. Photostable Ruthenium(II) Isocyanoborato Luminophores and Their Use in Energy Transfer and Photoredox Catalysis. *JACS Au* **2021**, *1* (6), 819–832. DOI: 10.1021/jacsau.1c00137.
- (18) Sell, A. C.; Wetzels, J. C.; Schmitz, M.; Maijenburg, A. W.; Woltersdorf, G.; Naumann, R.; Kerzig, C. Water-soluble ruthenium complex-pyrene dyads with extended triplet lifetimes for efficient energy transfer applications. *Dalton Trans.* **2022**, *51* (28), 10799–10808. DOI: 10.1039/D2DT01157C.

- (19) Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA quantum chemistry program package. *J. Chem. Phys.* **2020**, *152* (22), 224108. DOI: 10.1063/5.0004608.
- (20) Becke, A. D. Density - functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652. DOI: 10.1063/1.464913.
- (21) Miehlisch, B.; Savin, A.; Stoll, H.; Preuss, H. Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, *157* (3), 200–206. DOI: 10.1016/0009-2614(89)87234-3.
- (22) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297–3305. DOI: 10.1039/B508541A.
- (23) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8* (9), 1057–1065. DOI: 10.1039/b515623h.
- (24) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A ‘chain-of-spheres’ algorithm for the Hartree–Fock exchange. *Chem. Phys.* **2009**, *356* (1–3), 98–109. DOI: 10.1016/j.chemphys.2008.10.036.
- (25) Izsák, R.; Neese, F. An overlap fitted chain of spheres exchange method. *J. Chem. Phys.* **2011**, *135* (14), 144105. DOI: 10.1063/1.3646921.
- (26) Pantazis, D. A.; Chen, X.-Y.; Landis, C. R.; Neese, F. All-Electron Scalar Relativistic Basis Sets for Third-Row Transition Metal Atoms. *J. Chem. Theory Comput.* **2008**, *4* (6), 908–919. DOI: 10.1021/ct800047t.
- (27) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* **1998**, *102* (11), 1995–2001. DOI: 10.1021/jp9716997.
- (28) Miertuš, S.; Scrocco, E.; Tomasi, J. Electrostatic interaction of a solute with a continuum. A direct utilization of AB initio molecular potentials for the prevision of solvent effects. *Chem. Phys.* **1981**, *55* (1), 117–129. DOI: 10.1016/0301-0104(81)85090-2.
- (29) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104. DOI: 10.1063/1.3382344.
- (30) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32* (7), 1456–1465. DOI: 10.1002/jcc.21759.
- (31) Plasser, F. TheoDOR: A toolbox for a detailed and automated analysis of electronic excited state computations. *J. Chem. Phys.* **2020**, *152* (8), 84108. DOI: 10.1063/1.5143076.
- (32) Smidstrup, S.; Pedersen, A.; Stokbro, K.; Jónsson, H. Improved initial guess for minimum energy path calculations. *J. Chem. Phys.* **2014**, *140* (21), 214106. DOI: 10.1063/1.4878664.
- (33) Nocedal, J. Updating quasi-Newton matrices with limited storage. *Math. Comp.* **1980**, *35* (151), 773. DOI: 10.1090/S0025-5718-1980-0572855-7.
- (34) Santoro, A.; Sambiagio, C.; McGowan, P. C.; Halcrow, M. A. Synthesis and coordination chemistry of 1,1,1-tris-(pyrid-2-yl)ethane. *Dalton Trans.* **2015**, *44* (3), 1060–1069. DOI: 10.1039/c4dt02824d.
- (35) Manuta, D. M.; Lees, A. J. Solvent and substituent effects on the lowest energy excited states of $M(CO)_4(\text{diimine})$ ($M = \text{Cr, Mo, W}$) complexes. *Inorg. Chem.* **1983**, *22* (25), 3825–3828. DOI: 10.1021/ic00167a031.
- (36) Overton, C.; Connor, J. A. Binuclear 2,2'-bipyrimidine complexes derived from chromium, molybdenum and tungsten carbonyls. *Polyhedron* **1982**, *1* (1), 53–56. DOI: 10.1016/S0277-5387(00)81068-2.
- (37) Gimeno, L.; Queffélec, C.; Mall Haidaraly, K.; Blart, E.; Pellegrin, Y. Dehalogenation reaction photocatalyzed by homoleptic copper(I) complexes associated with strongly reductive sacrificial donors. *Catal. Sci. Technol.* **2021**, *11* (18), 6041–6047. DOI: 10.1039/D1CY01209F.

-
- (38) Braga, S. S.; Coelho, A. C.; Gonçalves, I. S.; Almeida Paz, F. A. (2,2' - Bipyridine)tetracarbonylmolybdenum(0). *Acta Crystallogr. E* **2007**, *63* (3), m780-m782. DOI: 10.1107/S1600536807007234.
- (39) Reichardt, C. Solvatochromic Dyes as Solvent Polarity Indicators. *Chem. Rev.* **1994**, *94* (8), 2319–2358. DOI: 10.1021/cr00032a005.
- (40) Burgess, J. Solvent effects on the visible absorption spectra of Mo(CO)₄(Bipy) and W(CO)₄(Bipy). *J. Organomet. Chem.* **1969**, *19* (1), 218–220. DOI: 10.1016/S0022-328X(00)87776-1.
- (41) Goetz, M.; Kerzig, C.; Naumann, R. An “all-green” catalytic cycle of aqueous photoionization. *Angew. Chem. Int. Ed.* **2014**, *53* (37), 9914–9916. DOI: 10.1002/anie.201405693.
- (42) Kerzig, C.; Goetz, M. Combining energy and electron transfer in a supramolecular environment for the “green” generation and utilization of hydrated electrons through photoredox catalysis. *Chem. Sci.* **2016**, *7* (6), 3862–3868. DOI: 10.1039/C5SC04800A.
- (43) Müller, P.; Brettel, K. Ru(bpy)(3)(2+) as a reference in transient absorption spectroscopy: differential absorption coefficients for formation of the long-lived (3)MLCT excited state. *Photochem. Photobiol. Sci.* **2012**, *11* (4), 632–636. DOI: 10.1039/C2PP05333K.
- (44) Boden, P.; Di Martino-Fumo, P.; Bens, T.; Steiger, S.; Albold, U.; Niedner-Schatteburg, G.; Gerhards, M.; Sarkar, B. NIR-Emissive Chromium(0), Molybdenum(0), and Tungsten(0) Complexes in the Solid State at Room Temperature. *Chem. Eur. J.* **2021**, *27* (51), 12959–12964. DOI: 10.1002/chem.202102208.
- (45) Boden, P.; Di Martino-Fumo, P.; Bens, T.; Steiger, S.; Albold, U.; Niedner-Schatteburg, G.; Gerhards, M.; Sarkar, B. Corrigendum: NIR-Emissive Chromium(0), Molybdenum(0), and Tungsten(0) Complexes in the Solid State at Room Temperature. *Chem. Eur. J.* **2023**, e202301532. DOI: 10.1002/chem.202301532.
- (46) Morse, P. M. Diatomic Molecules According to the Wave Mechanics. II. Vibrational Levels. *Phys. Rev.* **1929**, *34* (1), 57–64. DOI: 10.1103/PhysRev.34.57.
- (47) Kerzig, C.; Wenger, O. S. Sensitized triplet-triplet annihilation upconversion in water and its application to photochemical transformations. *Chem. Sci.* **2018**, *9* (32), 6670–6678. DOI: 10.1039/C8SC01829D.
- (48) Carmichael, I.; Hug, G. L. Triplet–Triplet Absorption Spectra of Organic Molecules in Condensed Phases. *J. Phys. Chem. Ref. Data* **1986**, *15* (1), 1–250. DOI: 10.1063/1.555770.

6.11 Supporting Information for Theoretical calculations supporting annihilator design and experimental findings (Section 3.2)



Supporting Information

Blue-to-UVB Upconversion, Solvent Sensitization and Challenging Bond Activation Enabled by a Benzene-Based Annihilator

T. J. B. Zähringer, J. A. Moghtader, M.-S. Bertrams, B. Roy, M. Uji, N. Yanai, C. Kerzig**

Supporting Information

Contents

1.	General experimental details and methods.....	2
1.1	Materials.....	2
1.2	Steady-state measurements	2
1.3	Excitation light sources.....	2
1.4	Determination of fluorescence quantum yields.....	3
1.5	Determination of the threshold intensity I_{th}	3
1.6	Upconversion quantum yields.....	4
1.7	Quenching rate constants	4
1.8	Determination of FRET parameters.....	5
1.9	Laser flash photolysis	6
1.10	Irradiation experiments.....	6
1.11	Fluorescence lifetime measurements	6
1.12	Chromatography.....	7
1.13	NMR spectroscopy	7
1.14	Gas chromatography and mass spectrometry	7
1.15	Preparation of deoxygenated solutions for photon upconversion studies	7
2.	Synthetic procedures.....	7
2.1	Synthesis of TIPS-ethynyl-benzene derivatives.....	7
2.2	Synthesis of 4CzIPN	9
3.	DFT calculations.....	10
4.	Photophysical properties of benzene and the TIPS-ethynyl substituted benzenes.....	12

5. Threshold intensity measurements.....	13
6. Additional control experiments and spectroscopic measurements of the UC-FRET sequence....	13
7. Additional spectroscopic data	16
8. NMR spectra and analytics.....	19
8.1 Spectra of benzene-derivatives and sensitizer.....	19
8.2 Irradiation experiments.....	23
8.3 Gas chromatography and mass spectrometry	27
9. Supporting references.....	27

1. General experimental details and methods

1.1 Materials

Unless specifically mentioned, all chemicals used for synthesis, irradiation experiments, or optical spectroscopy were commercially obtained and used as received. Tetrahydrofuran, 99.7%, VWR; (triisopropylsilyl)acetylene, 97%, Alfa Aesar; bis(triphenylphosphine)palladium(II) dichloride, 98%, Acros Organics; copper(I) iodide, 99.9%, Alfa Aesar; triphenylphosphine, 99%, Sigma-Aldrich; diisopropylamine, 99.9%, Sigma-Aldrich; 2,4,5,6-tetrafluoro-1,3-benzenedicarbonitrile, 97%, Alfa Aesar; carbazole, 95%, Alfa Aesar; sodium-bis(trimethylsilyl)amide 2 M in THF, 99.7%, Alfa Aesar; *p*-terphenyl, Alfa Aesar, 98%; 1,4-dibromobenzene, 98%, Alfa Aesar; bromobenzene, 99%, Sigma-Aldrich; 1,3,5-tribromobenzene, 98%, Acros Organics; acetone, 99.9%, VWR Chromanorm; cyclohexane, >99.5%, VWR Normapur; sodium sulfate, 99%, Acros Organics; diethyl ether, 99.5%, VWR; pinacolone, 97%, Thermo Scientific; C₆D₁₂, 99.5%, deuterio; toluene-d₈, 99.5%, deuterio; CDCl₃, 99.8%, deuterio; ethanol, 99.8%, VWR; coumarin 6, >98%, TCI; 1,2-diphenylethane, 98%, Thermo Scientific; 1,3-diphenylacetone, 99%, Thermo Scientific; ultrapure Millipore MilliQ water with a specific resistance of 18.2 MΩ cm.

Argon from Nippon Gases (5.0) or Air Liquid Japan (6.0) was used for removing dissolved oxygen before all experiments related to optical spectroscopy.

1.2 Steady-state measurements

Steady-state emission measurements at room temperature were performed using a Perkin Elmer FL-6500 spectrometer. Absorption spectra were recorded with a Perkin Elmer LAMBDA 365 UV-Vis spectrophotometer. All spectra were recorded at room temperature (295 ± 3 K) using quartz glass cuvettes. Emission spectra were corrected regarding the wavelength-dependent sensitivity of the instrument. Emissive chemicals were employed in very low concentrations to eliminate filter effects. Phosphorescence spectra at 77K were measured by using a JASCO FP-8700 spectrofluorometer.

1.3 Excitation light sources

The following light sources were employed for photon upconversion studies and application-related irradiation experiments: (i) a 447 nm cw laser (Roithner Lasertechnik, optical output: up to 1.1 W, with adjustable laser power and a beam size of ~0.10 cm², (ii) a 445 nm diode laser (75 mW, RGB Photonics), (iii) two 440 nm LEDs (Kessil Science, PR160L) with an average intensity reported as 352 mW cm⁻² (1 cm distance). Emission spectra of the LED and the 447 nm cw laser were measured by irradiating a water-containing cuvette in the FL-6500 instrument and recording the Rayleigh scattering light; the spectra so obtained are shown in Figure S1.

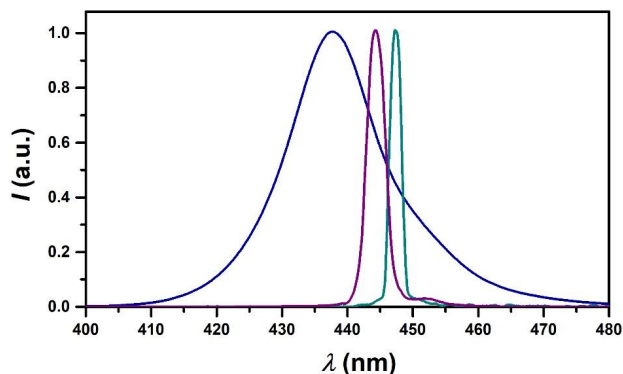


Figure S1. Emission spectra of the PR160L 440 nm LED from Kessil Science (blue), the 447 nm cw laser from Roithner Lasertechnik (green) and the 445 nm diode laser from RGB Photonics (purple). The emission spectra were measured by irradiating a water-containing cuvette in the emission spectrometer.

1.4 Determination of fluorescence quantum yields

The fluorescence quantum yield of **bTIPS-Bz** was determined in relation to a reference system **ref** (*p*-terphenyl in cyclohexane, $\Phi = 0.93$)^[1] by the comparison of their respective fluorescence emission spectra. In equation (1) Φ_i depicts the quantum yield, I the fluorescence intensity integrated over the wavenumber, A the absorption at the irradiation wavelength, and n the refractive index of the solvent of the corresponding system taken from literature.^[1] The fluorescence quantum yield for **bTIPS-Bz** was measured at four different excitation wavelengths (265, 270, 275 and 285 nm) and averaged over all results. Due to the high absorption coefficient of toluene below 300 nm, we could not determine the fluorescence quantum yield in the solvent mixture cyclohexane/toluene (9:1). However, we assume that the quantum yield is not significantly affected by the addition of 10% toluene. This is corroborated by very similar excited-singlet state lifetimes in neat cyclohexane and the above-mentioned solvent mixture containing toluene. The fluorescence quantum yield of **4CzIPN** in cyclohexane/toluene (9:1) was taken from the literature.^[2] The systems used to determine the fluorescence quantum yields were prepared with an optical density below 0.1 at the irradiation wavelengths to circumvent filter effects.

$$\Phi_{\text{Fl}} = \Phi_{\text{Fl,ref}} \cdot \frac{I}{I_{\text{ref}}} \cdot \frac{A_{\text{ref}}}{A} \cdot \frac{n^2}{n_{\text{ref}}^2} \quad (1)$$

1.5 Determination of the threshold intensity I_{th}

For TTA-UC emission spectra, a 445 nm diode laser (75 mW, RGB Photonics) was used as the excitation source. The laser power was controlled by combining the software (Ltune) and a variable neutral density filter and measured using a PD300-UV photodiode sensor (OPHIR Photonics). The laser beam was focused on a sample using a lens. The diameters of the laser beam ($1/e^2$) were measured at the sample position using a CCD beam profiler SP620 (OPHIR Photonics). A typical area of the laser beam spot estimated from the diameter was $2.1 \cdot 10^{-4} \text{ cm}^2$. The emitted light was monitored by a multichannel detector MCPD-9800 (Otsuka Electronics). A 425 nm short-pass filter was used between the sample and the detector. For I_{th} measurements, the emitted light was focused by an achromatic lens for detecting the upconverted emission from low excitation intensity. TTA-UC

emission spectra above 300 nm were calibrated by using a standard xenon lamp L7810-03 (HAMAMATSU). The UC solutions have been prepared in an argon-filled glovebox.

1.6 Upconversion quantum yields

The upconversion quantum yield was determined from the ratios of (integrated) upconverted photons and the integrated emission of reference systems with well-known quantum yields. For that two different methods/setups were employed as detailed below.

(i) A 1 cm quartz cuvette containing an argon-saturated **4CzIPN** solution (reference quantum yield, 0.90)^[2] in the absence of the annihilator was measured under identical conditions as the complete upconversion system. The 447 nm cw laser was employed and installed at a 90° angle with respect to the FL-6500 detector. The precise laser power was adjusted using a calibration sheet provided by the manufacturer. In some measurements, a neutral density filter from Newport was used to attenuate the luminescence signal in order to avoid over-saturation of the detector.

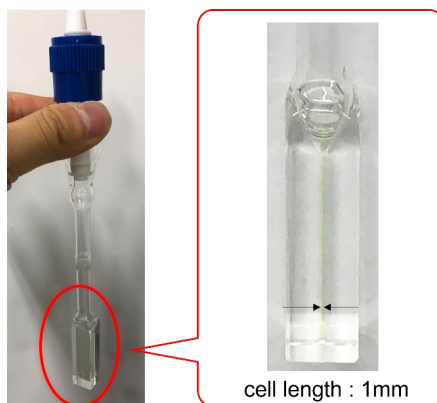


Figure S2. 1 mm quartz cuvette used for photon upconversion studies.

(ii) A 1 mm quartz cuvette (Figure S2) containing a 50 μM coumarin 6 solution was measured under identical conditions as the complete upconversion system. The 445 nm laser was employed and controlled as described in Section 1.5. The UC solutions have been prepared in an argon-filled glovebox. We measured the absolute fluorescence quantum yield of Coumarin 6 in cyclohexane:toluene (9:1) as 96.1% and used it for the calculation of Φ_{UC} .

$$\Phi_{\text{UC}} = \Phi_{\text{std}} \left(\frac{1 - 10^{-A_{\text{std}}}}{1 - 10^{-A_{\text{UC}}}} \right) \left(\frac{I_{\text{std}}}{I_{\text{UC}}} \right) \left(\frac{F_{\text{UC}}}{F_{\text{std}}} \right) \left(\frac{n_{\text{UC}}}{n_{\text{std}}} \right)^2 \quad (2)$$

The overall quantum yield Φ_{UC} was then determined according to equation (2). Where Φ , A , I , F , and n represent quantum yield, absorbance at either 447 nm or 445 nm, excitation intensity, integrated photoluminescence spectral profile, and solvent refractive index, respectively. The subscripts UC and std denote the parameters of the upconversion and standard systems. Note that the theoretical maximum of Φ_{UC} is 50%.

1.7 Quenching rate constants

The triplet-triplet energy transfer constant, k_{TET} , and FRET rates, k_{FRET} , were determined from Stern–Volmer experiments. The lifetime of the delayed sensitizer emission was measured with different concentrations c_q of **bTIPS-Bz** and fitted in a Stern–Volmer plot according to equation (3).

4

With the unquenched lifetime (7.9 μ s), the quenching rate constant k_{TET} was derived from the corresponding Stern–Volmer constant K_{SV} .

The FRET rates with the acceptors acetone and pinacolone were obtained by two different methods:

Method A: Either the kinetic emission traces at 318 nm (see main paper, Figure 5E) between 0 μ s and 300 μ s or the spectral upconversion emission of **bTIPS-Bz** between 300 nm and 400 nm (delay: 6 μ s, integration over 500 μ s, see main paper, Figure 5F) with varying quencher concentration were integrated and plotted in a Stern–Volmer graph. A linear fit was obtained by averaging the results of both (spectral and kinetic) measurements for each concentration. The LFP setup with 355 nm excitation described in Section 1.9 was used for these measurements.

Method B: The fluorescence lifetime (see Section 1.11 for the experimental setup) of **bTIPS-Bz** was measured with different concentrations c_q of acetone and fitted in a Stern–Volmer plot. Pinacolone could not be studied with this method due to its high absorption at our excitation wavelengths and resulting artifacts.

With the natural lifetime of **bTIPS-Bz** in Ar-saturated cyclohexane:toluene (9:1) (2.86 ns, see Figure S14), the quenching rate constant k_{FRET} was derived from the corresponding Stern–Volmer constant K_{SV} .

$$\frac{\tau_0}{\tau} = \frac{\phi_0}{\phi} = \frac{F_0}{F} = 1 + \tau_0 \cdot k_q \cdot c_q = 1 + K_{\text{SV}} \cdot c_q \quad (3)$$

1.8 Determination of FRET parameters

The spectral overlap integral $J(\lambda)$ between the absorption of the acceptors **AC** and **PC** with the annihilator **bTIPS-Bz** emission was obtained from equation (4).^[3]

$$J(\lambda) = \int_0^\infty \varepsilon_A(\lambda) \lambda^4 F_D(\lambda) d\lambda \quad (4)$$

With the molar absorption coefficient of the acceptor ε_A and the normalized fluorescence of the donor F_D .

$$J_{\text{AC}} = 2.5 \cdot 10^{10} \cdot \text{M}^{-1} \text{cm}^{-1} \text{nm}^4$$

$$J_{\text{PC}} = 5.8 \cdot 10^{10} \cdot \text{M}^{-1} \text{cm}^{-1} \text{nm}^4$$

The Förster radii, R_0 , of **AC** or **PC** as acceptor and **bTIPS-Bz** as donor were calculated by the following equation:^[3]

$$R_0 = 0.221 (\kappa^2 n^{-4} \Phi_D J(\lambda))^{\frac{1}{6}} \text{ (in } \text{\AA}) \quad (5)$$

With the orientation factor κ , the refractive index n , the fluorescence quantum yield of **bTIPS-Bz** and the respective spectral overlap integral $J(\lambda)$.

$$R_{0,\text{AC}} = 0.7 \text{ nm}$$

$$R_{0,\text{PC}} = 0.8 \text{ nm}$$

1.9 Laser flash photolysis

The LP980KS setup from Edinburgh Instruments equipped with an Nd:YAG laser from Litron (Nano LG 300-10) was employed for transient absorption and time-resolved emission spectroscopy. The frequency-tripled output with a wavelength of 355 nm served as the excitation source. The laser pulse duration was ~ 5 ns and the pulse frequency was 10 Hz. The typical pulse energy used for transient absorption and emission studies was 15 mJ. Detection of transient absorption spectra occurred on an ICCD camera from Andor. Kinetic traces at selected wavelengths were recorded using a photomultiplier tube. The spectroscopic experiments were performed at 293 K using a cuvette holder that allows temperature control. If not stated otherwise the TA spectra were integrated over 100 ns.

1.10 Irradiation experiments

The deoxygenated solutions were irradiated in Teflon-sealed NMR tubes with either the 447 nm cw laser or two 440 nm LEDs from Kessil (see excitation light sources for details) that were installed 90° to each other (Figure S3). During the experiment the NMR tube was kept at a constant temperature using a water bath in combination with a fan. Long-pass filters with a cut-off wavelength of 385 nm were used to filter out high-energy photons that might be emitted from the LEDs.



Figure S3. Setup for the irradiation experiments using two blue LEDs.

1.11 Fluorescence lifetime measurements

The *mini- τ* setup from Edinburgh Instruments (time-correlated single photon counting (TCSPC) technique) equipped with a pulsed LED (EPLED-300, excitation at ~ 293 nm) was employed for fluorescence lifetime measurements of **bTIPS-Bz** at 293 K. Stray light was removed with a long-pass filter with a cut-off wavelength of 320 nm from Newport and neutral density filters were used to avoid oversaturation of the detector.

Time-resolved upconversion lifetime measurements (Figure 3C, main paper) were carried out by using a time-correlated single-photon counting lifetime spectroscopy system, HAMAMATSU Quantaaurus-Tau C11367-21, C11567-02 and M12977-01. A xenon flashlamp (60W, pulse duration ≤ 3 μ s) equipped with a 445 nm band-pass filter served as light source. The solutions for these measurements have been prepared in an argon-filled glovebox.

1.12 Chromatography

For standard liquid column chromatography separation silica gel 60 M (0.040-0.063 mm Macherey-Nagel GmbH & Co., Düren, Germany) was used. Thin layer chromatography (TLC) was performed using "DC Kieselgel 60 F254" (Merck KGaA, Darmstadt, Germany) on aluminum and a UV lamp (Benda, NU-4 KL, λ = 254 nm and 365 nm, Wiesloch, Germany) was employed for detection. The resulting R_f values are given relative to the solvent.

1.13 NMR spectroscopy

For NMR spectroscopy a multinuclear magnetic resonance spectrometer of the type AV II 400 (Bruker, Karlsruhe, Germany) was employed. The chemical shifts are given as δ -values in ppm and they were referenced relative to the residue signal of the non-deuterated solvent. The following abbreviations were used: singlet (s), doublet (d), multiplet (m), and the coupling constant (J).

1.14 Gas chromatography and mass spectrometry

Gas chromatography was performed on an Agilent 8890 GC using a HP 5MS UI column (30 m x 0.25 mm x 0.25 μ m) and a flow of 1.2 ml/min helium. The flow was split to an FID and an Agilent 5977 GC/MSD. Injector temperature 250 °C, MS source temperature 250 °C, transfer line temperature 230 °C, quadrupole temperature 150 °C. Oven temperature program: Hold 40 °C for 2 min, heat at 50 °C to 320 °C and hold for 7.4 min.

1.15 Preparation of deoxygenated solutions for photon upconversion studies

Unless noted otherwise, the solutions for photon upconversion experiments were deoxygenated in custom-made Schlenk-cuvettes^[2] by five freeze-pump-thaw cycles using argon as an inert gas, liquid N₂ for cooling, and Schlenk line vacuum (down to 0.2 mbar).

2. Synthetic procedures

2.1 Synthesis of TIPS-ethynyl-benzene derivatives

The TIPS-ethynyl-functionalized benzenes were synthesized according to the Sonogashira coupling reaction analogous to the preparation of similar aromatic compounds.^[2,4] The exact quantities are listed for each benzene derivative below. The bromobenzene, Pd(PPh₃)₂Cl₂, CuI, PPh₃, and dry THF were added to a flame-dried round-bottom flask under argon flow. The flask was equipped with a condenser column. Diisopropylamine was added to the solution under constant stirring. The flask was then heated to 70 °C and (triisopropylsilyl)acetylene was added dropwise to the mixture. The mixture was held at 70 °C for 12 h under argon atmosphere. The completion of the reaction was tested with TLC. After cooling, the mixture was filtered and the solvent was removed under reduced pressure. The residue was redissolved in chloroform and washed twice with deionized water and twice with brine. The organic layer was dried with Na₂SO₄ and the solvent was removed under reduced pressure. If not stated otherwise, the product was purified via column chromatography (neat cyclohexane) and then if required recrystallized from ethanol/water (9:1). NMR spectra (see below) of all TIPS-ethynyl-benzenes derivatives agree with those reported in the literature.^[5]

1,4-bis((triisopropylsilyl)ethynyl)benzene (bTIPS-Bz): 1.418 g 1,4-dibromobenzene (4.30 mmol), 36.5 mg Pd(PPh₃)₂Cl₂ (0.052 mmol), 26.2 mg CuI (0.14 mmol), 36.1 mg PPh₃ (0.14 mmol), 28 mL dry THF, 13.5 mL diisopropylamine and 1.85 mL (triisopropylsilyl)acetylene (8.26 mmol); yield = 1.573 g, 3.59 mmol (84%) after column chromatography. Obtained as a colorless solid.

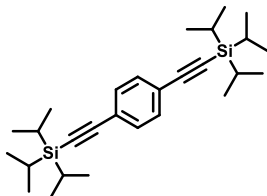
$R_f(\text{cyclohexane}) = 0.5$

GC-FID: purity > 99 %

EI-MS (*m/z*): calculated for [M + H]⁺: 438.314, found 438.350.

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.39 (s, 4H), 1.13 (s, 42H);

¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 131.9, 123.5, 106.8, 92.8, 18.8, 11.5.



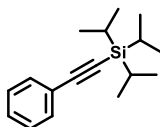
((triisopropylsilyl)ethynyl)benzene (TIPS-Bz)^[a] 675 mg bromobenzene (4.30 mmol), 18.26 mg Pd(PPh₃)₂Cl₂ (0.026 mmol), 13.1 mg CuI (0.069 mmol), 18 mg PPh₃ (0.069 mmol), 28 mL dry THF, 7 mL diisopropylamine and 0.93 mL (triisopropylsilyl)acetylene (4.13 mmol); yield = 354 mg, 1.37 mmol (32%).

[a] A colorless liquid was obtained from column chromatography, which was then distilled under vacuum (10⁻² mbar) at 80°C.

R_f(cyclohexane) = 0.75

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.29-7.32 (m, 3H), 7.47-7.49 (m, 2H), 1.13 (pseudo-s, 21H);

¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 132.2, 128.4, 128.32, 123.7, 107.2, 90.6, 18.8, 11.5.

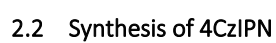


1,3,5-tris((triisopropylsilyl)ethynyl)benzene (tTIPS-Bz): 1,322 g 1,3,5-tribromobenzene (4.30 mmol), 54.8 mg Pd(PPh₃)₂Cl₂ (0.078 mmol), 39.3 mg CuI (0.21 mmol), 54.1 mg PPh₃ (0.21 mmol), 48 mL dry THF, 20 mL diisopropylamine and 2.78 mL (triisopropylsilyl)acetylene (12.39 mmol); yield = 2.38 g, 7.1 mmol (33%) after recrystallization. Obtained as a colorless solid.

R_f(cyclohexane) = 0.5

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.47 (s, 3H), 1.13 (pseudo-s, 63H);

¹³C NMR (400 MHz, CDCl₃): δ [ppm] = 135.0, 124.0, 105.2, 92.1, 18.7, 11.3.



The compound 4CzIPN was still available from our recent study.^[2] It was purified by sublimation prior to its use as sensitizer. The ¹H NMR spectrum agrees with that reported in the literature.^[6]

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.22(d, J_{HH} = 8 Hz, 2H), 7.74-7.67 (m, 8H), 7.51-7.47 (m, 2H), 7.33 (d, J_{HH} 8 Hz, 2H), 7.23-7.21 (m, 4H), 7.12-7.05 (m, 8H) 6.84-6.80 (m, 4H), 6.65-6.61 (m, 2H).



3. DFT calculations

The DFT calculations for structure optimization and frequency analysis were carried out using the Gaussian 09 software package^[7] with the B3LYP functional and the 6-311+G(d,p) basis set. No negative vibrational frequencies were observed in the optimized structures indicating the successful convergence on minimum structures. Initially, singlet ground states were optimized and the resulting structures served as the starting point for the corresponding triplet state calculations. Spin densities of the triplet states were obtained by single-point calculations following successful optimizations. The calculated triplet energies, $E_T(\text{DFT})$, were determined by comparing the energies of the optimized singlet ground states to those of the corresponding triplet states.^[8] The TIPS-ethynyl substituents add numerous degrees of rotational freedom and consequently require huge computational effort. For the initial screening of the annihilators used in this work, we replaced the TIPS-ethynyl by TMS-ethynyl substituents simplifying the calculations significantly. We found similar E_T values, deviating by 0.01 eV when comparing respective mono- and di-substituted TIPS-ethynyl and TMS-ethynyl. Based on these results, the triplet energy for **tTIPS-Bz** (for which we could not obtain suitable optimized structures and energies) was extrapolated from **tTMS-Bz**.

Time-dependent DFT calculations with identical functional and basis were used to calculate the vertical excitation energies for simulating the triplet-triplet absorption spectrum of **bTIPS-Bz**. The predicted transitions and their oscillator strengths are displayed in Figure 3B (main paper). The calculated triplet absorption spectrum shows a global maximum at 361 nm, which is in good agreement with the experimental triplet absorption spectrum peaking at 348 nm.

Table S1. Computed triplet energies (in eV or kJ/mol) for benzene and corresponding TIPS- or TMS-derivatives.

Compound	$E_T(\text{DFT})^{[a]}$ [eV]	$E_T(\text{lit.})^{[b]}$ [eV]	$E_T(\text{corr.})^{[c]}$ [eV]	$E_T(\text{corr.})^{[d]}$ [kJ mol ⁻¹]
Benzene (Bz)	3.83	3.9	-	-
TIPS-Bz	3.01	-	3.06	295
TMS-Bz	3.02	-	3.07	296
bTIPS-Bz	2.53	-	2.57	248
bTMS-Bz	2.54	-	2.58	249
tTIPS-Bz	n.a.	-	2.97 ^[e]	287 ^[e]
tTMS-Bz	2.92	-	2.98	288

[a] DFT-calculated triplet energy at the B3LYP/6-311+G(d,p) level of theory. [b] Experimental triplet energy from ref^[9]. [c] Calculated triplet energy corrected by the underestimation factor from benzene (i.e., calculated E_T multiplied by 1.02). [d] Energies converted to kJ/mol. [e] Estimated value from comparison of TIPS and TMS derivatives.

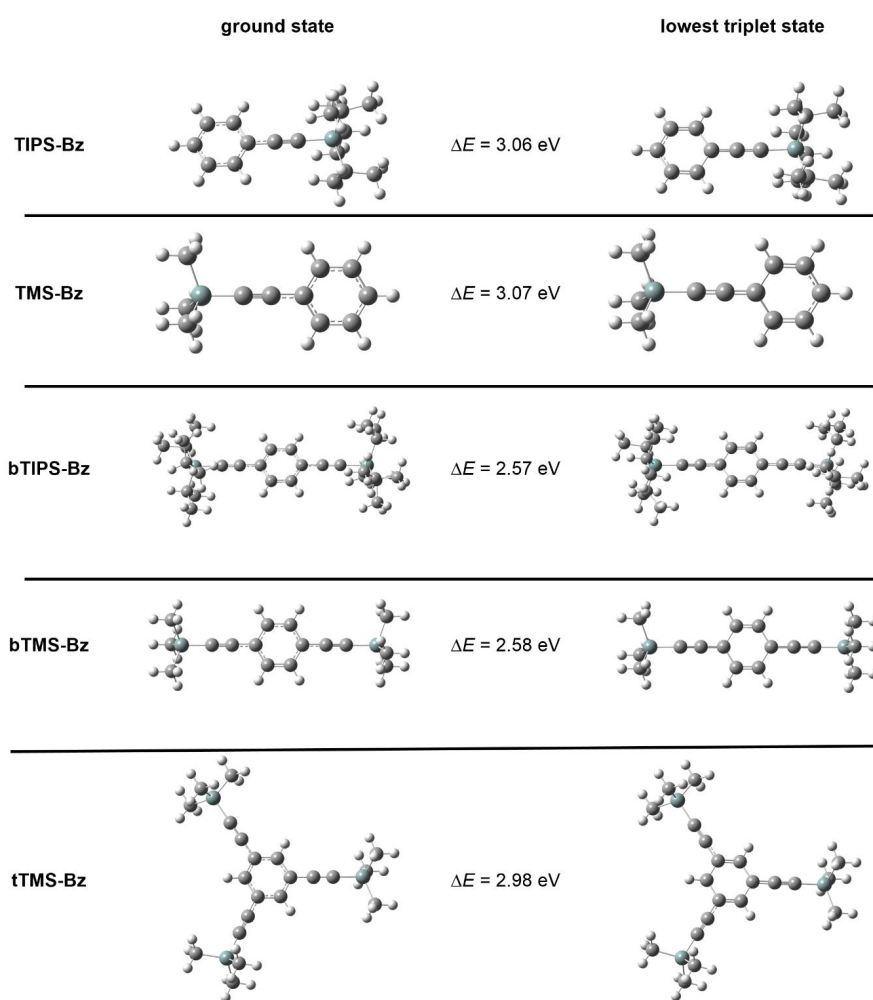


Figure S4. Optimized ground state (left) and lowest triplet state (right) structures of TIPS-Bz, TMS-Bz, bTIPS-Bz, bTMS-Bz and tTMS-Bz with their calculated triplet energies, $E_T(\text{DFT})$.

4. Photophysical properties of benzene and the TIPS-ethynyl substituted benzenes

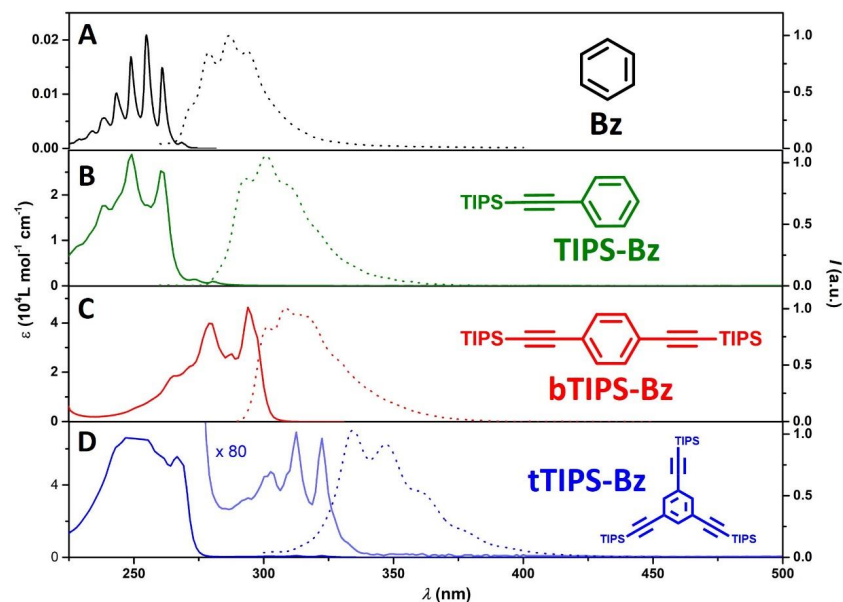


Figure S5. Absorption (solid lines) and normalized photoluminescence (dotted lines) spectra of benzene (Bz) (panel A)^[a], TIPS-Bz (panel B), bTIPS-Bz (panel C) and tTIPS-Bz (panel D) in cyclohexane. [a] Taken from ref.^[10].

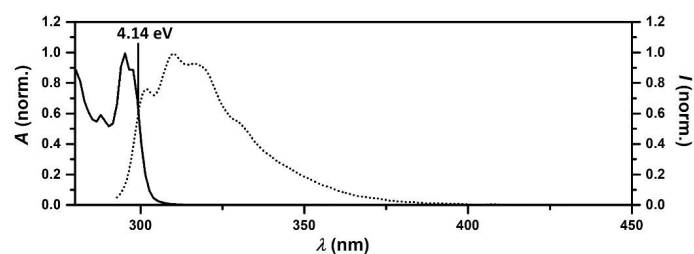


Figure S6. Absorption (solid lines) and normalized photoluminescence (dotted lines) spectrum of bTIPS-Bz in cyclohexane:toluene (9:1). The absorption spectrum could not be recorded below 280 nm owing to the toluene background absorption.

5. Threshold intensity measurements

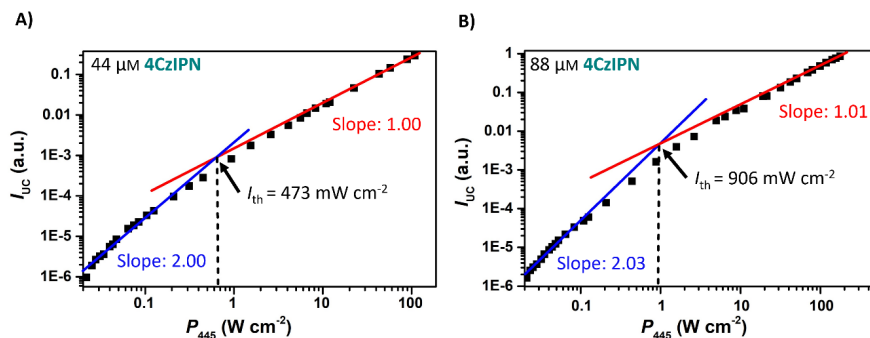


Figure S7. Normalized UC emission of deoxygenated solutions containing A) 44 or B) 88 μM **4CzIPN** and 10 mM **bTIPS-Bz** in cyclohexane:toluene (9:1) using a 445 nm cw laser for excitation. The UC signal was plotted against the laser power on a double-logarithmic scale. The threshold intensity I_{th} was determined from the crossing point of the linear (slope ~ 1) and the quadratic (slope ~ 2) fit.

6. Additional control experiments and spectroscopic measurements of the UC-FRET sequence

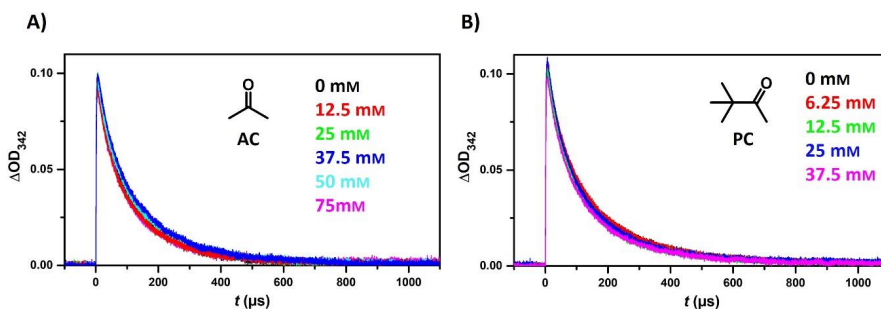


Figure S8. Kinetic traces of the **bTIPS-Bz** triplet state recorded at 342 nm after 355 nm excitation of 20 μM **4CzIPN** and 10 mM **bTIPS-Bz** in Ar-saturated cyclohexane:toluene (9:1) with different concentrations of acetone (A) and pinacolone (B). The measurements were recorded with the same solutions as in Figure 5 E/F of the main paper.

Figure S8 A/B show the kinetic traces of the **bTIPS-Bz** triplet state with increasing carbonyl (acetone and pinacolone) concentrations. Only slight variances of the lifetime and concentration with no clear trends are observed that most likely stem from minor laser fluctuations and/or residual oxygen impurities. It can therefore be concluded that the triplet-triplet annihilation process is unaffected by the addition of the carbonyls and thus the decreasing UC emission does not originate from unproductive quenching of the sensitizer or annihilator triplet.

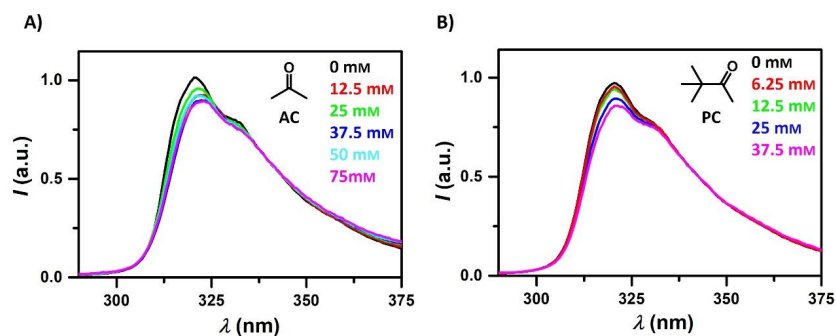


Figure S9. Normalized time-gated (delay, 6 μ s; integration over 500 μ s) emission spectra after 355 nm laser excitation of 20 μ M **4CzIPN** and 10 mM **bTIPS-Bz** in Ar-saturated cyclohexane:toluene (9:1) with different concentrations of (A) pinacolone and (B) acetone. The emission spectra were scaled to identical intensity at 340 nm.

The kinetic traces of the upconversion emission in Figure 5E (main paper) were recorded at a central detection wavelength of 318 nm (monochromator slit width, 17 nm). This wavelength was selected as it provides the best signal quality, being the maximum emission and avoids stray laser light (355 nm). However, at this wavelength the carbonyls acetone and pinacolone already show minor absorption.

$$\varepsilon_{318}(\text{AC}) = 2 \cdot \text{M}^{-1}\text{cm}^{-1}$$

$$\varepsilon_{318}(\text{PC}) = 5 \cdot \text{M}^{-1}\text{cm}^{-1}$$

Calculating the absorption with the highest concentration used in Figure 5 E/F and the average optical pathlength we obtain the following values:

$$A_{318}(\text{AC}) = 2 \cdot \text{M}^{-1}\text{cm}^{-1} \cdot 75 \text{ mM} \cdot 0.5 \text{ cm} = 0.075$$

$$A_{318}(\text{PC}) = 5 \cdot \text{M}^{-1}\text{cm}^{-1} \cdot 37.5 \text{ mM} \cdot 0.5 \text{ cm} = 0.094$$

These simple calculations suggest that less than 20% of the emission attenuation in Figure 5E is due to reabsorption rather than FRET. This is further supported when the emission spectra with increasing quencher concentrations are scaled to an identical intensity at a wavelength where the carbonyl compounds do not absorb (shown in Figure S9).

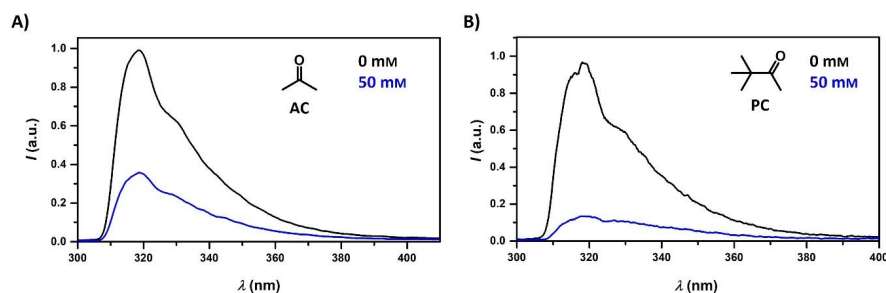


Figure S10. Normalized upconversion emission spectra of deoxygenated solutions containing 44 μM **4CzIPN** and 10 mM **bTIPS-Bz** in the absence and presence of 50 mM **AC** (A) or **PC** (B) in cyclohexane:toluene (9:1) using a cw laser for excitation at 447 nm (laser power 100 mW).

Additional UC emission quenching experiments were performed with a cw laser for excitation at 447 nm. A solution containing 44 μM **4CzIPN** and 10 mM **bTIPS-Bz** was irradiated in the absence and presence of 50 mM **AC** (A) or **PC** (B) in cyclohexane:toluene (9:1) (Figure S10). The UC signal decreases when the carbonyls are added and the quenching is about twice as efficient with **PC** compared to **AC**. These qualitative results are in perfect agreement with the LFP measurements from Figure 5 (main paper). However, we regard the LFP measurements as more reliable for extracting quenching rate constants because of the observed Norrish fragmentation for **PC** under cw excitation conditions (note that it takes about 1 min to record a spectrum displayed in Figure S10), which does not take place upon excitation with a single 355 nm laser pulse.

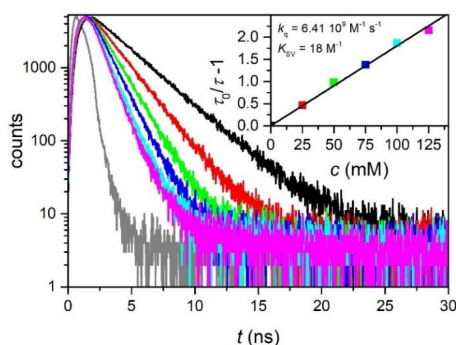


Figure S11. Lifetime-based fluorescence quenching experiments of 15 μM **bTIPS-Bz** with varying acetone concentrations in air-saturated cyclohexane upon pulsed LED (293 nm, grey trace corresponds to IRF) excitation. Inset: Corresponding Stern–Volmer plot.

Lifetime-based Stern–Volmer fluorescence quenching experiments of **bTIPS-Bz** were conducted with varying acetone concentrations in neat and air-saturated cyclohexane (Figure S11). Oxygen removal was not carried out to ensure exact concentrations of the volatile quencher. The quenching constant $k_q = 6.41 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was calculated using the Stern–Volmer equation (equation 3) and the fluorescence lifetime of **bTIPS-Bz** (2.81 ns) in air-saturated cyclohexane. This slightly higher FRET rate compared to the rate constant ($k_{\text{FRET}} = 5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) obtained by the UC-FRET sequence in Figure 5D of the main paper most likely stems from the different methods of preparation and the slightly different solvent. We assume that the volatile acetone is removed in small amounts by the thorough freeze-pump-thaw method that was carried out with the UC-FRET solutions in Figure 5E/F yielding a slightly lower quenching efficiency.

7. Additional spectroscopic data

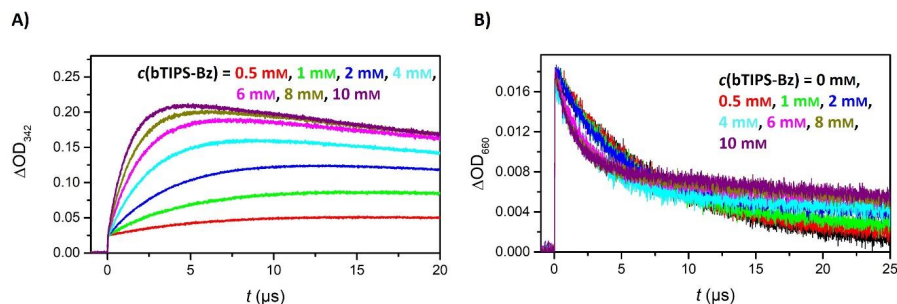


Figure S12. Time-resolved transient absorption measurements after 355 nm laser excitation of solutions containing 20 μM **4CzIPN** in Ar-saturated cyclohexane:toluene (9:1) with different **bTIPS-Bz** concentrations recorded (A) at 342 nm (B) at 660 nm. The measurements were carried out with the same solutions as in Figure 3A (main paper).

The time-resolved transient absorption measurements in Figure S12 were carried out with the same solutions as in Figure 3 of the main paper. The triplet concentration of **bTIPS-Bz** recorded at 342 nm increases with increasing annihilator concentration, as expected (Figure S12A). At a given annihilator concentration, the $^3\text{bTIPS-Bz}$ formation occurs with slightly faster rate constants than the delayed emission quenching of **4CzIPN** (Figure 3A of the main paper). These minor discrepancies are attributed to the subsequent $^3\text{bTIPS-Bz}$ decay complicating the kinetics. Furthermore, the triplet decay of **4CzIPN** was recorded at 660 nm and shortens with increasing annihilator concentration. However, the weak signal is superimposed with the strong absorption of the long-lived $^3\text{bTIPS-Bz}$ species (Figure S12B) (compare, the transient absorption spectra in Figure 3A of the main paper and the predicted $^3\text{bTIPS-Bz}$ transitions). The **4CzIPN** triplet lifetime and its delayed emission (that allows us to indirectly monitor triplet quenching without artifacts of quenching products as in Figure S12) are known to be in excellent correlation and yields practically the same result.^[11] In line with that observation, the τ_0 value in our solvent mixture (7.9 μs) is identical regardless of the detection method ($^3\text{4CzIPN}$ transient absorption at 660 nm or delayed emission at 477 nm). Hence, the (delayed) luminescence lifetime of **4CzIPN** was used for a straightforward kinetic analysis (Figure 3A of the main paper).

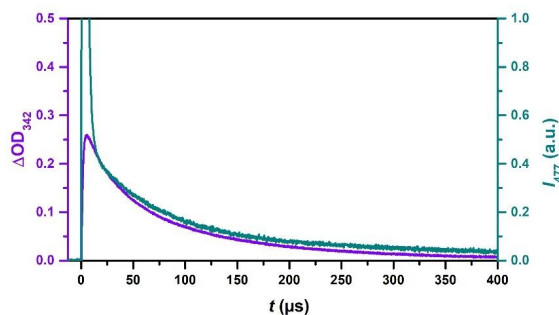


Figure S13. Time-resolved transient absorption and emission measurements of a solution containing 20 μM **4CzIPN** with 10 mM **bTIPS-Bz** in Ar-saturated cyclohexane:toluene 9:1 after excitation with 355 nm laser pulses. Purple curve: Triplet state decay of **bTIPS-Bz** at 342 nm; cyan curve: Elongated emission of **4CzIPN** as a result of back triplet-triplet energy transfer monitored at 477 nm.

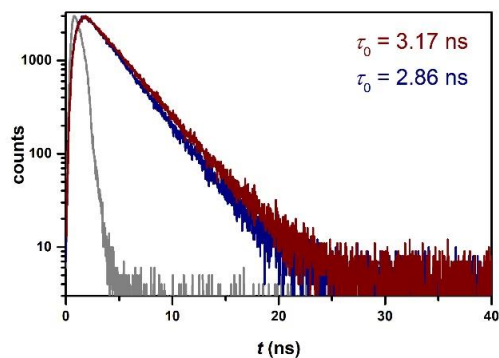


Figure S14. Fluorescence lifetime measurements of 15 μM **bTIPS-Bz** in Ar-saturated neat cyclohexane (dark red) and in cyclohexane:toluene (9:1) (dark blue). Grey trace corresponds to IRF.

Figure S14 displays the fluorescence lifetime measurement of 15 μM **bTIPS-Bz** in neat cyclohexane (dark red) and in a solvent mixture of cyclohexane:toluene (9:1) (dark blue). With the addition of the co-solvent toluene, the lifetime decreases from 3.17 ns to 2.86 ns. The fluorescence lifetime measured in cyclohexane:toluene (9:1) was used to determine the FRET rate constant that is shown in the Stern-Volmer plot (Figure 5B) of the main paper.

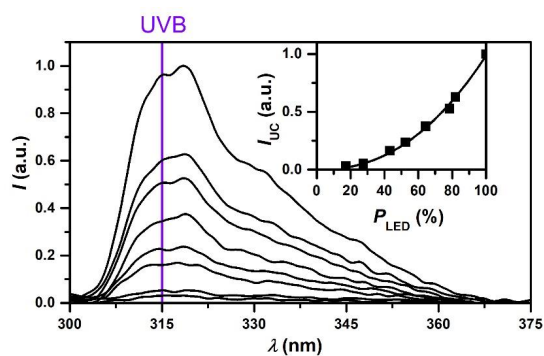


Figure S15. Normalized photon upconversion emission with deoxygenated solutions containing 44 μM 4CzIPN and 10 mM **bTIPS-Bz** in cyclohexane:toluene (9:1) using a blue LED (440 nm) as excitation source. Inset: Normalized upconversion emission plotted against the relative LED power.

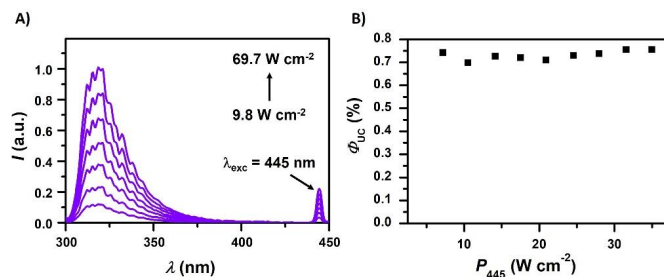


Figure S16. Photon upconversion studies with deoxygenated solutions containing 44 μM **4CzIPN** and 10 mM **bTIPS-Bz** in cyclohexane:toluene (9:1) using a cw laser for excitation at 445 nm. A) Power-dependent spectra of the normalized upconverted emission. B) External upconversion quantum yield, Φ_{UC} , plotted against the laser power density.

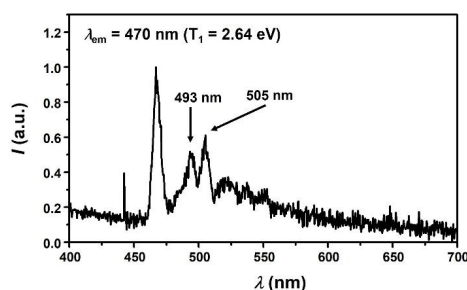


Figure S17. Phosphorescence spectrum of 10 mM **bTIPS-Bz** recorded at 77K in 2-methyltetrahydrofuran.

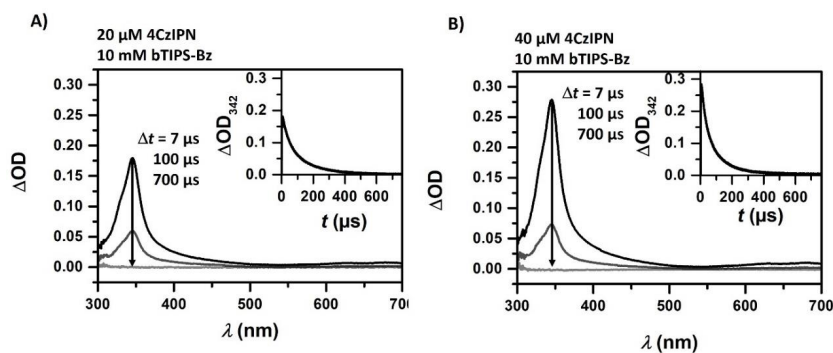


Figure S18. Transient absorption measurements of a solution containing 20 μM (A) or 40 μM (B) **4CzIPN** with 10 mM **bTIPS-Bz** in Ar-saturated cyclohexane:toluene (9:1) after excitation with 355 nm laser pulses. Insets: Kinetic measurements at 342 nm.

Figure S18 shows transient absorption spectra of the upconversion solution (**4CzIPN**–**bTIPS-Bz**) with detection window delays of 7, 100 and 700 μs . The strong absorption of triplet-excited **bTIPS-Bz** peaking at 342 nm fully decays after 700 μs (Inset). No spectroscopic signatures of long-lived species that would originate from electron transfer (such as sensitizer bleach or radical ion absorption bands) are detected. Even at higher concentrations of **4CzIPN** (40 μM) (which strongly increases the signal intensities and the probability for reactions between singlet-excited **bTIPS-Bz** and **4CzIPN**) no new species appear.

8. NMR spectra and analytics

8.1 Spectra of benzene-derivatives and sensitizer

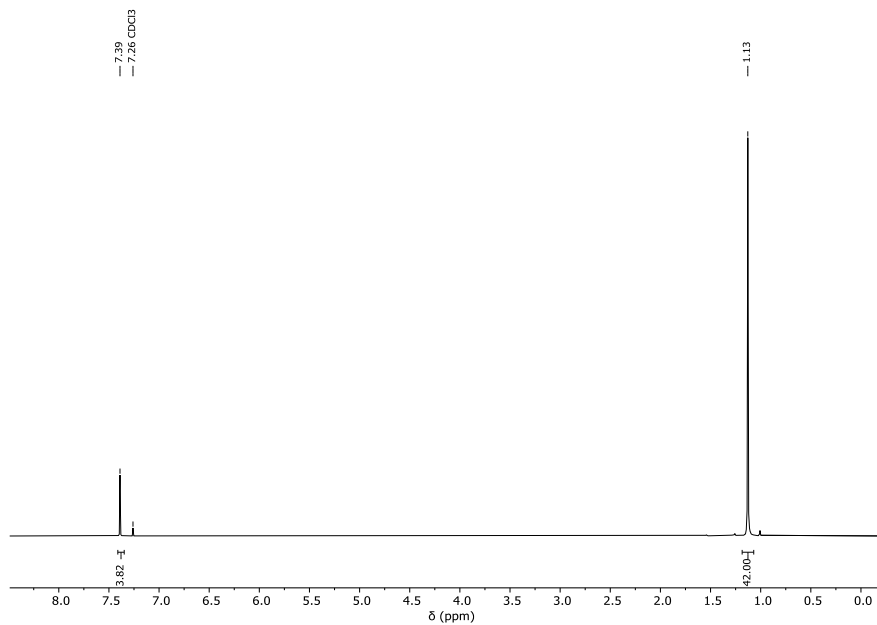


Figure S19. ^1H NMR spectrum of 1,4-bis((triisopropylsilyl)ethynyl)benzene (bTIPS-Bz).

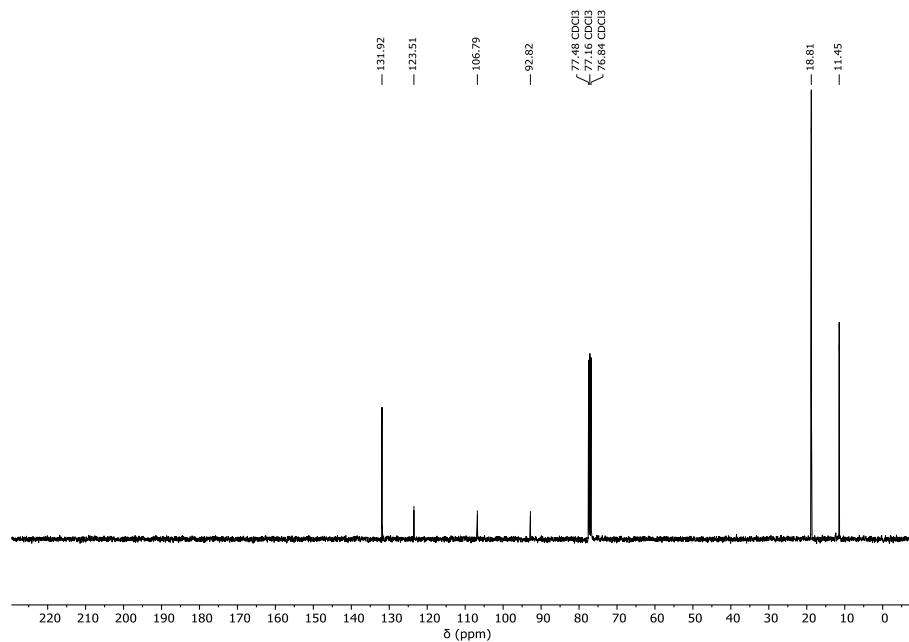


Figure S20. ¹³C NMR spectrum of 1,4-bis((triisopropylsilyl)ethynyl)benzene (**bTIPS-Bz**).

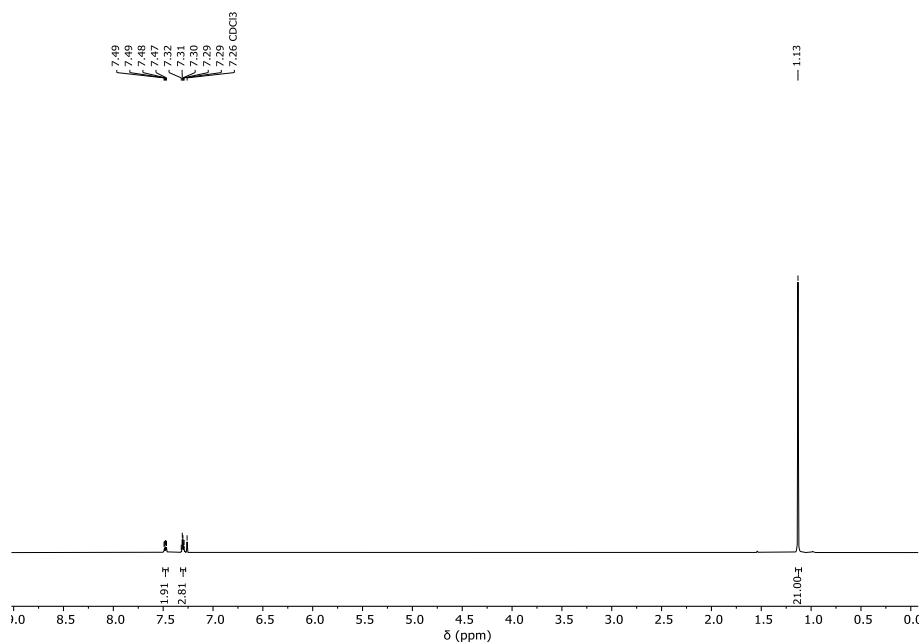


Figure S21. ¹H NMR spectrum of triisopropyl(phenylethynyl)silane (**TIPS-Bz**).

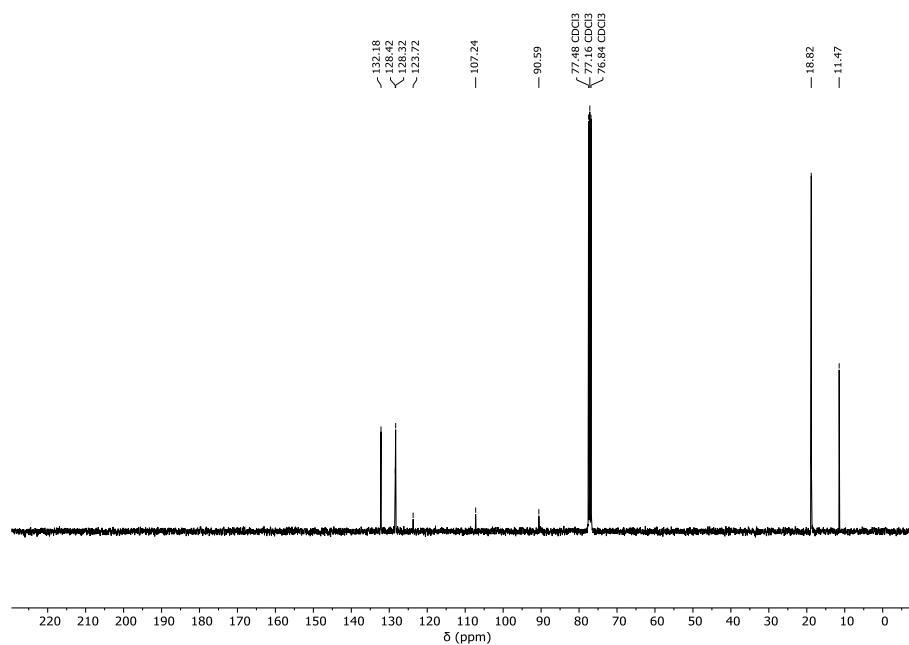


Figure S22. ¹³C NMR spectrum of triisopropyl(phenylethynyl)silane (TIPS-Bz).

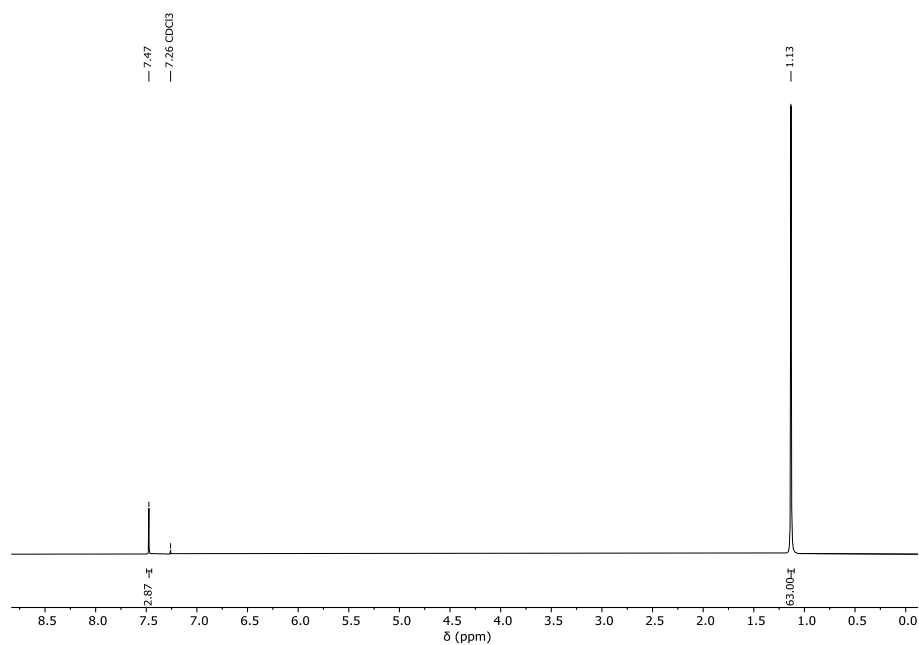


Figure S23. ¹H NMR spectrum of 1,3,5-tris((triisopropylsilyl)ethynyl)benzene (tTIPS-Bz).

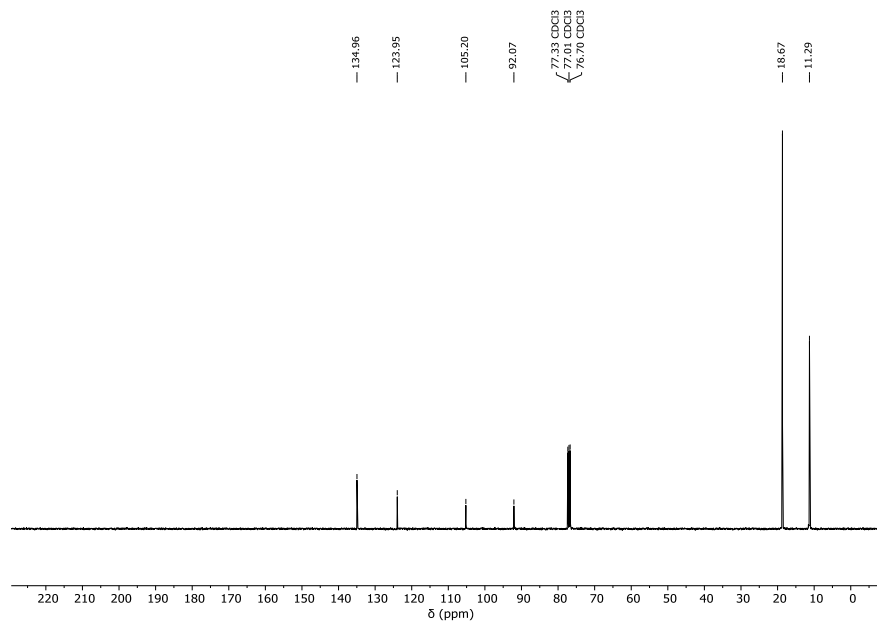


Figure 24. ¹³C NMR spectrum of 1,3,5-tris((triisopropylsilyl)ethynyl)benzene (tTIPS-Bz).

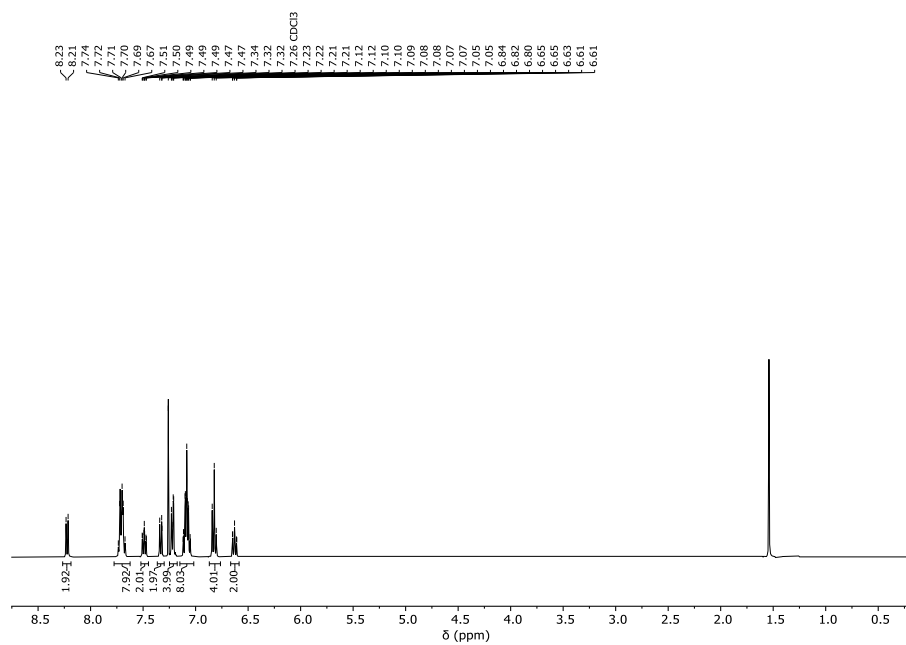


Figure S25. ¹H NMR spectrum of 4CzIPN.

8.2 Irradiation experiments

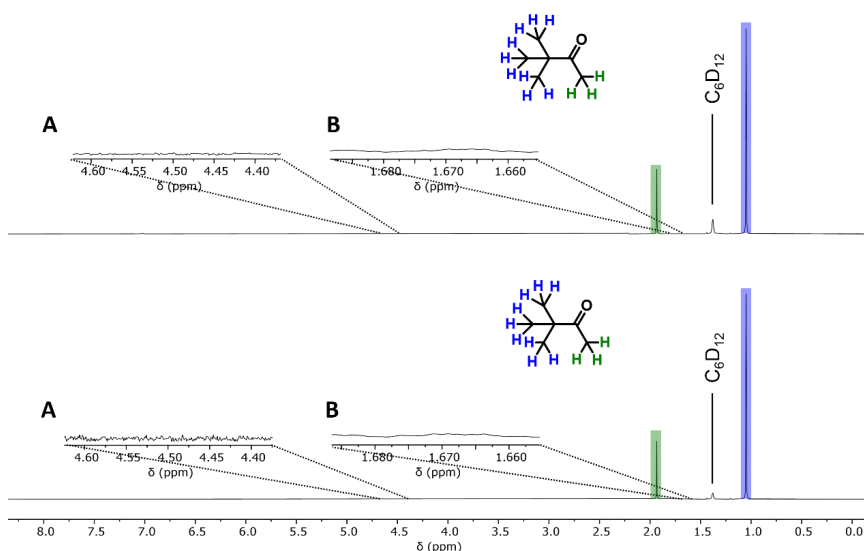


Figure S26. ^1H NMR experiment of 100 μM **4CzIPN** and 100 mM pinacolone in Ar-saturated cyclohexane:toluene (9:1) before (top panel) and after (bottom panel) 30 min of irradiation at 447 nm with 1.1 W. Insets: ^1H NMR region of isobutylene as a stable product of the UC-FRET-driven Norrish reaction. A) septet region; B) triplet region.

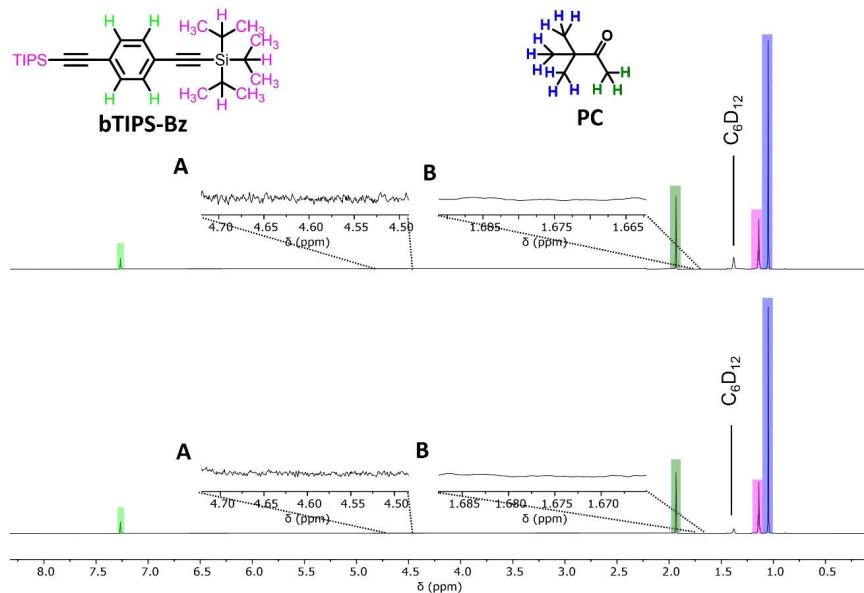


Figure S27. ^1H NMR experiment of 10 mM **bTIPS-Bz** and 100 mM pinacolone in Ar-saturated cyclohexane:toluene (9:1) before (top panel) and after (bottom panel) 30 min of irradiation at 447 nm with 1.1 W. Insets: ^1H NMR region of isobutylene as a stable product of the UC-FRET-driven Norrish reaction. A) septet region; B) triplet region.

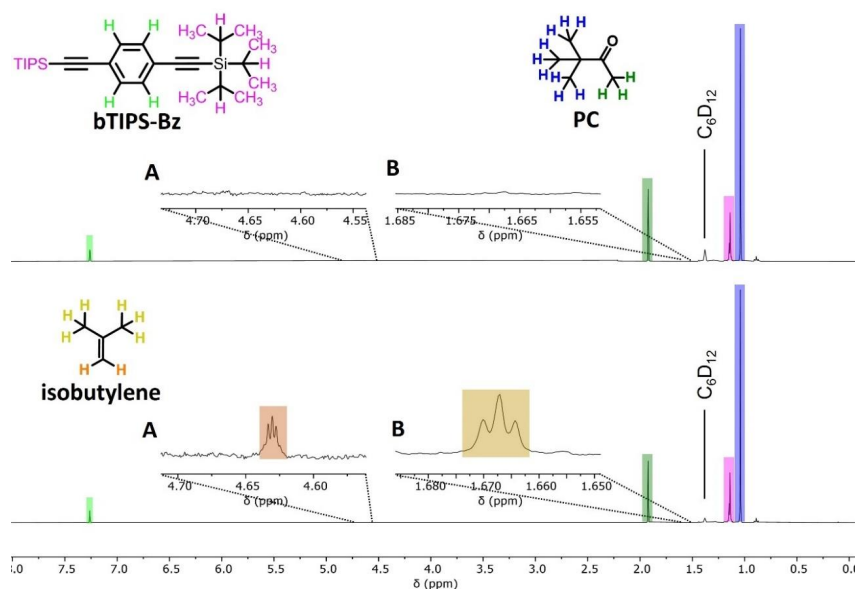


Figure S28. ^1H NMR experiment of 10 mM **bTIPS-Bz**, 100 μM **4CzIPN**, and 100 mM pinacolone in Ar-saturated cyclohexane:toluene (9:1) before (top panel) and after (bottom panel) 30 min of irradiation at 447 nm with 1.1 W. Insets: ^1H NMR region of isobutylene as a stable product of the UC-FRET-driven Norrish reaction. A) septet region; B) triplet region.^[12]

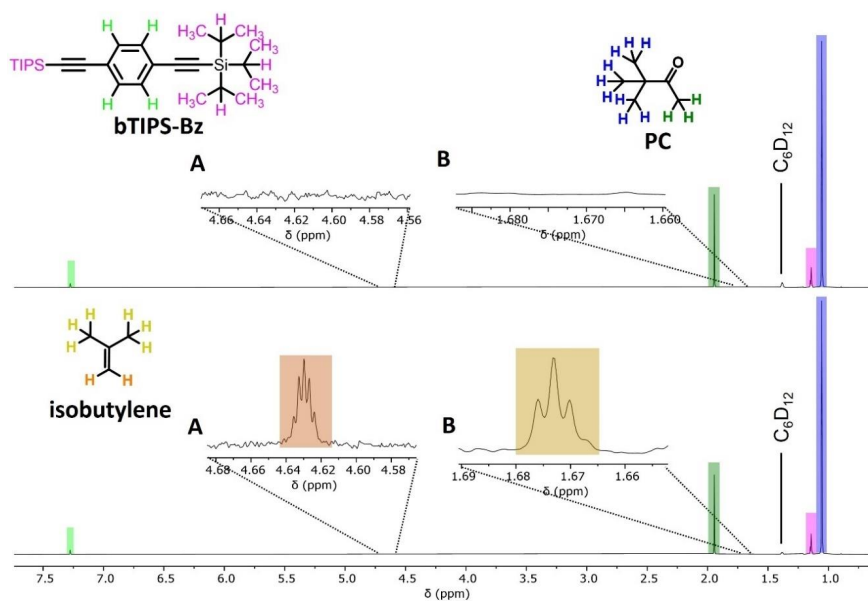


Figure S29. ^1H NMR experiment of 10 mM **bTIPS-Bz**, 100 μM **4CzIPN**, and 100 mM pinacolone in Ar-saturated cyclohexane:toluene (9:1) before (top panel) and after (bottom panel) 1 h of irradiation at 440 nm with two LEDs. Insets: ^1H NMR region of isobutylene as a stable product of the UC-FRET-driven Norrish reaction. A) septet region; B) triplet region.^[12]

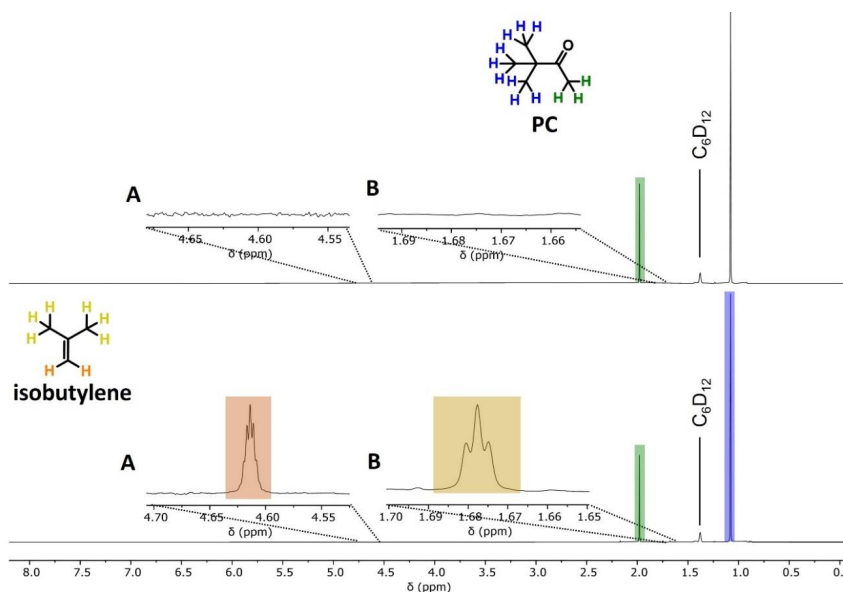


Figure S30. ^1H NMR experiment of 100 mM pinacolone in Ar-saturated cyclohexane before (top panel) and after (bottom panel) 15 min of irradiation with a UV lamp (Benda, NU-4 KL, $\lambda = 254$ nm). In contrast to the setup shown in Figure S3 with direct NMR tube irradiation, a quartz cuvette has been used for these irradiation experiments to ensure that the UV photons penetrate the reaction flask. Insets: ^1H NMR region of isobutylene as a stable product of the UC-FRET-driven Norrish reaction. A) septet region; B) triplet region.^[12]

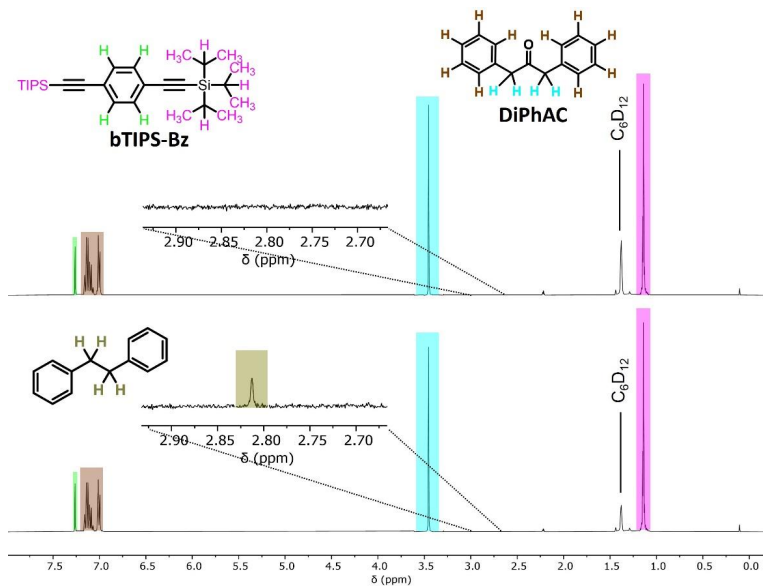


Figure S31. ^1H NMR experiment of 10 mM bTIPS-Bz, 100 μM 4CzIPN, and 50 mM 1,3-diphenylacetone in Ar-saturated cyclohexane:toluene (9:1) before (top panel) and after (bottom panel) 1 h of irradiation at 440 nm with two LEDs (with the setup shown in Figure S3). Inset: ^1H NMR region of 1,2-diphenylethane as a stable product of the UC-FRET-driven Norrish reaction.

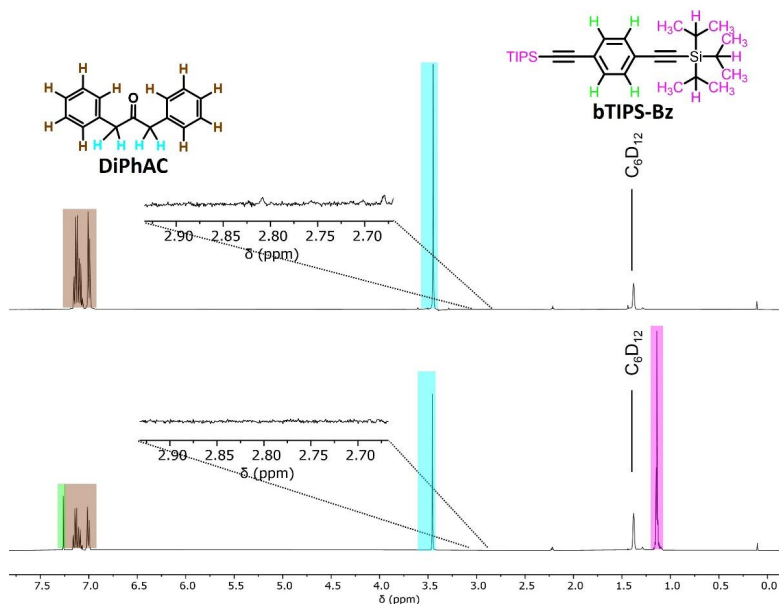


Figure S32. ^1H NMR experiment of 10 mM **bTIPS-Bz** with 50 mM 1,3-diphenylacetone (top panel) and 100 μM **4CzIPN** with 50 mM 1,3-diphenylacetone (bottom panel) in Ar-saturated cyclohexane:toluene (9:1) after 1 h of irradiation at 440 nm with two LEDs (control experiments). Inset: ^1H NMR region of 1,2-diphenylethane as a stable product of the UC-FRET-driven Norrish reaction.

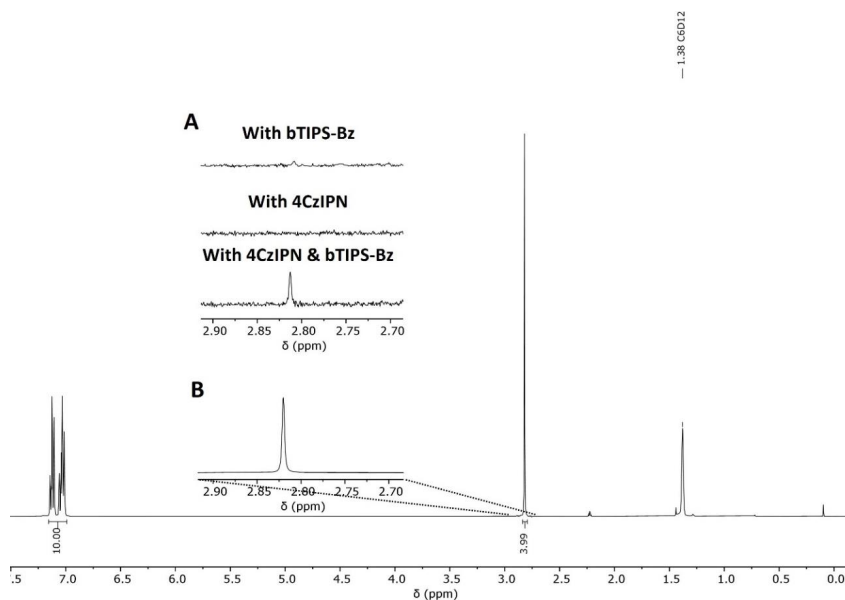


Figure S33. ^1H NMR of 1,2-diphenylethane in cyclohexane:toluene (9:1). Insets: ^1H NMR region of benzylic hydrogens. A) ^1H NMR spectra of irradiation and control experiments (taken from Figures S31 and S32). The signal was scaled to the benzylic hydrogens of 1,3-diphenylacetone. B) ^1H NMR of an authentic sample of the 1,2-diphenylethane reference.

8.3 Gas chromatography and mass spectrometry

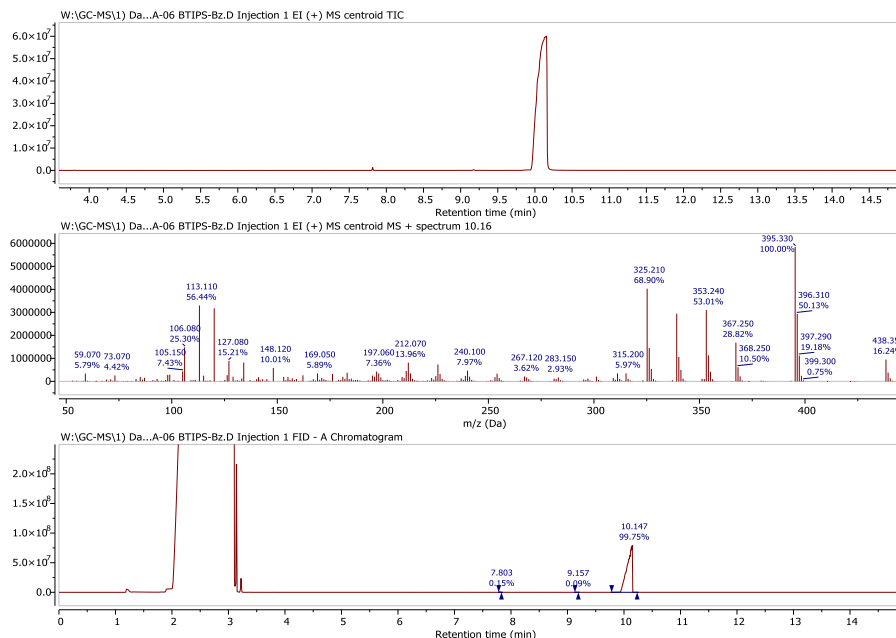


Figure S34. GC analysis and EI-MS spectrum of bTIPS-Bz.

9. Supporting references

- [1] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, J. Michl, V. Balzani, *Handbook of photochemistry*, CRC/Taylor & Francis, Boca Raton, **2006**.
- [2] T. J. B. Zähringer, M.-S. Bertrams, C. Kerzig, *J. Mater. Chem. C* **2022**, *10*, 4568.
- [3] J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Springer, New York, NY, **2006**.
- [4] N. Harada, Y. Sasaki, M. Hosoyamada, N. Kimizuka, N. Yanai, *Angew. Chem. Int. Ed.* **2021**, *60*, 142.
- [5] a) B. Feng, Y. Yang, J. You, *Chem. Commun.* **2020**, *56*, 790; b) E. A. Ziemann, J. B. Mietner, M. Deffner, N. van Steerteghem, K. Clays, C. Herrmann, J. Heck, *Eur. J. Inorg. Chem.* **2015**, *2015*, 1111.
- [6] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, *492*, 234.
- [7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. (Ed.) *Gaussian Inc. Wallingford CT*, **2009**.
- [8] a) V. Gray, A. Dreos, P. Erhart, B. Albinsson, K. Moth-Poulsen, M. Abrahamsson, *Phys. Chem. Chem. Phys.* **2017**, *19*, 10931; b) C. Fischer, C. Kerzig, B. Zilte, O. S. Wenger, C. Sparr, *ACS Catal.* **2020**, *10*, 210; c) L. Vaghi, F. Rizzo, J. Pedrini, A. Mauri, F. Meinardi, U. Cosentino, C. Greco, A. Monguzzi, A. Papagni, *Photochem. Photobiol. Sci.* **2022**, *21*, 913.
- [9] J. P. Doering, *J. Chem. Phys.* **1969**, *51*, 2866.
- [10] I. B. Berlman, *Handbook of fluorescence spectra of aromatic molecules. 2.ed*, Academic Press, New York, N., **1971**.
- [11] F. B. Dias, T. J. Penfold, A. P. Monkman, *Methods Appl. Fluoresc.* **2017**, *5*, 12001.
- [12] Steven J. Peters, Trisha M. Blood, Mark E. Kassabaum, *Eur. J. Org. Chem.* **2009**, *2009*, 6104.

6.12 Supporting Information for Insights into properties of triplet excited ligand-centered states in heteroleptic platinum(II) complexes (Section 3.3)

Supporting Information

Cyclometalated Spirobifluorene Imidazolylidene Platinum(II) Complexes with Predominant ^3LC Emissive Character and High Photoluminescence Quantum Yields

Tim Riesebeck^a, Maria-Sophie Bertrams^b, Sergej Stipurin^a, Kai Konowski^a,
Christoph Kerzig^{*b} and Thomas Strassner^{*a}

^a Physikalische Organische Chemie, Technische Universität Dresden, 01069 Dresden, Germany;

^b Department of Chemistry, Johannes Gutenberg University, 55128 Mainz, Germany

*Prof. Dr. Thomas Strassner
Tel: (+49)351-463-38571.
Fax: (+49)351-463-39679.
E-mail: thomas.strassner@tu-dresden.de

*Jun.-Prof. Dr. Christoph Kerzig
Tel: (+49)6131-39-22479
E-mail: ckerzig@uni-mainz.de

Table of Contents

General Procedures	S-3
Experimental Procedures	S-7
NMR Spectra	S-11
Solid State Structure Details	S-21
Thermogravimetric Analysis	S-25
Additional Emission Measurements	S-26
Energy Transfer Experiments	S-31
Emission Quantum Yields in Solution	S-32
Additional Spectra in PMMA	S-33
Computational Details	S-34
Electrochemistry	S-38
References	S-39

General Procedures

All compounds were synthesized in flame dried Schlenk tubes under an atmosphere of argon unless otherwise noted. Solvents of at least 99.0% purity were used in all reactions in this study. Dimethylformamide (DMF) were dried using standard techniques and stored over molecular sieve (3 Å). Dichloro(cycloocta-1,5-diene)-platinum(II) was prepared according to a modified literature procedure.¹ Sodium (2Z)-4-oxo-2-penten-2-olate and Bis-1,3-(2,4,6-trimethylphenyl)propan-1,3-dione were prepared according to literature known methods.² Further chemicals were obtained from common suppliers and used without further purification. ¹H, ¹³C and ¹⁹⁵Pt spectra were acquired on Bruker Avance 300, Bruker DRX 500 and Bruker Avance 600 NMR spectrometers. ¹H and ¹³C spectra were referenced internally (¹H: 7.26, ¹³C 77.0 for CDCl₃; ¹H: 2.50, ¹³C: 39.43 for DMSO-d₆). ¹⁹⁵Pt spectra were referenced externally by using potassium tetrachloro-platinate(II) in D₂O (PtCl₄²⁻: -1617.2). Chemical shifts are given in ppm, coupling constants in Hz. Elemental analyses were performed by the microanalytical laboratory of our institute on a FlashSmart elemental analyzer from thermoscientific. Melting points were determined by using a Wagner and Munz PolyTherm A system and are not corrected. Electrospray ionization MS spectra were recorded using a LC-MS coupled device by Hewlett Packard (HPLC: 1100, mass detector: Esquire-LC, electrospray ionization).

Photoluminescence measurements

The 2 wt% emitter films were prepared by doctor blading a solution of an emitter in a 10 wt% PMMA solution in dichloromethane on a quartz substrate with a 60 µm doctor blade. The film was dried and the emission was measured under nitrogen atmosphere. Excitation was conducted in a wavelength range of 250-400 nm (Xe lamp with a monochromator), and the emission and quantum yields were measured with the absolute photoluminescence quantum yield spectrometer Quantaurus from Hamamatsu (model C11347-01) utilizing an integrating sphere. Absorption spectra were measured on a Perkin Elmer Lambda 365 UV-vis spectrometer in dichloromethane solutions with an analyte concentration of 5 x 10⁻⁵ mol/l. For measurements at 77 K an emitter was dissolved in 2-methyltetrahydrofuran (5 x 10⁻⁴ mol/l) in a quartz cuvette. The solution was degassed and the atmosphere was exchanged for argon. After freezing the prepared sample, the cuvette was inserted in a quartz finger dewar containing liquid nitrogen.

Solid-state structure determination

Preliminary examination and data collection for single crystals of compound **4a** and **4b** were carried out on a Bruker D8 VENTURE (KAPPA goniometer, PHOTON detector) single crystal-diffractometer equipped with an Oxford Cryosystem (Cryostream 800) cooling system at the window of a sealed x-ray tube using monochromated Mo-K_α (λ = 0.71073 Å) radiation (Incoatec IµS3.0 microfocus source equipped with multilayer optics). Intensity data were extracted using the APEX3 suite³ including the SAINT software package.⁴ The reflections were merged and corrected from Lorentz, polarization and decay effects and absorption correction was applied based on multiple scans.⁵ The

structure was solved by a combination of dual space⁶, direct methods with the aid of difference Fourier synthesis and were refined against all data using SHELXTL-XTMP⁷. Hydrogen atoms were assigned to ideal positions using the SHELXTL-XTMP riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXTL-XTMP weighting scheme. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.⁸ All calculations were performed with the APEX3 suite³ including SAINT software package⁴, the HELX program package⁹, PLATON¹⁰ and Mercury¹¹.

Computational details

The Gaussian16¹² (Rev A.03) package was used to perform all quantum chemical calculations employing standard functionals, basis sets and models. Detailed information on the computational settings along with literature references can be found in the respective sections below. All given ground state structures were verified as true minima by vibrational frequency analysis and the absence of a single imaginary vibrational frequencies and the absence of negative eigenvalues. UV/Vis spectra and electronic transitions were calculated using TD-DFT methods (singlet, nstates=50, CPCM, solvent=dichloromethane) as implemented in the Gaussian16 package. Calculated geometries were visualized with GaussView¹³. The coordinates of the optimized structures are given below.

Optical spectroscopy - Steady-state measurements (Mainz)

Absorption spectra were recorded using a LAMBDA 365 and emission spectroscopy was carried out with a FL-6500 (both from Perkin Elmer). All steady-state absorption and emission measurements were performed at room temperature (295 ± 2 K) and the emission spectra were corrected for the wavelength-dependent sensitivity of the emission spectrometer. The fluorescence quantum yields in solution were measured against known standard compounds (perylene in EtOH¹⁴ and Irppy in H₂O¹⁵). To avoid filter effects, the absorption was adjusted below 0.1 at the excitation wavelengths and in the overlap region of absorption and luminescence spectra. Emission spectra were measured at three different excitation wavelengths, out of which the average value was calculated. Finally, two correction factors were included: i) different refractive indices of the solvents and ii) different optical densities at the excitation wavelengths such that the following well-known formula (Eqn. 1)^[14] was used to determine the fluorescence quantum yields (ϕ ... quantum yield, I ... integrated luminescence intensity, A ... optical density at the excitation wavelength and n ... refractive index of the solvent; subscript "r" refers to the parameters of the reference compound):

$$\phi = \phi_r \frac{I}{I_r} \frac{A_r}{A} \frac{n^2}{n_r^2}$$

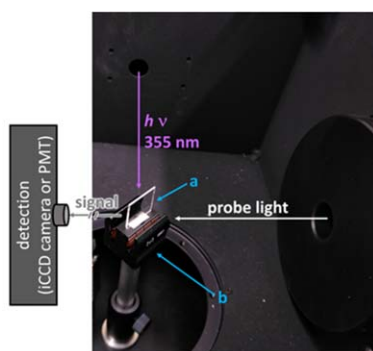
Eqn. 1

S-4

Laser flash photolysis (Mainz)

For the laser flash photolysis (LFP) measurements, an LP980-KS apparatus from Edinburgh Instruments was used. As excitation source a frequency-tripled Nd:YAG laser from Litron (Nano LG 300-10) with ~10 ns pulses and a pulse frequency of 10 Hz (unless indicated otherwise) was used. The energy of the 355 nm laser pulse was modified to intensities between 10 mJ and 15 mJ in solution (7.5-15 mJ for measurements in PMMA matrix). Kinetic traces were recorded at a single wavelength with a photomultiplier tube, and for measuring transient absorption (TA) and emission spectra, an iCCD camera from Andor was employed. Unless stated otherwise, TA spectra were time-integrated for 100 ns and detected with a time delay of 10-30 ns (50 ns for PMMA) after the laser pulse. The concentrations for LFP measurements were adjusted such that the solutions have absorption values between 0.1 and 0.2 at the laser wavelength 355 nm using cuvettes with 1 cm path length. Unless otherwise indicated, the LFP measurements were carried out at 20°C employing a cuvette holder that allows precise temperature control using the TC1 controller from Quantum North West.

Measurements in PMMA matrix were performed by employing a custom-made holder for the quartz substrate (2 wt% Pt-complex in PMMA, identical samples were used for the solid state photophysical characterization summarized in Table 1 of the main paper). The position of the quartz substrate was adjusted carefully: i) the quartz substrate was positioned at an angle such that possible reflections of the exciting laser-beam can be controlled, ii) the excitation beam (355 nm) and the light originating from the probe lamp were aligned to achieve a suitable beam overlap on the quartz substrate such that iii) the probe light reaches the detector at an optimal position (see depiction below).



Depiction of the experimental setup for LFP measurements: with PMMA films including the sample quartz substrate (blue arrow, a) and the sample holder (blue arrow, b). The light paths are indicated by three arrows: violet arrow, excitation laser beam; white arrow, light of the probe lamp; grey arrow, outgoing signal.

Samples for spectroscopy in solution were degassed for 10 min with a gentle stream of argon (Nippon Gases 5,0). Control absorption spectra ensured no changes in concentration caused by the purging procedure. Degassing for about 30 min or preparing the solutions with freeze-pump-thaw cycles did not increase the excited-state lifetimes, indicating that our general procedure with 10 min argon purging was suitable for obtaining reliable results.

Fitting of the kinetic traces was performed with the software package from Edinburgh Instruments. Biexponential fitting functions were used for traces that showed systematic derivations in the residuals of initial monoexponential fits. The relative errors for all lifetimes are estimated to be below 10%. In most cases, several kinetic traces or even measurements at different detection wavelengths were averaged to obtain more reliable results.

Irradiation experiments (Mainz)

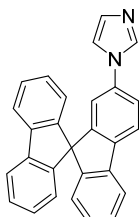
For the *cis-trans* isomerization reaction, a stock solution containing *trans*-methylcinnamate (51 mM) and the reference compound (dimethyl sulfone) was prepared in DCM-*d*₂. The stock solution was divided into three parts, one containing no photocatalyst, and the other two containing either **4a** or **4b** (1 mol% of the substrate concentration). All three solutions were degassed by four freeze-pump-thaw cycles followed by a transfer into argon flushed NMR-tubes, which were sealed with a septum cap. Throughout the irradiation, the NMR-tubes were positioned in front of a 370 nm LED from Kessil (KSPR160L-370).¹⁶ The temperature was maintained by a water bath. The progress of the reaction was tracked by ¹H-NMR measurements on a Bruker Avance 300 spectrometer.

Electrochemistry

Cyclic voltammetry experiments were carried out using a Biologic SP-150 potentiostat in degassed, dry DMF solutions, employing a platinum wire counter electrode, a glassy carbon working electrode and a Ag/Ag⁺ pseudo reference electrode. All complexes were measured as 1 mM solutions along with 0.1 M supporting electrolyte N(*n*-Bu)₄ClO₄. For the cyclovoltammetry we used a sweep rate of 100 mV/s, the DPV data were measured at a sweep rate of 50 mV/s. All measurements were internally referenced against Fc/Fc⁺.

Experimental procedures

1-(9,9'-spirobi[fluoren]-2-yl)-1H-imidazole (2)



2.18 g (5.41 mmol) 2-Bromo-9,9'-spirobi[9H-fluorene] (**1**), 0.442 g (6.49 mmol, 1.2 eq.) imidazole, 0.972 g (7.03 mmol, 1.3 eq.) potassium carbonate and 0.195 g (1 mmol, 0.185 eq.) copper(I)iodide were placed in a flame-dried 25 ml Schlenk flask, equipped with a reflux condenser. The atmosphere was exchanged with argon in three cycles. The solid materials were dissolved in 7 ml dry, degassed DMF and the reaction was heated to 160 °C and stirred for 24 h. Subsequently, the solvent was removed *in vacuo* and the product was purified by flash column chromatography with an eluent mixture of dichloromethane with 5% methanol. The analytically pure product was obtained after drying *in vacuo* as colorless solid (1 g, 48%).

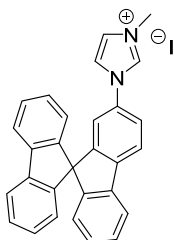
M.p.: 185 °C

¹H-NMR in DMSO-*d*₆ (300 MHz) δ = 8.18 (d, *J* = 8.3 Hz, 1H), 8.12 – 7.97 (m, 4H), 7.74 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.59 (t, *J* = 1.4 Hz, 1H), 7.48 – 7.35 (m, 3H), 7.17 – 7.11 (m, 3H), 6.97 (s, 1H), 6.88 (d, *J* = 2.1 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 7.6 Hz, 1H) ppm.

¹³C-NMR in DMSO-*d*₆ (75 MHz) δ = 149.7, 148.7, 147.6, 141.4, 140.2, 140.1, 136.6, 135.5, 129.7, 128.2, 128.1, 128.0, 123.5, 123.3, 121.9, 120.8, 120.7, 120.6, 118.1, 115.3, 65.6 ppm.

MS(ESI) calc'd [M+H]⁺ 383.1543 **Found:** 383.1546

1-(9,9'-spirobi[fluoren]-2-yl)-3-methyl-1*H*-imidazol-3-ium iodide (3)



In a 100 ml pressure tube, 1g (2.61 mmol) 1-(9,9'-spirobi[fluoren]-2-yl)-1*H*-imidazole (**2**) were dissolved in 6 ml THF. Then, 0.2 ml (3.27 mmol, 1.25 eq.) iodomethane were added to the solution via syringe. The tube was sealed and the reaction was stirred in air for 24 h at 90 °C. Afterwards, the reaction was allowed to cool down to room temperature and diethyl ether was added until a light-orange solid precipitated. The solid was filtered and washed excessively with THF and diethyl ether. The orange-colored product was dried in vacuo (1.3 g, 95%).

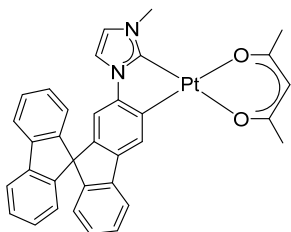
M.p.: 275 °C

¹H-NMR in DMSO-*d*₆ (300 MHz) δ = 9.54 (s, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.19 (t, *J* = 1.8 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.85 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.49 – 7.41 (m, 3H), 7.23 – 7.14 (m, 3H), 7.08 (d, *J* = 2.1 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 3.79 (s, 3H) ppm.

¹³C-NMR in DMSO-*d*₆ (75 MHz) δ = 150.0, 148.9, 147.1, 142.8, 141.4, 139.5, 136.1, 134.2, 130.0, 128.3, 128.2, 128.1, 124.0, 123.6, 123.5, 122.1, 122.0, 121.3, 120.9, 120.8, 116.9, 65.5, 35.8 ppm.

MS(ESI) calc'd [M-I]⁺ 397.1699 **Found:** 397.1701

[Acetylacetonato- κ O, κ O']-[1-(9,9'-spirobi[fluoren]- κ C²)-3-methyl-1H-imidazolin-2-ylidene- κ C²]platinum(II) (**4a**)



In a flame-dried 100 ml Schlenk tube, 0.21 g (0.4 mmol) 1-(9,9'-spirobi[fluoren]-2-yl)-3-methyl-1H-imidazol-3-ium iodide (**3**) and 0.046 g (0.2 mmol, 0.5 eq.) silver(I) oxide were dissolved in 10 ml dry DMF and stirred at room temperature for 24 h in an argon atmosphere. Then, 0.15 g (0.4 mmol, 1 eq.) Pt(COD)Cl₂ were added and the reaction was continued stirring for 24 h at room temperature. Subsequently, the reaction was heated to 115 °C and stirred for further 24 h. Finally, the reaction was allowed to cool to 50 °C and 0.097 g (0.8 mmol, 2 eq.) sodium acetylacetonate were added to the reaction mixture which was stirred at the same temperature for another 24 h. The solvent was removed *in vacuo* and the crude product was taken up in dichloromethane and filtered through a plug of Celite® and afterwards purified by flash column chromatography with an eluent mixture of isohexanes and dichloromethane (1:1 v/v). The analytically pure product was obtained as an orange solid after washing with pentane (3x5 ml) and drying *in vacuo* (151 mg, 54%).

M.p.: >300 °C

¹H-NMR in Methylene Chloride-d₂ (600 MHz) δ 8.24 (s, 1H), 7.90 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.88 (dt, *J* = 7.7, 0.9 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.12 (td, *J* = 7.5, 1.1 Hz, 2H), 7.04 (td, *J* = 7.4, 1.1 Hz, 1H), 6.98 (d, *J* = 2.2 Hz, 1H), 6.75 (dt, *J* = 7.6, 0.8 Hz, 2H), 6.71 (d, *J* = 2.1 Hz, 1H), 6.61 (dt, *J* = 7.5, 0.8 Hz, 1H), 6.34 (s, 1H) 5.58 (s, 1H), 4.00 (s, 3H), 2.17 (s, 3H), 1.99 (s, 3H) ppm.

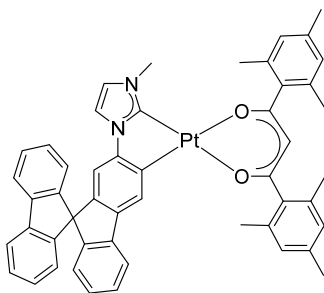
¹³C-NMR in Methylene Chloride-d₂ (151 MHz) δ 185.7, 185.6, 149.7, 149.3, 147.6, 144.6, 143.0, 142.3, 138.1, 128.3, 128.2, 128.1, 127.1, 124.5, 123.8, 123.5, 121.5, 120.6, 120.3, 114.9, 106.4, 102.4, 66.4, 35.3, 28.3, 28.2 ppm.

¹⁹⁵Pt-NMR in CDCl₃ (64 MHz) δ = -3424.80 ppm.

MS(ESI) calc'd [M+H]⁺ 690.1715 **Found:** 690.1725

Anal. calc'd. for C₃₄H₂₆N₂O₂Pt: C 59.21%; H 3.80%, N 4.06% **Found:** C 59.51%; H 3.87%, N 3.85%

[1,3-Bis(2,4,6-trimethylphenyl)propane-1,3-dionato- κ O, κ O'] [1-(9,9'-spirobi[fluoren]-2-yl)-3-methyl-1H-imidazolin-2-ylidene- κ C²]platinum(II) (**4b**)



In a flame-dried 100 ml Schlenk tube, 0.42 g (0.8 mmol) 1-(9,9'-spirobi[fluoren]-2-yl)-3-methyl-1H-imidazol-3-ium iodide (**3**) and 0.092 g (0.4 mmol, 0.5 eq.) silver(I) oxide were dissolved in 20 ml dry DMF and stirred at room temperature for 24 h in an argon atmosphere. Then, 0.3 g (0.8 mmol, 1 eq.) Pt(COD)Cl₂ were added and the reaction was continued stirring for 24 h at room temperature. Subsequently, the reaction was heated to 115 °C and stirred for further 24 h. Finally, the reaction was allowed to cool to 50 °C and 0.493 g (1.6 mmol, 2 eq.) 1,3-bis(2,4,6-trimethylphenyl)propane-1,3-dione and 0.18 g (1.6 mmol, 2 eq.) potassium *tert*-butoxide were added to the reaction mixture which was stirred at the same temperature for another 24 h. The solvent was removed *in vacuo* and the crude product was taken up in dichloromethane and filtered through a plug of Celite® and afterwards purified by flash column chromatography with an eluent mixture of isohexanes and dichloromethane (2:1 v/v). The analytically pure product was obtained as a yellow solid after washing with pentane (3x5 ml) and drying *in vacuo* (366 mg, 50%).

M.p.: >300 °C

¹H-NMR in CDCl₃ (300 MHz) δ = 8.20 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.36 (td, *J* = 7.5, 1.0 Hz, 2H), 7.27 (td, *J* = 7.5, 1.0 Hz, 1H), 7.11 (td, *J* = 7.5, 1.0 Hz, 2H), 7.03 – 6.90 (m, 4H), 6.83 (s, 2H), 6.78 (d, *J* = 7.5 Hz, 2H), 6.66 – 6.57 (m, 2H), 6.34 (s, 1H), 5.71 (s, 1H), 3.88 (s, 3H), 2.45 (s, 6H), 2.37 (s, 3H), 2.34 (s, 6H), 2.29 (s, 3H) ppm.

¹³C-NMR in CDCl₃ (75 MHz) δ = 184.9, 184.7, 149.5, 149.0, 148.8, 147.0, 144.5, 142.6, 141.8, 139.9, 139.4, 138.2, 137.7, 137.5, 134.4, 133.8, 128.5, 128.2, 127.9, 127.7, 127.5, 126.7, 124.5, 123.5, 123.5, 120.8, 120.1, 119.9, 114.7, 107.5, 106.4, 66.0, 35.1, 21.4, 21.3, 20.3, 19.7 ppm.

¹⁹⁵Pt-NMR in CDCl₃ (64 MHz) δ = -3366.55 ppm.

MS(ESI) calc'd [M+H]⁺ 898.2967 **Found:** 898.2928

Anal. calc'd. for C₅₀H₄₂N₂O₂Pt: C 66.88%; H 4.71%, N 3.12% **Found:** C 66.75%; H 4.64%, N 3.17%

NMR Spectra

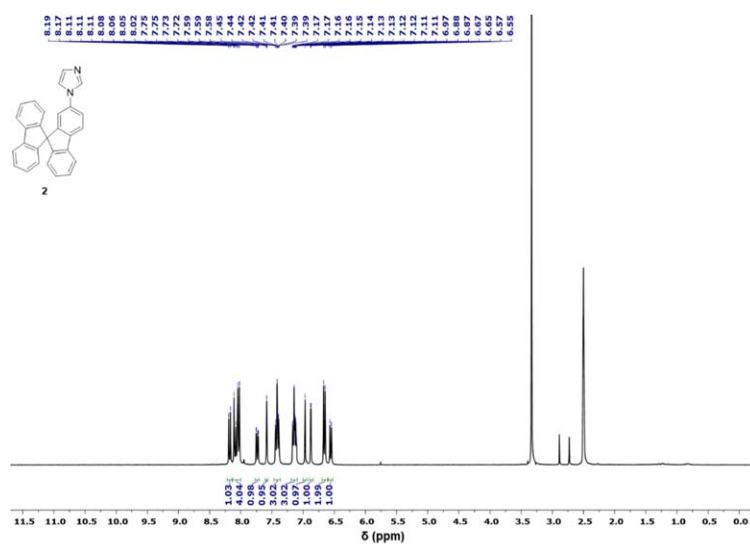


Figure S1: ¹H-NMR spectrum of **2**.

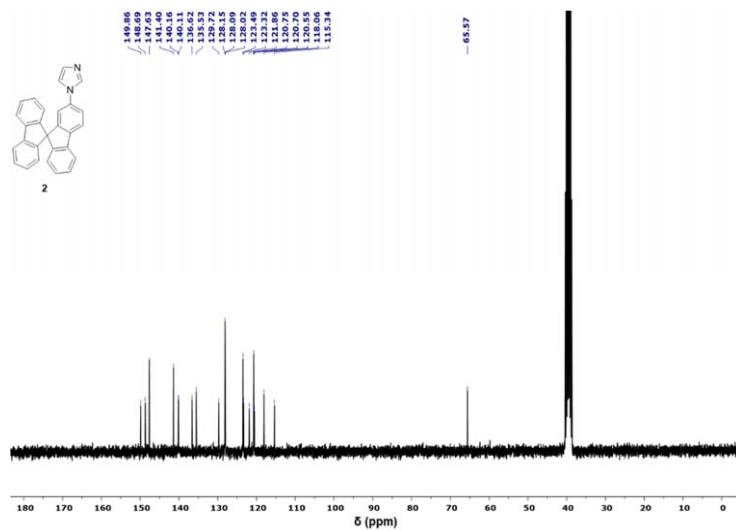


Figure S2: ¹³C-NMR spectrum of **2**.

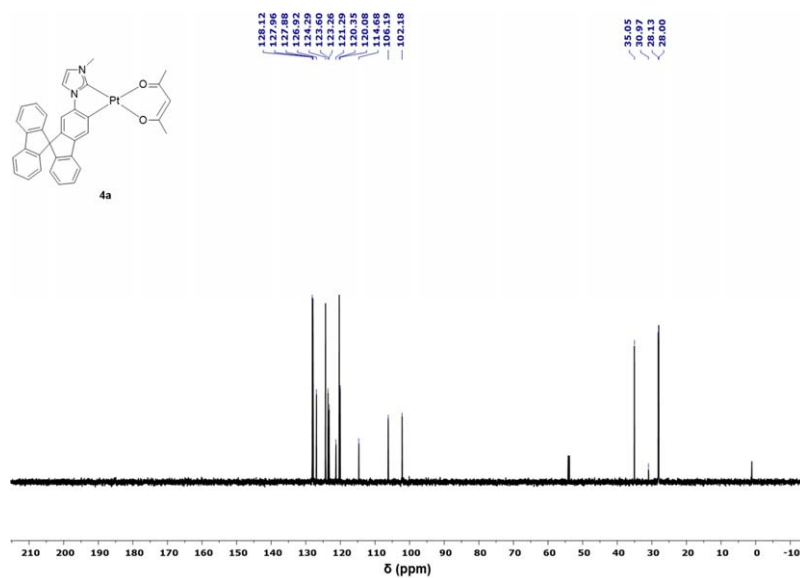


Figure S7: ¹³C-NMR (DEPT 135) spectrum of 4a.

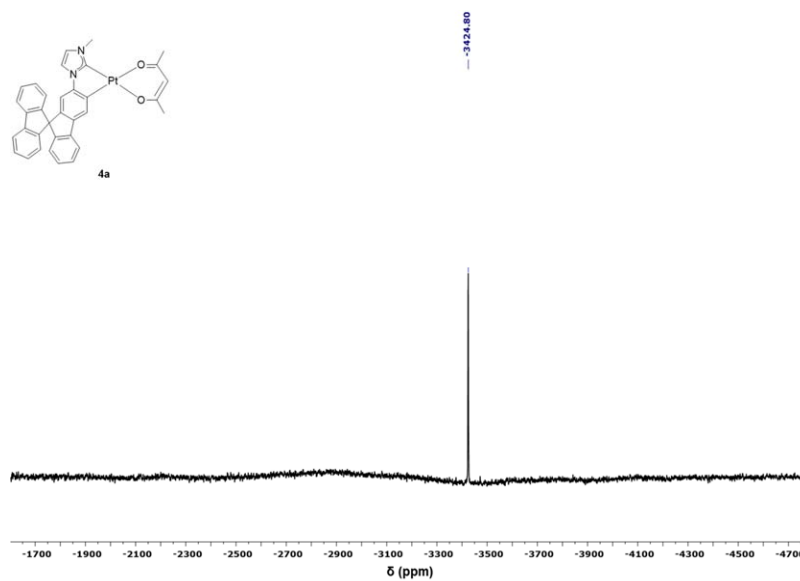


Figure S8: ¹⁹⁵Pt-NMR spectrum of 4a.

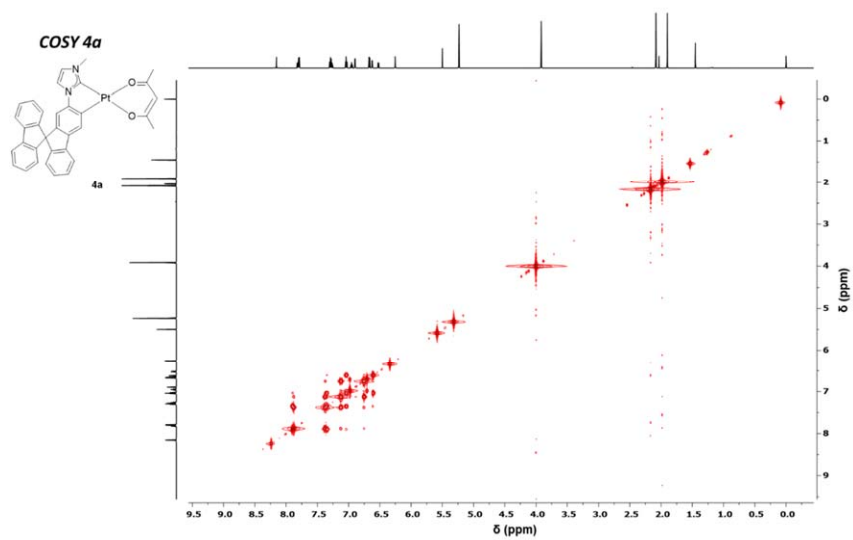


Figure S9: COSY-NMR spectrum of **4a**.

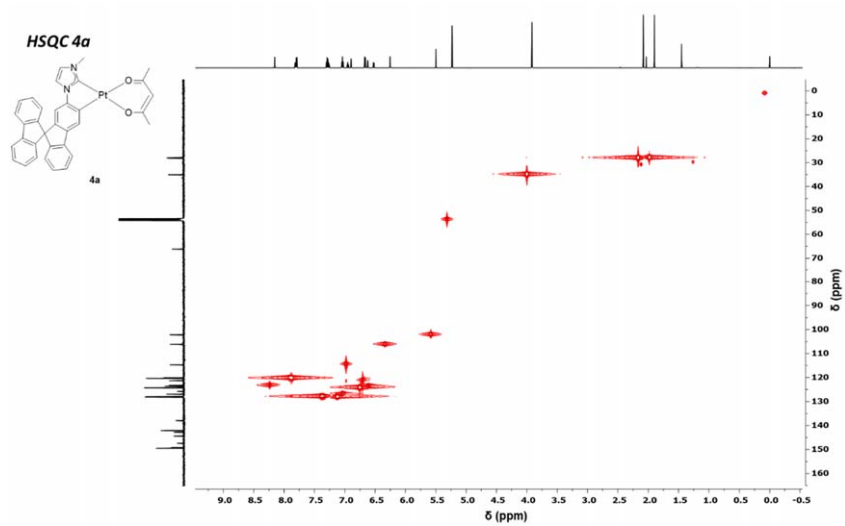


Figure S10: HSQC-NMR spectrum of **4a**.

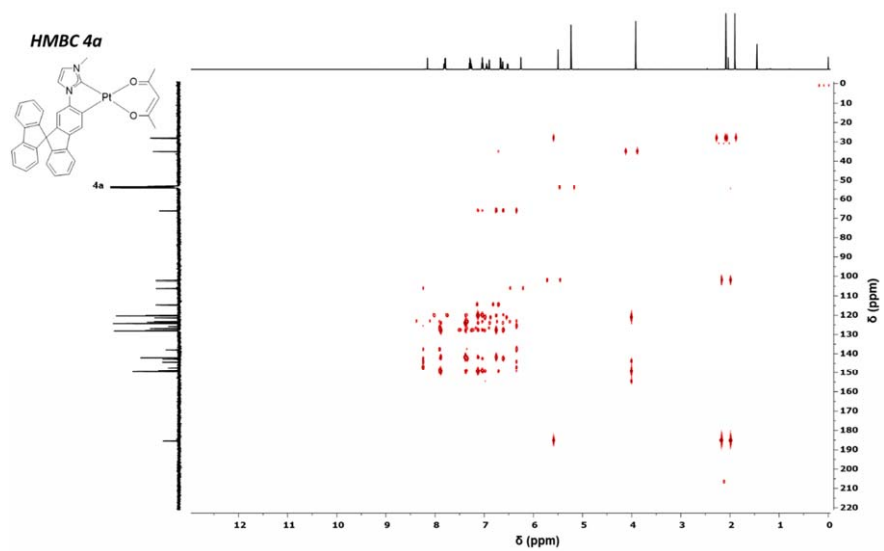


Figure S11: HMBC-NMR spectrum of **4a**.

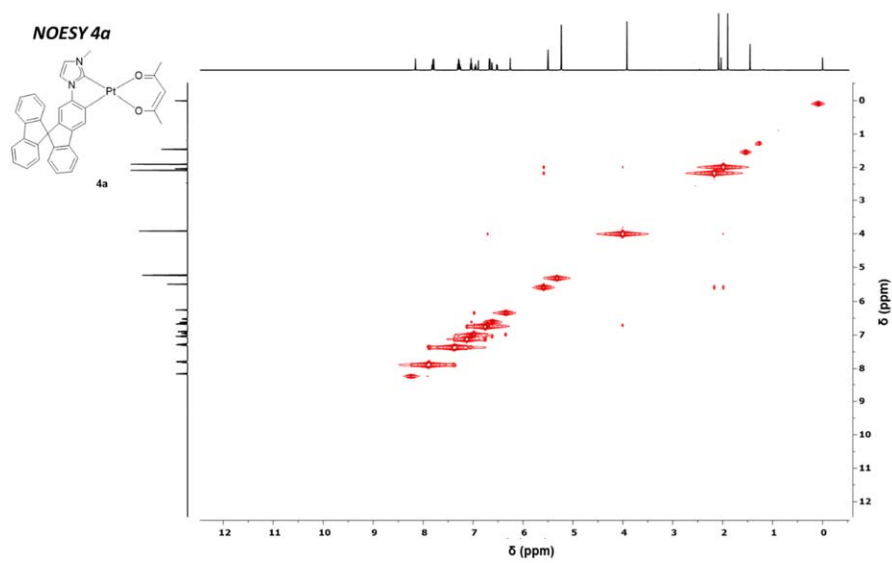


Figure S12: NOESY-NMR spectrum of **4a**.

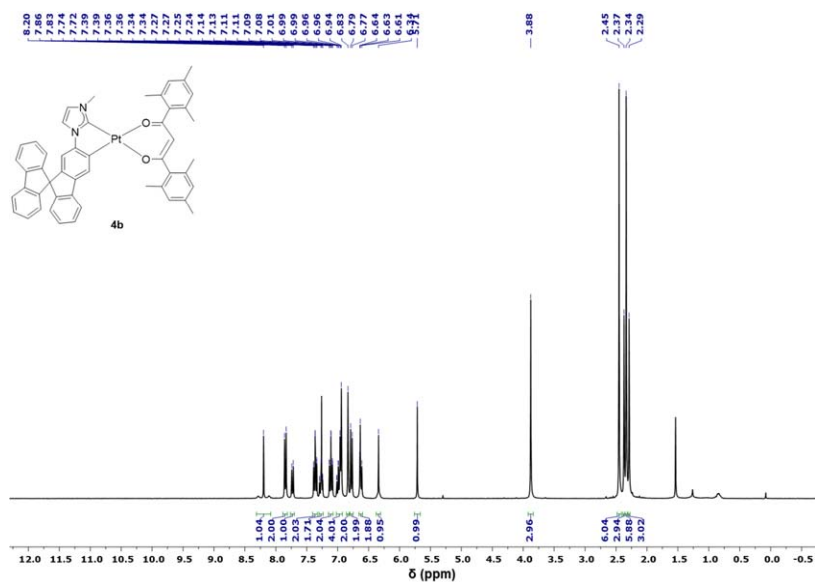


Figure S13: ^1H -NMR spectrum of **4b**.

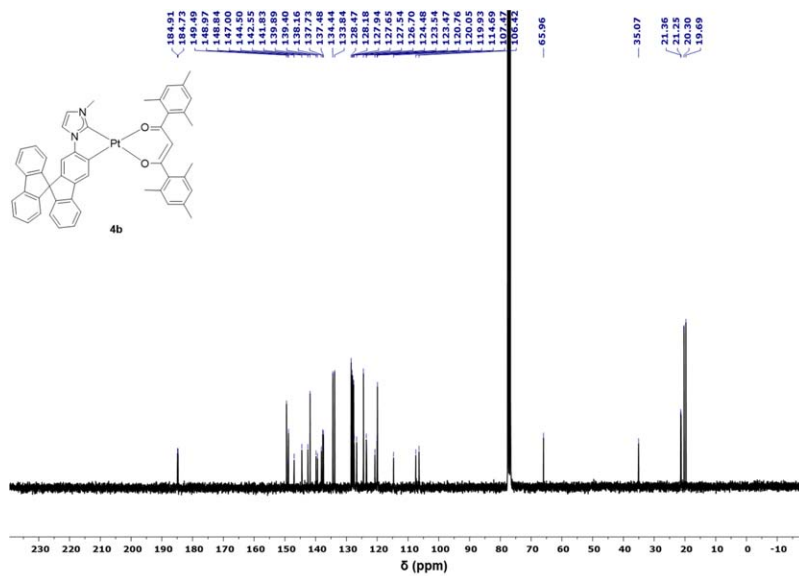


Figure S14: ^{13}C -NMR spectrum of **4b**.

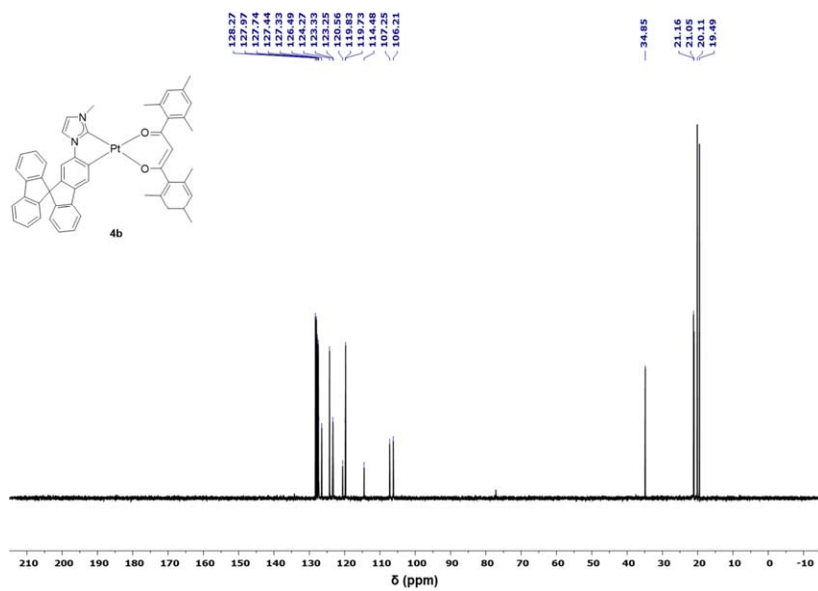


Figure S15: ^{13}C -NMR (DEPT 135) spectrum of **4b**.

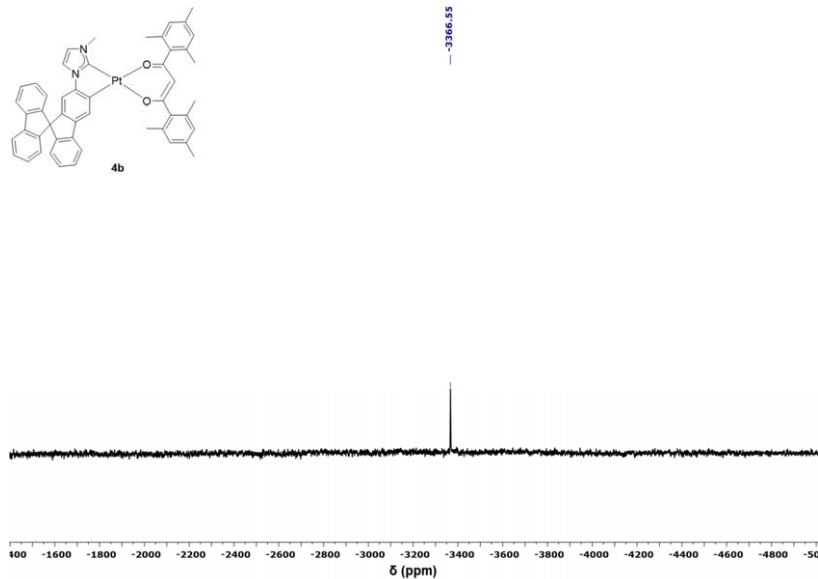


Figure S16: ^{195}Pt -NMR spectrum of **4b**.

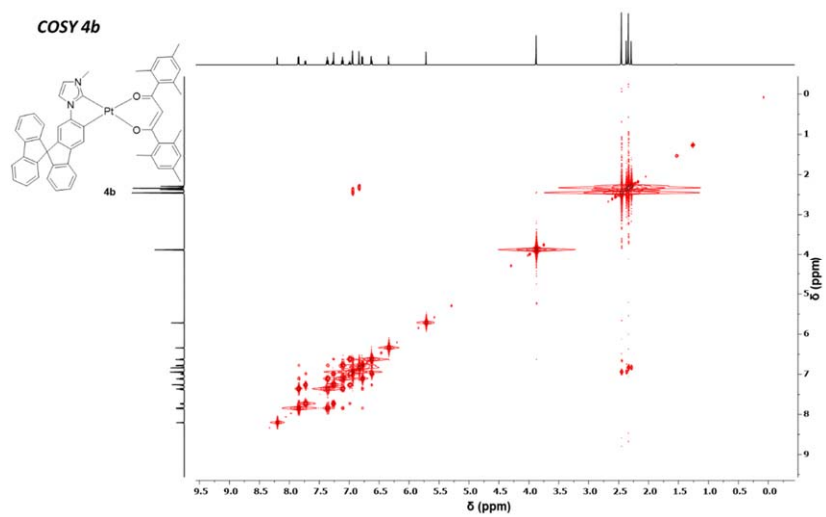


Figure S17: COSY-NMR spectrum of **4b**.

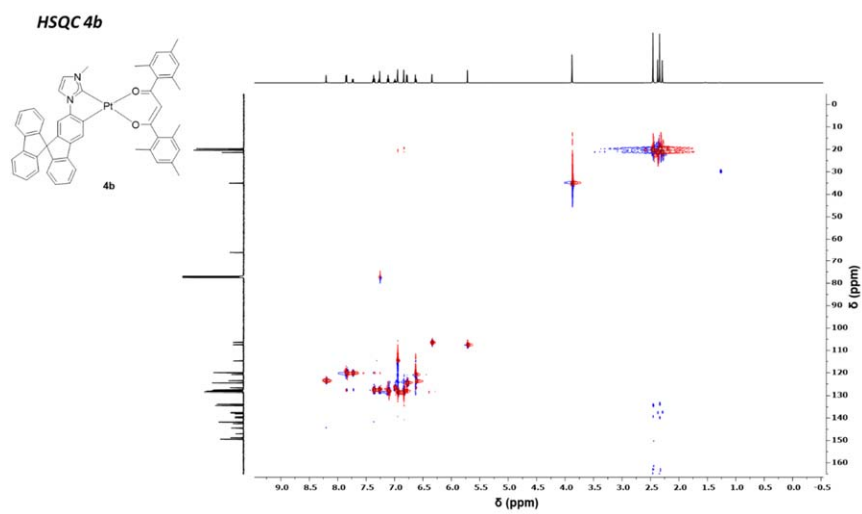


Figure S18: HSQC-NMR spectrum of **4b**.

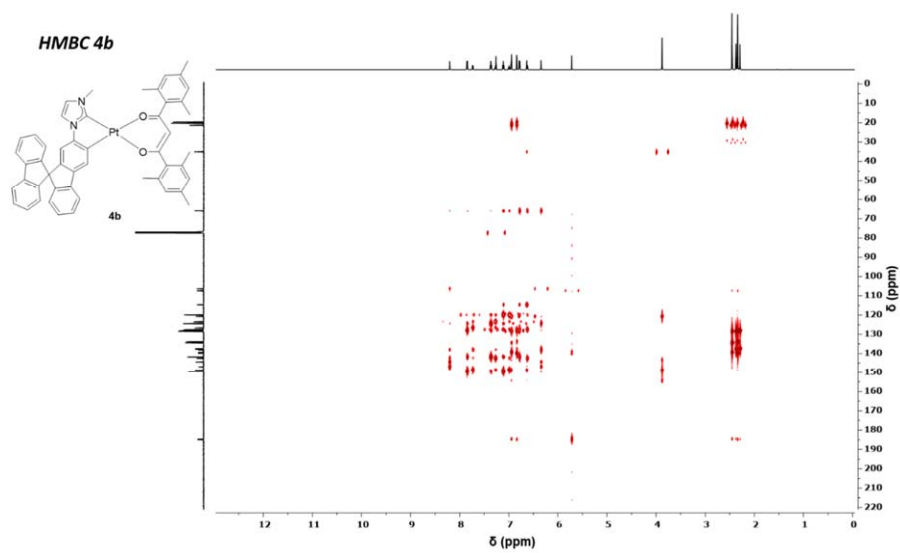


Figure S19: HMBC-NMR spectrum of **4b**.

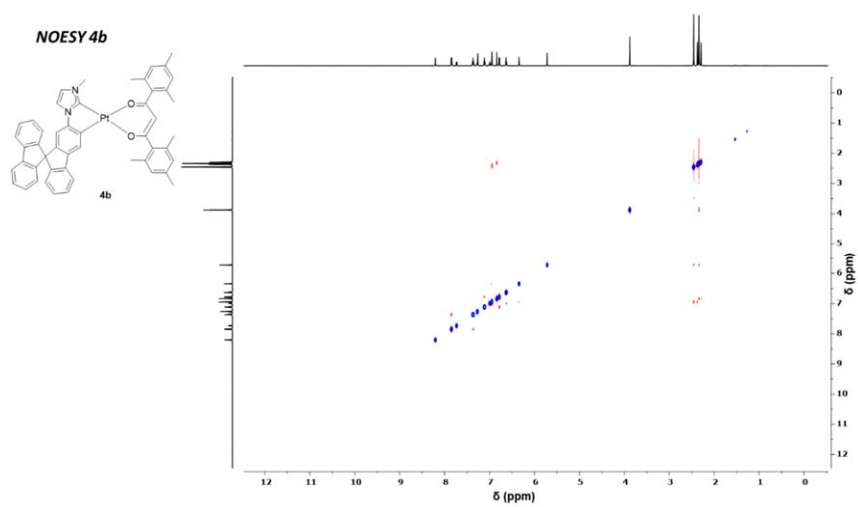
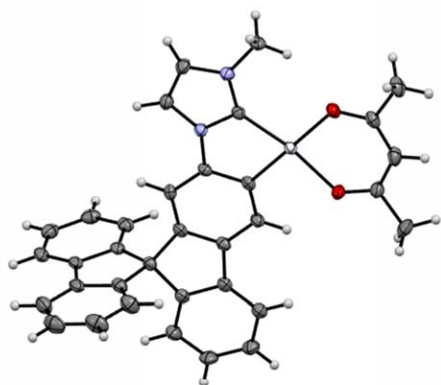


Figure S20: NOESY-NMR spectrum of **4b**.

Solid State Structure Details

Complex **4a**

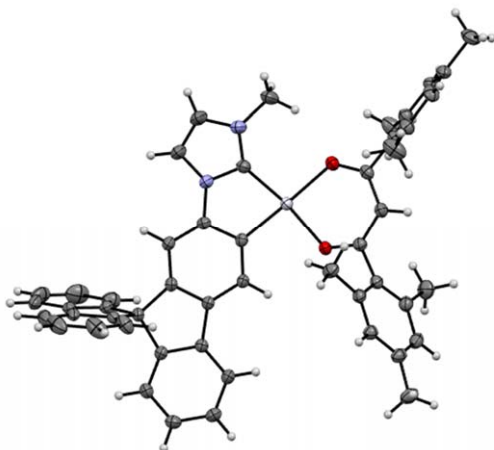


CCDC #	2179090
Empirical formula	C _{34.50} H ₂₇ Cl N ₂ O ₂ Pt
Formula weight	732.12
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 14.5200(8) Å a = 85.780(2)°. b = 15.3331(8) Å b = 65.603(2)°. c = 15.8400(8) Å g = 61.794(2)°.
Volume	2797.6(3) Å ³
Z	4
Density (calculated)	1.738 Mg/m ³
Absorption coefficient	5.147 mm ⁻¹
F(000)	1436
Crystal size	0.199 x 0.122 x 0.073 mm ³
Theta range for data collection	2.523 to 28.323°.
Index ranges	-19<=h<=19, -20<=k<=20, -21<=l<=21

S-21

Reflections collected	233175
Independent reflections	13941 [R(int) = 0.0654]
Completeness to theta = 25.242°	99.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13941 / 0 / 736
Goodness-of-fit on F ²	1.055
Final R indices [I > 2sigma(I)]	R1 = 0.0240, wR2 = 0.0484
R indices (all data)	R1 = 0.0350, wR2 = 0.0533
Extinction coefficient	n/a
Largest diff. peak and hole	1.212 and -1.142 e.Å ⁻³

Complex **4b**



CCDC #	2179091
Empirical formula	C ₅₀ H ₄₂ N ₂ O ₂ Pt
Formula weight	897.94
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n

S-22

Unit cell dimensions	a = 15.5749(10) Å	a = 90°.
	b = 17.3730(12) Å	b = 112.876(2)°.
	c = 15.7354(10) Å	g = 90°.
Volume	3922.8(4) Å ³	
Z	4	
Density (calculated)	1.520 Mg/m ³	
Absorption coefficient	3.620 mm ⁻¹	
F(000)	1800	
Crystal size	0.220 x 0.136 x 0.110 mm ³	
Theta range for data collection	2.353 to 28.430°.	
Index ranges	-20 ≤ h ≤ 20, -23 ≤ k ≤ 23, -20 ≤ l ≤ 20	
Reflections collected	291836	
Independent reflections	9746 [R(int) = 0.0362]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9746 / 0 / 503	
Goodness-of-fit on F ²	1.081	
Final R indices [I > 2σ(I)]	R1 = 0.0159, wR2 = 0.0396	
R indices (all data)	R1 = 0.0192, wR2 = 0.0421	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.900 and -0.498 e.Å ⁻³	

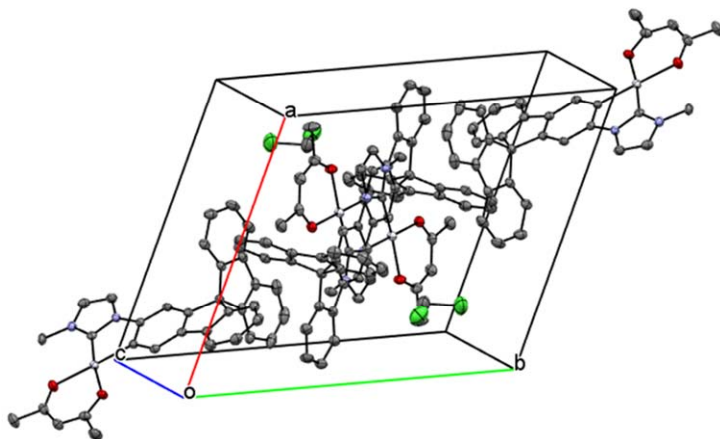


Figure S21: Solid state packing of **4a**. H-atoms are omitted for clearance.

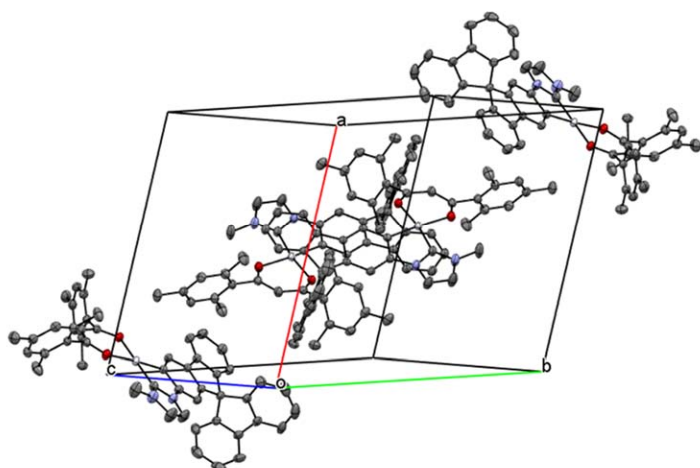


Figure S22: Solid state packing of **4b**. H-atoms are omitted for clearance.

Thermogravimetric Analysis Data

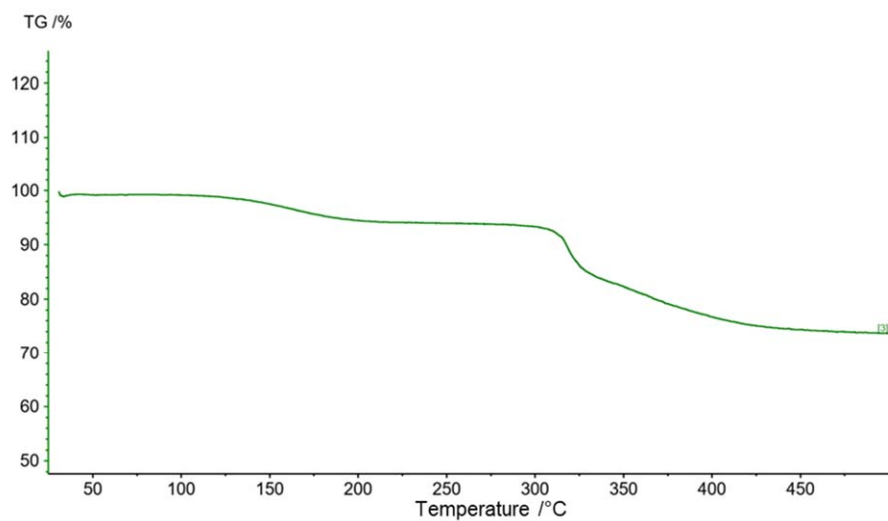


Figure S23: Thermogravimetric analysis of **4a** recorded at a heat rate of 5K/min under an argon atmosphere.

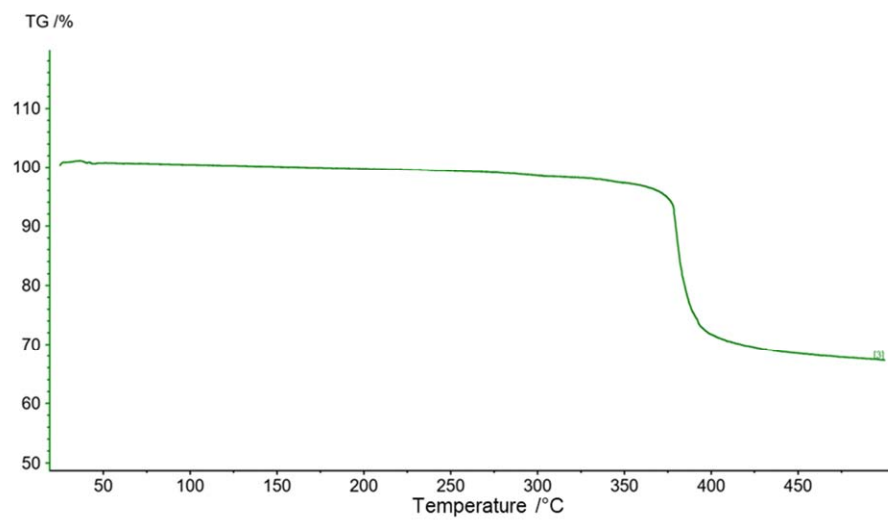


Figure S24: Thermogravimetric analysis of **4b** recorded at a heat rate of 5K/min under an argon atmosphere.

Additional Emission Measurements

The measurements of **4a** and **4b** in PMMA matrix were performed with the same quartz substrates as used for quantum yield determination (with a Hamamatsu system, model C11347-01, as described above). With the custom-made set-up (compare p. S-6 depiction of the experimental setup), all measurement modes could be performed like those in solution, except kinetic absorption measurements (too low signal intensity).

Comparison of emission spectra – PMMA vs. solution: The emission spectra of **4a** and **4b** were recorded in different solvents (THF and DCM) and in PMMA matrix. The three different environments do not have any impact on the maxima of the spectra or their relative intensities (Figure S25).

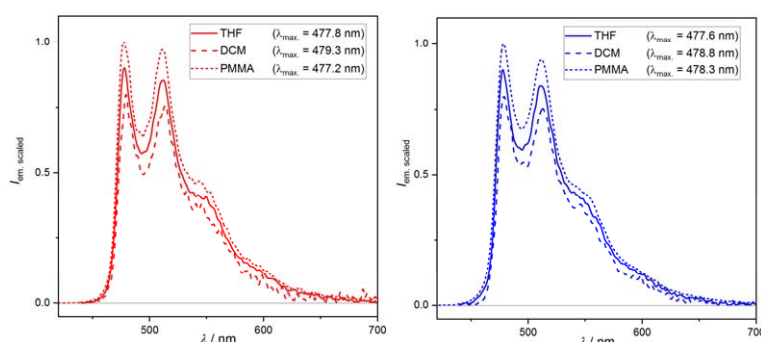


Figure S25: Emission spectra of **4a** (left side, red) and **4b** (right side, blue) in solution (THF, solid lines or DCM dashed lines) and PMMA matrix (dotted lines). All spectra were recorded on the FL-6500 and excited at wavelengths between 300-355 nm

Comparison of emission lifetimes – PMMA vs. solution: The emission lifetimes of **4a** and **4b** in PMMA are slightly longer compared to those measured in solution. For these measurements, the best-fit function is biexponential, which is caused by effects originating from the solid-state-nature of the PMMA matrix combined with the high intensity of the 355 nm laser pulses. As an approximation for the excited-state lifetimes τ_0 of **4a** and **4b** in PMMA, the two lifetimes, from each fit were averaged, and weighted according to their relative contribution (Figures S26 and S27 as well as Table S1). Generally, the measurements in PMMA matrix were accompanied by scattering effects, which could not be eliminated entirely (Figure S27). A slightly longer excited state lifetime was observed for **4a**, compared to that of **4b**, which is in line with the results obtained in solution.

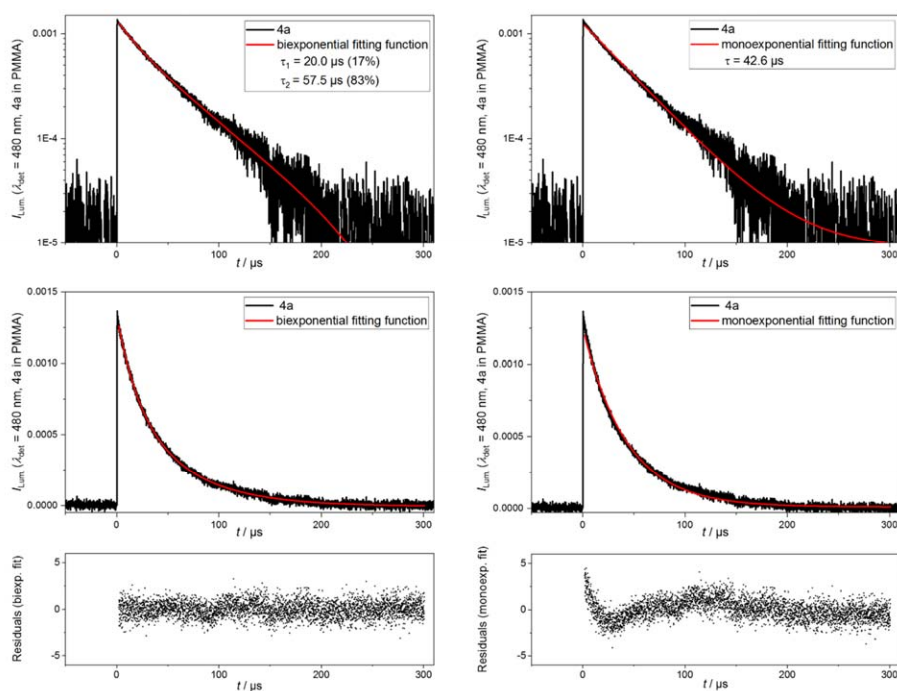


Figure S26: Kinetic emission data of **4a** in PMMA matrix after 355 nm excitation. Upper panel: mono- (right) and biexponential (left) fitting functions, plotted on a log-scale including the resulting lifetimes and their relative contributions. Middle panel: mono- (right) and biexponential (left) fitting functions, plotted on a linear scale. Lower panel: Residuals resulting from the fits displayed above.

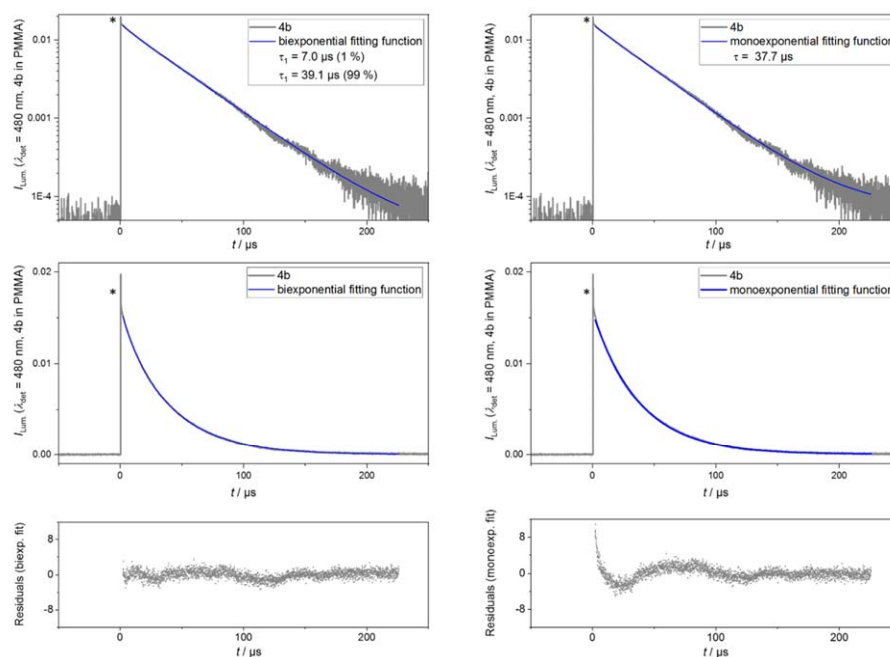


Figure S27: Kinetic emission data of **4b** in PMMA matrix after 355 nm excitation. Upper panel: mono- (right) and biexponential (left) fitting functions, plotted on a log-scale including the resulting lifetimes and their relative contributions. Middle panel: mono- (right) and biexponential fitting functions, plotted on a linear scale. Lower panel: Residuals resulting from the fits displayed above. *Asterisk indicates scattering light from the laser pulse.

For comparison, the emission lifetimes of **4a** and **4b** in THF solution are plotted on a log-scale in Figure S28, including the corresponding residuals (for linear-scale kinetics see main paper). In contrast to what has been described for the PMMA samples, we did not observe any systematic deviations from monoexponential fitting functions of the kinetic traces for the complexes in solution.

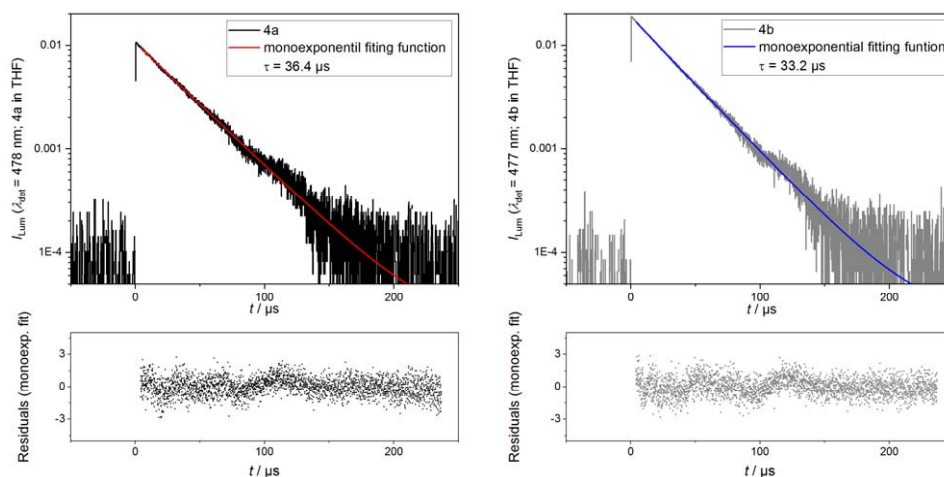


Figure S28: Upper panel: Kinetic emission data of **4a** (left) **4b** (right) in THF on a log-scale (for linearly scaled plot see Figure 6, main paper); Lower panel: Residuals resulting from the fits of the data sets shown above.

Table S1: Excited-state lifetimes of unquenched **4a** and **4b** in THF solution and PMMA matrix.

	4a ($\lambda_{\text{det.}}$ / nm)	4b ($\lambda_{\text{det.}}$ / nm)
$\tau_{\text{em.}}$ (PMMA) / μs	52.1 (480) ^[a]	38.8 (480) ^[a]
$\tau_{\text{em.}}$ (THF) / μs	36.4 (478)	33.2 (477)

^[a] Detected with a laser frequency of 1 Hz and at low laser intensities to avoid too high local excited state concentrations that could result in a more pronounced biexponential decay owing to self-quenching. Amplitude-weighted average excited-state lifetimes.

Temperature dependency of the emission spectra: In addition to the solvent dependency, the emission of **4a** and **4b**, was investigated at different temperatures. For both complexes, the position of the spectra and the relative intensities remain virtually identical for temperatures between 5 °C and 30 °C (Figure S29). The temperature was adjusted using the temperature-controlled cuvette holder of the LP980-KS setup.

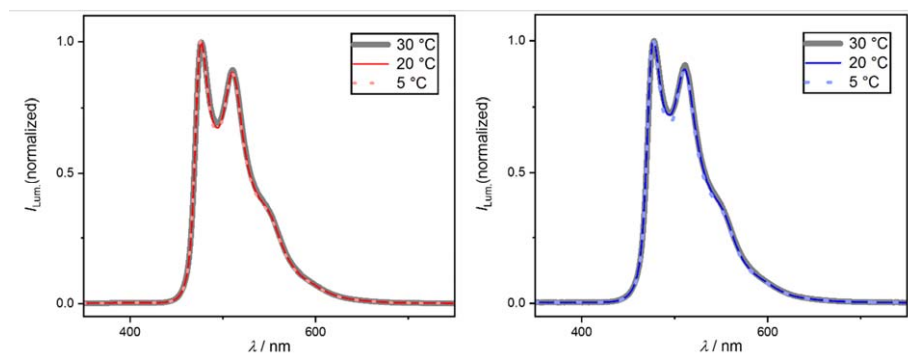


Figure S29: Normalized emission spectra of **4a** (left; red and grey curves; time delay after 355 nm laser excitation 100 ns, integrated over 30 μ s) and **4b** (right; blue and grey curves; time delay after 355 nm laser excitation 20 ns, integrated over 150 μ s) in degassed THF solution after 355 nm laser excitation.

Energy transfer experiments

LFP measurements on the TTET with *p*-terphenyl

Both platinum(II) complexes show TTET reactivity, and upon *p*-terphenyl addition the corresponding 3p -terphenyl signature^{14,17,18} was observed in the TA spectra (see main paper for **4a** and Figure S30 for **4b**).

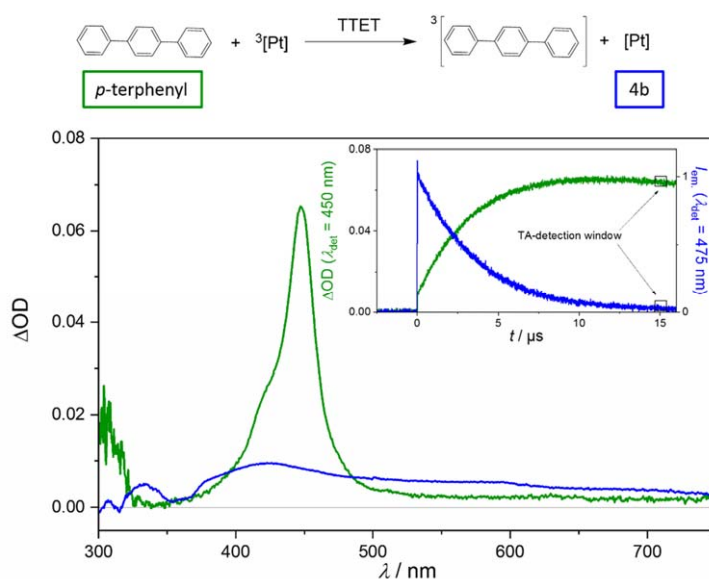


Figure S30: Reaction scheme of TTET from $^3[\text{4b}]$ to *p*-terphenyl. Main: TA spectra of $^3[\text{4b}]$ (blue trace, time delay 20 ns) and 3p -terphenyl after TTET (green, time delay 15 μs), inset: emission decay of $^3[\text{4b}]$ with 1 mM *p*-terphenyl (blue trace) and corresponding 3p -terphenyl formation (green trace).

Irradiation experiments

The *cis-trans* isomerization of methyl-cinnamate, catalyzed by either of the platinum(II) complexes (see SI section General Procedures for details) was tracked using ^1H -NMR spectroscopy. For both complexes, *cis*-yields of about 43 % were observed after 1 hour of 370 nm irradiation (Figure S31 and Table S2). A *cis-trans*-ratio of 1:1 was observed after 1 hour of irradiation that did not change upon further irradiation. This implies the presence of a photostationary state. Control experiments without the platinum sensitizers did not show any conversion (left spectra in Figure S31).

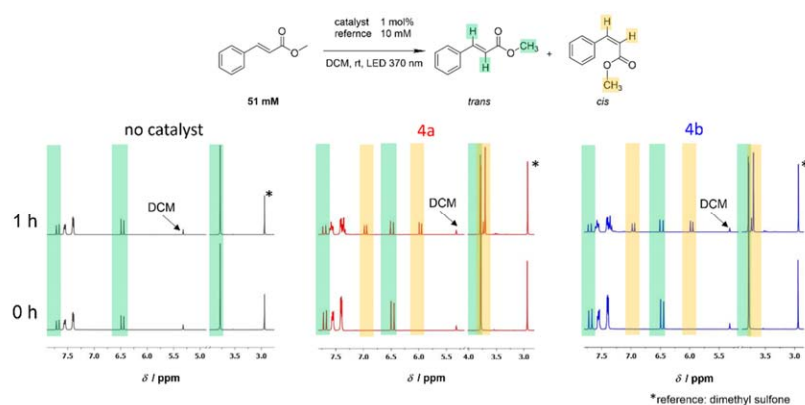


Figure S31: Reaction scheme and conditions for the isomerization reaction and ^1H -NMR spectra before (0 h) and after 1 h of 370 nm LED irradiation. The color code indicates the protons that were assigned to the different isomers. For quantitative analysis the integral of the reference (dimethyl sulfone at 2.94 ppm, marked with an asterisk) was compared to the peaks corresponding to the *trans*-isomer (marked in green) or to the peaks of the *cis*-isomer (marked in orange). For the *cis*-isomer, only the two high field signals (singlet at 3.70 ppm and doublet at 5.95 ppm) were considered, due to overlapping signals at the low-field doublet (doublet at 6.94 ppm).

Table S2: Quantitative ^1H -NMR analysis of irradiation experiments (for reaction conditions see text and Fig. S31).

Time	no catalyst (cis/trans ^[a])	4a (cis/trans ^[a] ; cis yield ^[b])	4b (cis/trans ^[a] ; cis yield ^[b])
0 h	(0/1)	(0/1)	(0/1)
1 h	(0/1)	(50/50; 42%)	(51/49; 44%)

^[a]cis/trans corresponds to direct ratio of the integrated peaks; ^[b] corresponds to the absolute amount of *cis*-isomer within the reaction solution.

Emission quantum yields in solution

The quantum yields of complexes **4a** and **4b** were determined in THF relative to literature-known substances in solution (perylene in EtOH¹⁴ and Irspyy in H₂O¹⁵). All spectra were recorded at three different excitation wavelengths (355 nm, 360 nm and 370 nm); the results of these triple determinations were averaged and are listed in Table S3. In solution the quantum yields are lower compared to the results in PMMA matrix (compare main paper). The quantum yields are very similar for both compounds, which is in line with all other observations related to the excited state properties of the two platinum(II) complexes.

Table S3: Relative quantum yield determination of **4a** and **4b** in deoxygenated THF solution vs. two reference compounds.

Reference compound	4a	4b
vs perylene (in EtOH, 92 %) ^[a]	28.3 % (± 0.6 %)	33.2 % (± 0.6 %)
vs Irspdy (in H ₂ O; 73 %) ^[b]	29.1 % (± 0.6 %)	34.1% (± 0.1 %)

^[a] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, Handbook of Photochemistry, 3rd Ed., CRC Press, 2006.

^[b] C. Kerzig, X. Guo, O. S. Wenger, *J. Am. Chem. Soc.* 2019, 141, 2122–2127.

Additional Spectra in PMMA

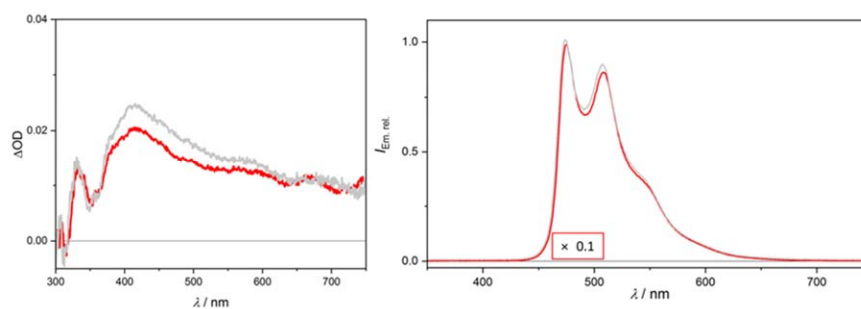


Figure S32: Comparative spectra (TA, left and emission, right), of **4a** in PMMA (red) or THF (grey). For better comparison, the emission spectra (recorded with the LFP setup and an integration time of 50 μ s for PMMA matrix and 160 μ s for THF solution) were scaled.

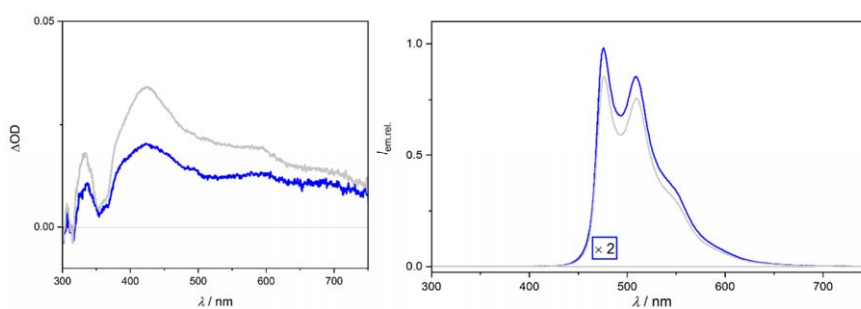


Figure S33: Comparative spectra (TA, left and emission, right), of **4b** in PMMA (red) or THF (grey). For better comparison, the emission spectra (recorded with the LFP setup and an integration time of 50 μ s for PMMA matrix and 150 μ s for THF solution) were scaled.

Computational Details

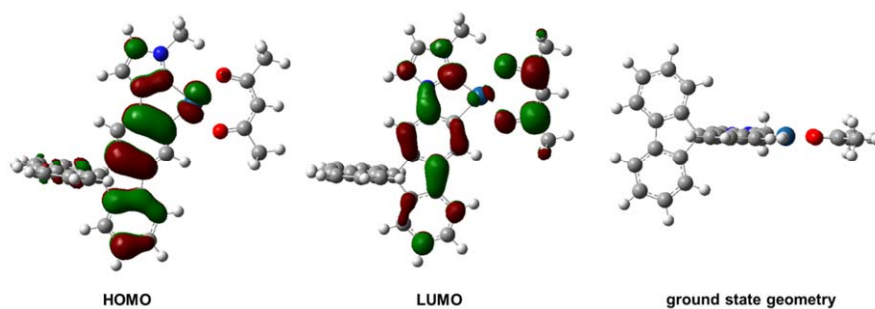


Figure S34: Calculated frontier molecular orbitals for the ground state of **4a** (left and center, isoval: MO = 0.03). Optimized geometry for the ground state of **4a** (right).

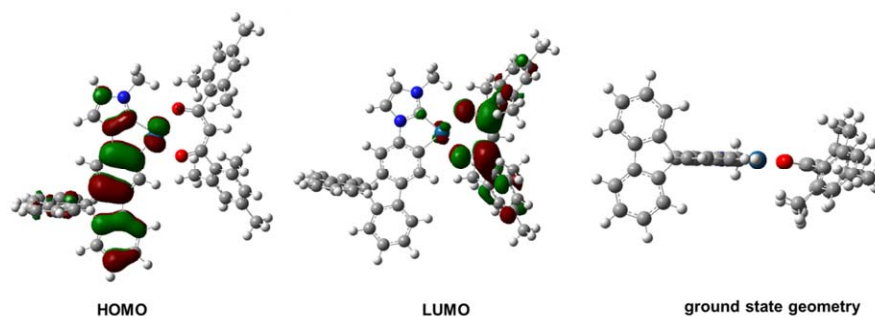


Figure S35: Calculated frontier molecular orbitals for the ground state of **4b** (left and center, isoval: MO = 0.03). Optimized geometry for the ground state of **4b** (right).

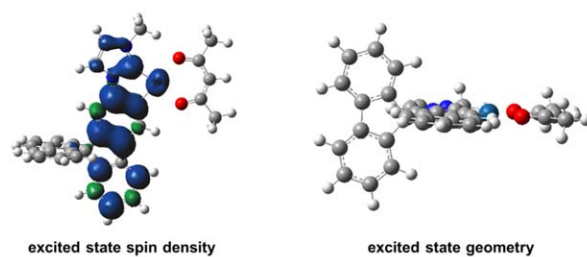


Figure S36: Calculated spin density of the triplet state of **4a** (left, isoval: MO = 0.03, density = 0.002). Optimized geometry for the excited triplet state of **4a** (right).

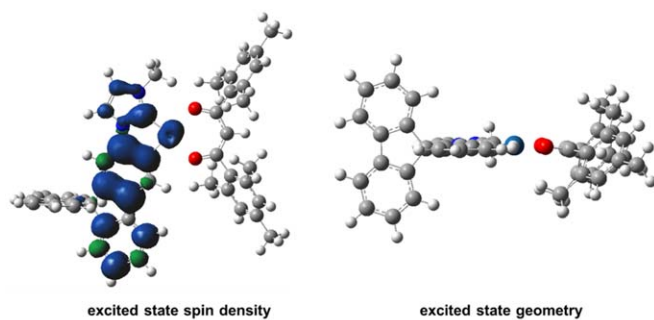


Figure S37: Calculated spin density of the triplet state of **4b** (left, isoval: MO = 0.03, density = 0.002). Optimized geometry for the excited triplet state of **4b** (right).

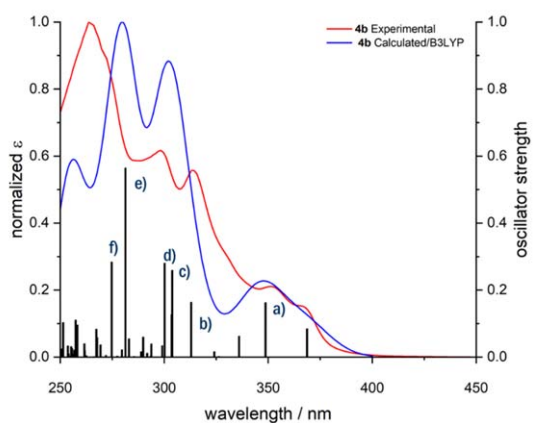
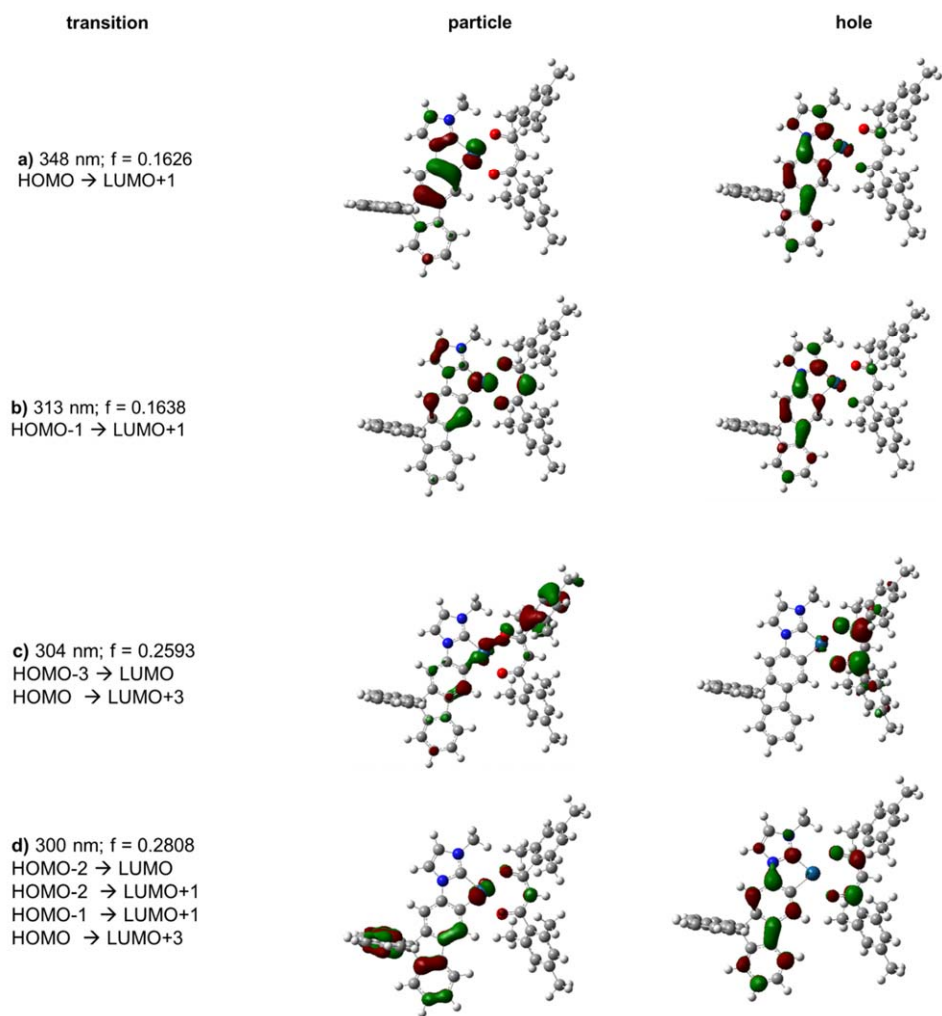


Figure S38: Comparison of experimental (blue) and calculated (red, 0.333 eV half-width) absorbance spectrum of **4b**. Transitions (a-f) are represented by oscillator strengths (black) as obtained from the calculations (cf. Figure S39).



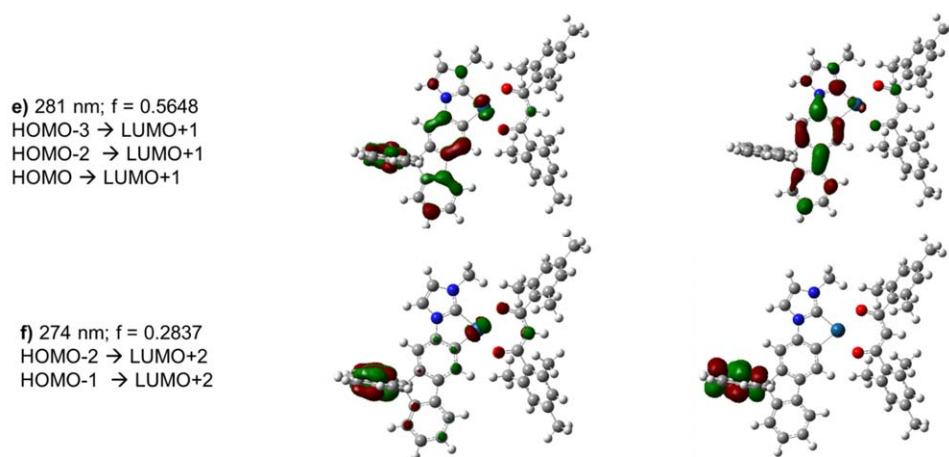


Figure S39: NTO analysis (isoval MO = 0.04) of complex **4b** for the transitions (a-f) labeled in Figure S38.

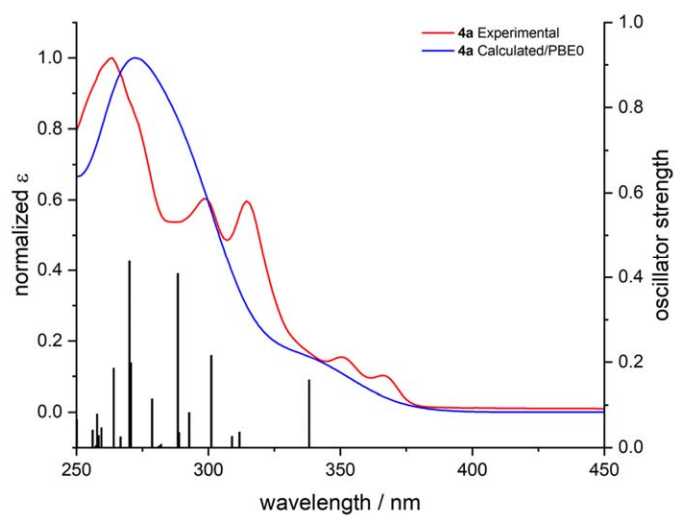


Figure S40: Comparison of experimental (blue) and, based on PBE0, calculated (red, 0.333 eV half-width) absorbance spectrum of **4a**. Transitions are represented by oscillator strengths (black) as obtained from the calculations.

Electrochemistry

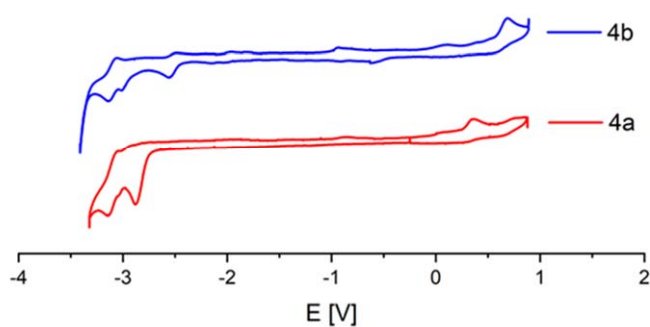


Figure S41: Stacked cyclic voltammograms of complexes **4a** (red) and **4b** (blue) measured in deoxygenated DMF solutions (1 mM analyte concentration) at room temperature and internally referenced against Fc/Fc^+ , based on the obtained reference waves with ferrocene (cf. Fig. S41). Cyclic voltammograms were recorded at a sweep rate of 100 mV/s at room temperature.

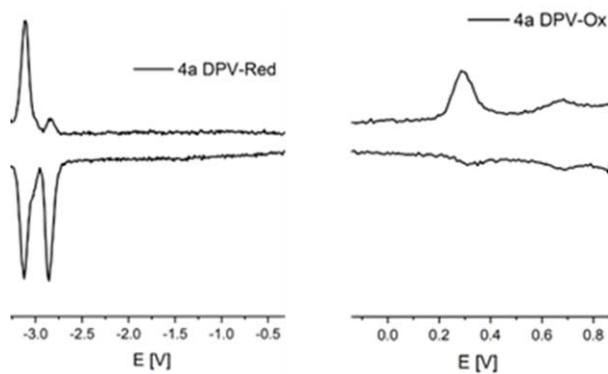


Figure S42: Differential pulse voltammograms of the first (quasi-reversible) reductive (left) and first (quasi-reversible) oxidative (right) event of **4a** referenced internally against Fc/Fc^+ . Voltammograms were recorded in deoxygenated DMF solutions (1mM analyte) at room temperature with a sweep rate of 50 mV/s.

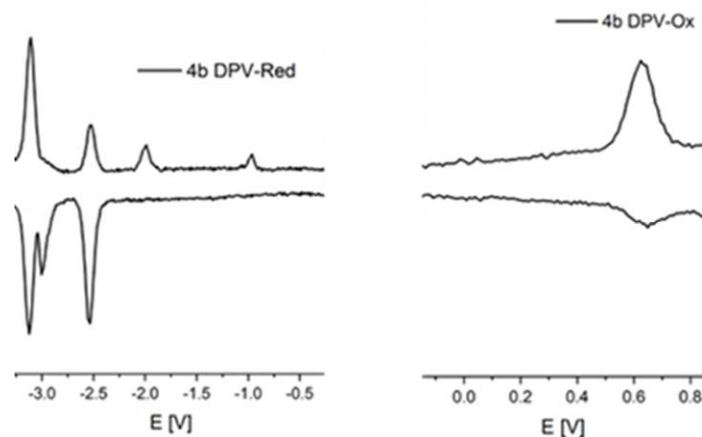


Figure S43: Differential pulse voltammograms of the first (quasi-reversible) reductive (left) and first (quasi-reversible) oxidative (right) event of **4b** referenced internally against **Fc/Fc***. Voltammograms were recorded in deoxygenated DMF solutions (1mM analyte) at room temperature with a sweep rate of 50 mV/s.

References

- (1) Drew, D.; Doyle, J. R.; Shaver, A. G. *Cyclic Diolefin Complexes of Platinum and Palladium*; John Wiley & Sons, Inc, 2007.
- (2) Zhang, C.; Yang, P.; Yang, Y.; Huang, X.; Yang, X.-J.; Wu, B. High-Yield Synthesis of 1,3-Dimesitylpropane-1,3-dione: Isolation of Its Aluminum Complex as a Stable Intermediate. *Synth. Commun.* **2008**, *38*, 2349–2356.
- (3) Bruker AXS Inc. *Bruker Crystallographic Suite APEX3*; Madison, Wisconsin, USA, 2017.
- (4) Bruker AXS Inc. *Bruker Integration Engine SAINT*; Madison, Wisconsin, USA, 2017.
- (5) Sheldrick, G. M. *SADABS Multi Scan Absorption*; University of Goettingen, Goettingen, Germany, 2016.
- (6) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* **2015**, *71*, 3–8.
- (7) Sheldrick, G. M. SHELXT - integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015**, *71*, 3–8.
- (8) Hahn, T. *Space-group symmetry*, 3., rev. ed.; International tables for crystallography / publ. for the International Union of Crystallography; Vol. A; Kluwer Acad. Publ: Dordrecht, 1992.
- (9) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. A* **2008**, *64*, 112–122.
- (10) Spek, A. L. Structure validation in chemical crystallography. *Acta Crystallogr. D* **2009**, *65*, 148–155.
- (11) Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.; Wood, P. A.; Mercury 4.0: from visualization to analysis, design and prediction. *J. Appl. Crystallogr.* **2020**, *53*, 226–235.

-
- (12) M. J. Frisch G. W. Trucks H. B. Schlegel G. E. Scuseria M. A. Robb J. R. Cheeseman G. Scalmani V. Barone B. Mennucci G. A. Petersson H. Nakatsuji M. Caricato X. Li H. P. Hratchian A. F. Izmaylov J. Bloino G. Zheng J. L. Sonnenberg M. Hada M. Ehara K. Toyota R. Fukuda J. Hasegawa M. Ishida T. Nakajima Y. Honda O. Kitao H. Nakai T. Vreven J. A. Montgomery Jr. J. E. Peralta F. Ogliaro M. Bearpark J. J. Heyd E. Brothers K. N. Kudin V. N. Staroverov T. Keith R. Kobayashi J. Normand K. Raghavachari A. Rendell J. C. Burant S. S. Iyengar J. Tomasi M. Cossi N. Rega J. M. Millam M. Klene J. E. Knox J. B. Cross V. Bakken C. Adamo J. Jaramillo R. Gomperts R. E. Stratmann O. Yazyev A. J. Austin R. Cammi C. Pomelli J. W. Ochterski R. L. Martin K. Morokuma V. G. Zakrzewski G. A. Voth P. Salvador J. J. Dannenberg S. Dapprich A. D. Daniels O. Farkas J. B. Foresman J. V. Ortiz J. Cioslowski D. J. Fox *Gaussian 09 Revision D.01 Gaussian Inc. Wallingford CT 2013*, 2013.
- (13) Dennington, R.; Keith, T. A.; Millam, J. M. *GaussView, Version 6.0*; Semichem Inc., Shawnee Mission, KS, 2016.
- (14) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*; CRC Press, 2006.
- (15) Kerzig, C.; Guo, X.; Wenger, O. S. Unexpected Hydrated Electron Source for Preparative Visible-Light Driven Photoredox Catalysis. *J. Am. Chem. Soc.* **2019**, *141*, 2122–2127.
- (16) Bertrams, M.-S.; Kerzig, C. Converting p-terphenyl into a novel organo-catalyst for LED-driven energy and electron transfer photoreactions in water. *Chem. Commun.* **2021**, *57*, 6752–6755.
- (17) Carmichael, I.; Hug, G. L. Triplet–Triplet Absorption Spectra of Organic Molecules in Condensed Phases. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1–250.
- (18) Kocia, R. Pulse radiolysis studies of intermediates derived from p-terphenyl in the oxygenated methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide ionic liquid. *Int. J. Chem. Kinet.* **2019**, *51*, 958–964.

Maria-Sophie Bertrams

Curriculum Vitae

Personal Information

Name	Maria-Sophie Bertrams
Date / Place of Birth	02.09.1993 / Waldshut
Address	
E-Mail	mbertra@uni-mainz.de

School and Education

2007 – 2012	Apprenticeship for carpentry in addition to school), in Heimschule Kloster Wald, Degree: carpenter ()
2003 – 2011	Secondary school, in Heimschule Kloster Wald, Degree: A-levels ()

Studies and University

01.10.2020 – today	PhD-thesis; group of , University of Mainz
28.10.2019 – 21.04.2020	Masterthesis; group of , University of Basel Title: "Photochemistry with novel <i>p</i> -terphenyl-based catalysts: sustainable photocatalytic applications and mechanistic insights"
08.2018 – 05.2020	Master-studies chemistry, University of Basel Degree: Master of Science in Chemistry ()
02.2016 – 08.2018	Bachelor-studies chemistry, University of Basel, Degree: Bachelor of Science in Chemistry ()
08.2014 – 02.2016	Bachelor-studies biology, University of Basel
02.2014 – 08.2014	Bachelor-studies chemistry, University of Zürich

Jobs and Internships

08.06. – 19.06.2020	Internship at hospital „Hochrheinklinikum Waldshut“
16.09. – 27.09.2020	Internship at the emergency medical service station in Waldshut
Summer 2014, 2015, 2016, 2017	Holiday-job at the German postal service "Deutsche Post"
09.2012 – 03.2014	Social year at the University clinic in Freiburg, abdominal surgery section

Interests and Activities

Red Cross section Tiengen	Since 2015 acting member of a Red Cross organization; advanced training as paramedic
Languages	German (native language), English, Latin, French (basic skills)
Music	Playing piano; Musical director of the group „Himmelwärts“ (Seelsorgeeinheit St. Verena Waldshut-Tiengen)
Sports	Jogging, racing cycle

Publications

- Schmitz, M.; Bertrams, M.-S.; Sell, A.; Glaser, F.; Kerzig, C.; 2024, *J. Chem. Am. Soc.*; submitted.
- Fritsch, L.; Vukadinovic, Y.; Lang, M.; Naumann, R.; Bertrams, M.-S.; Kruse, A.; Schoch, R.; Müller, P.; Neuba, A.; Dierks, P.; Lochbrunner, S.; Kerzig, C.; Heinze, K.; Bauer, M.; 2024, *ChemPhotoChem*; e202300281; DOI: 10.1002/cptc.202300281
- Kitzmann, W.; Bertrams, M.-S.; Boden, P.; Fischer, A. C.; Klauer, R.; Sutter, J.; Naumann, R.; Förster, C.; Nieder-Schatteburg, G.; Bings, N. H.; Hunger, J.; Kerzig, C.; Heinze, K.; 2023; *Journal of the American Chemical Society*; **145**; 16597-16609; DOI:10.1021/jacs.3c03832
- Bertrams, M.-S.; Hermainski, K.; Mörsdorf, J.-M.; Ballmann, J.; Kerzig, C.; 2023; *Chemical Science*; **14**; 8583-8591; DOI:10.1039/D3SC01725G
- Zähringer, T. J. B.; Moghtader, J. A.; Bertrams, M.-S.; Roy, B.; Uji, M.; Yanai, N.; Kerzig, C.; 2023; *Angewandte Chemie International Edition*; **62**; e202215340; DOI: 10.1002/anie.202215340
- Riesebeck, T.; Bertrams, M.-S.; Stipurin, S.; Konowski, K.; Kerzig, C.; Strassner, T.; 2022; *Inorganic Chemistry*; **61**; 15499-15509; DOI: 10.1021/acs.inorgchem.2c02141
- Zähringer, T. J. B.; Bertrams, M.-S.; Kerzig, C.; 2022; *Journal of Materials Chemistry C*; **10**; 4568 – 4573, DOI: 10.1039/D1TC04782E
- Bertrams, M.-S.; Kerzig, C.; 2021; *Chemical Communications*; **57**; 6752 – 6755, DOI: 10.1039/D1CC01947C
- Pfund, B.; Steffen, D. M.; Schreier, M. R.; Bertrams, M.-S.; Ye, C.; Börjesson, K.; Wenger, O. S.; Kerzig, C.; 2020; *Journal of the American Chemical Society*; **23**, 10468 – 10476, DOI: 10.1021/jacs.0c02835
- Becker, M.; Bertrams, M.-S.; Constable, E. C.; Housecroft, C. E.; 2020; *Materials*; **13**; 1547, DOI: 10.3390/ma13071547
- Joss, D.; Bertrams, M.-S.; Häussinger, D.; 2019, *Chemistry – A European Journal*; **25**; DOI: 10.1002/chem.201901692

Supervision of Practical Courses, Research-Internships and Theses

- | | |
|--|---|
| 14.08.2023 (6 weeks)
[redacted]; Internship | "Reactivity control via exchanging Ir-dyads for their metal-complex congeners" |
| 18.04.2022 (3 months)
[redacted]; Bachelor Thesis | "Novel annihilator-sensitizer couples for photon upconversion in water" |
| 10.01.2022 (6 weeks)
[redacted]; Internship | "Electron- and Energy Transfer Processes in Micellar Systems" |
| 13.09.2021 (6 weeks)
[redacted]; Internship | "Spin-Effekte in photoinduzierten Elektronentransfer-Reaktionen"
(English: Spin-effects in photoinduced electron transfer reactions) |
| 28.07.2021 (6 weeks)
[redacted]; Internship | "Intramolecular triplet-triplet energy transfer enhanced triplet triplet annihilation upconversion with long lived organic triplet states in molecular dyads" |
| 15.05.2021 (6 weeks)
[redacted]; Internship | "Untersuchung der Auswirkung von Coulomb-Wechselwirkung auf photokatalytische Energie-und Elektronentransfermechanismen"
(English: Exploration of the effect of Coulomb-interactions on photocatalytic energy- and electron transfer mechanisms) |

Maria-Sophie Bertrams

Winter semester 2020/21, Summer semester 2021, Winter semester 2021/22	Practical course M2 for bachelor students in education; 1-2 days for 6 weeks
Summer semester 2022 Winter semester 2022/23 Sommer semester 2023 Winter semester 2023/24	Practical course M12 for bachelor students in education; 1-2 days for 6 weeks Seminar on the photochemistry experiment for the practical course M12 for master students in education

Conferences

26.02.-28.02.2024 18 th KCT, Innsbruck	„Merging photoactive metal complexes with organic chromophores to achieve reactivity control”; Talk
18.02.-22.02.2024 CECP, Bad Hofgastein	„Switching from electron transfer to energy transfer photochemistry with molecular dyads”; Poster
21.12.2023 Joint Seminar of Inorg. Chem. Uni Mainz	„Transient absorption spectroscopy for exploring triplet reactivity”; Talk
01.12.2023 Christmas Symposium, Basel	„Switching from electron transfer to energy transfer photochemistry with molecular dyads”; Poster
04.10.-06.10.2023 1 st Light Induced Transformations, Regensburg	„Energy and electron transfer photochemistry in water – controlling the quenching pathway in photocatalysis”; Poster
19.09.-21.09.2022 28 th Lecture Conference on Photochemistry, Düsseldorf	„Energy and electron transfer photochemistry in water – controlling the quenching pathway and photocatalytic applications”; Poster
13.02.-17.02.2022 CECP, Bad Hofgastein	“Exploring p-terphenyl derivatives for LED-driven photocatalysis in water”; Talk
24.06.2021 Joint Seminar of Inorg. Chem. Uni Mainz, online	“Water-soluble p-terphenyl derivatives for sustainable photoredox chemistry”; Talk
29.03.-01.04.2021 JCF Springsymposium, online	. “A p-terphenyl derivative as versatile organo-photocatalyst for sustainable electron and energy-transfer reactions”; Poster
19.10.2020 CYSS: Light Driven Catalysis, online	“An SO ₂ -bridged p-terphenyl as versatile organo-photocatalyst under sustainable reaction conditions”; Poster
14.09. - 15.09.2020 27 th Lecture Conference on Photochemistry, online	“How an SO ₂ -bridge enables intersystem crossing and photocatalytic applications of a water-soluble p-terphenyl derivative”; Poster
01.03. – 03.03.2020 Koordinationschemie Treffen, Uni Freiburg	“Sustainable photoredox chemistry with novel p-terphenyl-based catalysts”; Poster

Further activities

28.04.2022, 27.04.2023	Talk for “Girls day” with the program “Meet female scientists”
20.01.2023, 01.02.2024	Co-supervision of a lab-visit for pupils with the “Nat-Lab” of the University Mainz

Date: 28.04.2024

Signature: _____

