

Molecular Rubies – Photocatalysis and Energy Tuning

Dissertation zur Erlangung des Grades eines

Doctor rerum naturalium (Dr. rer. nat.)

des Fachbereichs 09

Chemie, Pharmazie, Geographie und Geowissenschaften

der Johannes Gutenberg-Universität Mainz

im Promotionsfach Chemie

vorgelegt von

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geboren in Mainz.

September 2025

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Molecular Rubies — Photocatalysis and Energy Tuning

Dissertation

Date of submission: 09th of September 2025

First reviewer: [REDACTED]

Second reviewer: [REDACTED]

Date of the oral exam:

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This thesis was written in the period from April 2021 to September 2025 at the Department of Chemistry of the Johannes Gutenberg University Mainz under the supervision [REDACTED]

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Abstract

To a photochemist, light is energy waiting to be used chemically. Doing so requires the use of photoactive compounds such as photocatalysts (PCs). PCs are capable of absorbing light and storing part of its energy for a certain period of time, during which their reactivity is heightened. Most PCs are transition metal complexes (TMCs) containing noble metals such as ruthenium or iridium. These elements are very rare and expensive, which inherently impedes their use in large-scale photochemistry. By comparison, chromium is much more abundant and could serve as a promising replacement in photochemical applications.

The first part of this work includes a total of four studies, which explore the utilization of highly emissive chromium(III) complexes with long excited-state (ES) lifetimes, so-called *Molecular Rubies*, in photocatalysis. In addition, unique strengths and/or reactivities of these compounds may be identified.

The initial study presented in this work explores the use of the tripodal *Molecular Ruby* $[\text{Cr}(\text{tpe})_2]^{3+}$ as a photoredox catalyst in a radical cation [4+2] cycloaddition reaction (tpe = 1,1,1-tris(pyrid-2-yl)ethane). This complex possesses a strongly oxidizing and extremely long-lived ES ($E_{\text{red}}^* = 1.25 \text{ V}$; $\tau_0 = 3.5 \text{ ms}$), which should permit bimolecular reactivity via electron transfer. Over the course of the study, $[\text{Cr}(\text{tpe})_2]^{3+}$ succeeded in catalyzing the radical cation cycloaddition, displaying a high level of photostability and outperforming the noble metal complex $[\text{Ru}(\text{bpz})_3]^{2+}$ (bpz = 2,2'-bipyrazine). Additionally, a combination of photocatalytic experiments and spectroscopic methods shed light on the reaction mechanism, particularly the role of oxygen as a redox-shuttle.

Building on the promising results of the preceding study, a more complex photocatalytic system is explored. The light-induced fixation of SO_2 into organic molecules in two three-component reactions yielded sulfones and sulfonamides, respectively. Mechanistic investigations via laser flash photolysis revealed that the success of these multi-component reactions partially stemmed from vastly different cage-escape yields between individual substrates.

In the third study a unique tool for future mechanistic investigations was created. The parent complex $[\text{Cr}(\text{tpe})_2]^{3+}$ was substituted with one or two trifluoromethyl-groups, respectively. The thereby obtained complexes $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ and $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ display almost unaltered coordination geometries and emission energies. In contrast, their reduction potentials are shifted +100 mV per CF_3 -group. Tuning the reduction potential while leaving the emission energy untouched is highly unusual. In these chromium(III) complexes this endeavour succeeded, due to the

spatial separation of the metal-centered ESs and the ligand-centered reduction. When looking at electron transfer reactions, the only variable that changes between these compounds is the reduction potential and thus the thermodynamic driving force. The series of complexes obtained from this research should thus permit studies on the isolated effect of the driving force on e.g. cage-escape yields.

Aiming to expand the impact of this now established catalyst, $[\text{Cr}(\text{tpe})_2]^{3+}$ was used to address some common challenges associated with the scalability of photocatalysis. These include high cost, limited stability/recyclability of noble metal catalysts, the need for sophisticated irradiation setups due to their high absorptivity (e.g. flow-reactors) as well as their often poor performance in water. To overcome these hurdles, simple, cheap and scalable syntheses from abundant materials were developed for both tpe and $[\text{Cr}(\text{tpe})_2]^{3+}$. The complex was utilized in a number of laboratory-scale photocatalytic transformations, which were conducted in standard glassware. This setup took advantage of the complex's low absorptivity, which facilitates the use of longer optical paths. The complex was recycled in up to >90% yield, which underlines its high level of stability. Furthermore, the chromium(III) complex was successfully employed as a photoredox catalyst in water, showing neither solubility/stability issues nor detrimental shortening of its ES lifetime.

The second part of this work consists of a study that investigates the properties of the newly developed $[\text{Cr}(\text{dgpy})_2]^{3+}$. In this compound, two of the pyridine moieties typical for *Molecular Rubies* are replaced with saturated, cyclic guanidines. Photo-physical characterization of this complex showed a red-shift of the emission energy, relative to polypyridyl complexes. This was attributed to a stronger *nephelauxetic effect*. Fast, non-radiative decay was observed for this compound, which resulted in a short ES lifetime and low quantum yield. These observations were attributed to thermally activated back-intersystem crossing to its distorted ^4ES and to intramolecular energy transfer to the C–H oscillators of its guanidine moieties.

The research conducted in this work establishes the *Molecular Ruby* $[\text{Cr}(\text{tpe})_2]^{3+}$ as a highly promising photocatalyst. Its desirable properties include strong oxidative power, a long ES lifetime, accessibility, stability, solubility in different solvents and its tendency to favor simple reactor designs. With the help of this compound, crucial mechanistic information was gained regarding catalyst reoxidation and cage-escape. Future studies on these aspects of the catalytic cycle will be facilitated owing to the development of the derivatives $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ and $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ and their shifted reduction potentials. In a separate effort, the development and characterization of $[\text{Cr}(\text{dgpy})_2]^{3+}$ has provided deep insight into ES decay mechanisms of chromium(III) complexes. The design of new, highly-emissive *Molecular Rubies* will benefit from the information obtained from this compound. The knowledge gained from this work solidifies the relevance of TMCs containing earth-abundant metals in the fields of photocatalysis and fundamental photophysical research.

Kurzzusammenfassung

Für den Photochemiker ist Licht Energie, die darauf wartet chemisch genutzt zu werden. Dazu bedarf es photoaktiver Materialien wie Photokatalysatoren, welche in der Lage sind Licht zu absorbieren und dessen Energie für eine bestimmte Zeit zu speichern. In diesem Zeitfenster ist die Reaktivität des Katalysators erhöht. Die meisten Photokatalysatoren sind Komplexe edler Übergangsmetalle wie Ruthenium oder Iridium. Diese Elemente sind sehr selten und teuer, was ihre Anwendbarkeit für Photochemie in großem Maßstab inhibiert. Häufiger vorkommende Metalle wie Chrom könnten in diesem Kontext Abhilfe schaffen.

Der erste Teil dieser Arbeit besteht aus vier Studien, die die Anwendung von stark emissiven Chrom(III)-Komplexen (sog. *Molekularen Rubinen*) mit langlebigen angeregten Zuständen (AZ) in der Photokatalyse untersuchen. Zudem könnten einzigartige Stärken und/oder Reaktivitäten dieser Verbindungen entdeckt werden.

Die erste Studie untersucht die Verwendung des tripodalen *Molekularen Rubins* $[\text{Cr}(\text{tpe})_2]^{3+}$ als Photokatalysator in einer radikal-kationischen [4+2]-Cycloaddition ($\text{tpe} = 1,1,1\text{-tris}(\text{pyrid-2-yl})\text{ethan}$). Der Komplex besitzt stark oxidierende und langlebige AZ ($E_{\text{red}}^* = 1.25 \text{ V}$; $\tau_0 = 3.5 \text{ ms}$), die bimolekulare Reaktivität über Elektronentransfer ermöglichen sollten. In dieser Studie fungierte $[\text{Cr}(\text{tpe})_2]^{3+}$ erfolgreich als Katalysator der Cycloaddition, wobei es durch seine hohe Photostabilität dem Edelmetallkomplex $[\text{Ru}(\text{bpz})_3]^{2+}$ überlegen war ($\text{bpz} = 2,2'\text{-bipyrazin}$). Zusätzlich konnte mittels photokatalytischer Experimente und spektroskopischer Methoden molekularer Sauerstoff als Redox-Shuttle identifiziert werden.

Nach den vielversprechenden Ergebnissen der vorigen Studie wurden zwei komplexere Dreikomponenten-Reaktionen untersucht. Durch die lichtinduzierte Fixierung von SO_2 in organische Moleküle, konnten so Sulfone und Sulfonamide hergestellt werden. Untersuchungen der Mechanismen mittels Laser-Flash-Photolyse zeigten, dass der Erfolg dieser Reaktionen auf stark unterschiedlichen Cage-Escape-Ausbeuten der verschiedenen Substrate beruhte.

In der dritten Studie konnte ein einzigartiges Werkzeug für zukünftige mechanistische Untersuchungen geschmiedet werden. $[\text{Cr}(\text{tpe})_2]^{3+}$ wurde mit einer bzw. zwei Trifluormethyl-Gruppen substituiert. Die so erhaltenen Komplexe $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ und $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ zeigen nahezu unveränderte Koordinationsgeometrien und Emissionsenergien. Im Gegensatz dazu sind ihre Reduktionspotentiale um +100 mV pro CF_3 -Gruppe verschoben. Die Verschiebung des Reduktionspotentials unabhängig von der Emissionsenergie ist höchst ungewöhnlich, gelingt aber in diesen Komplexen durch die räumliche Trennung der metallzentrierten AZ und der ligandenzentrierten Reduktion. In Elektronentransfer-Reaktionen ändert sich zwischen diesen Komplexen

lediglich das Reduktionspotential und somit die thermodynamische Triebkraft. Diese Verbindungsreihe sollte in zukünftigen Studien dazu genutzt werden können, den isolierten Einfluss der Triebkraft auf z.B. Cage-Escape-Ausbeuten zu untersuchen.

Um den Einfluss des nun etablierten Katalysators $[\text{Cr}(\text{tpe})_2]^{3+}$ zu erweitern, wurde dieser genutzt, um gängige Herausforderungen in der Skalierbarkeit von Photokatalyse zu adressieren. Diese umfassen hohe Kosten, begrenzte Stabilität und Wiederverwendbarkeit molekularer Edelmetall-Katalysatoren, die Notwendigkeit komplexer Bestrahlungsaufbauten (z.B. Flow-Reaktoren) aufgrund ihrer hohen molaren Extinktionskoeffizienten sowie ihre oft schlechte Leistungsfähigkeit in Wasser. Um diese Hürden zu überwinden, wurden simple, kostengünstige und skalierbare Synthesen basierend auf gut verfügbaren Materialien für tpe und $[\text{Cr}(\text{tpe})_2]^{3+}$ entwickelt. Der Komplex wurde in mehreren photokatalytischen Reaktionen auf einer Laborskala verwendet, wobei herkömmliche Glasgeräte genutzt werden konnten. Dieser Aufbau nutzt den niedrigen Extinktionskoeffizienten des Komplexes, welcher längere optische Weglängen begünstigt. Der Komplex wurde in Ausbeuten von bis zu >90% wiedergewonnen, was seine Stabilität unterstreicht. Zudem wurde $[\text{Cr}(\text{tpe})_2]^{3+}$ erfolgreich als Photokatalysator in Wasser verwendet und zeigte weder Einbußen bezüglich Löslichkeit, Stabilität oder Langlebigkeit seiner AZ.

Der zweite Teil dieser Arbeit besteht aus einer Studie, in welcher die Eigenschaften von $[\text{Cr}(\text{dgy})_2]^{3+}$ untersucht wurden. In dieser Verbindung sind zwei der für *Molekular Rubine* gängigen Pyridin-Einheiten durch gesättigte, cyclische Guanidine ausgetauscht. Die photophysikalische Charakterisierung des Komplexes zeigte eine Rotverschiebung der Emissionsenergie, relativ zu Polypyridyl-Komplexen. Diese Beobachtung wurde einem ausgeprägteren *nephelauxetischen Effekt* zugeordnet. Schnelle, strahlungslose Relaxation wurde beobachtet, was sich in einer kurzen Lebenszeit sowie niedrigen Quantenausbeute äußerte. Diese Ergebnisse wurden über thermisch aktiviertes *back-Intersystem Crossing* zum verzerrten ^4AZ und über intramolekularen Energietransfer zu den C–H-Oszillatoren der Guanidin-Einheiten erklärt.

Diese Forschungsarbeit etabliert den *Molekularen Rubin* $[\text{Cr}(\text{tpe})_2]^{3+}$ als vielversprechenden Photokatalysator, welcher viele wünschenswerte Eigenschaften wie synthetische Zugänglichkeit und hohe Stabilität aufweist. Mit dieser Verbindung konnten essentielle Informationen über Katalysator-Reoxidation und Cage-Escape erhalten werden. Zukünftige Studien dieser mechanistischen Aspekte können erweitert und vertieft werden, dank der neu entwickelten Komplexe $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ und $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ und ihrer verschobenen Reduktionspotentiale. In einer separaten Arbeit wurden mithilfe der neuen Verbindung $[\text{Cr}(\text{dgy})_2]^{3+}$ tiefe Einblicke in strahlungslose Relaxationsprozesse von Chrom(III)-Komplexen gewonnen. Die Entwicklung neuer *Molekularer Rubine* wird von den so gewonnenen Informationen profitieren. Das in dieser Arbeit erlangte Wissen festigt die Relevanz von Übergangsmetallkomplexen häufig vorkommender Metalle im Bereich photokatalytischer und photophysikalischer Forschung.

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List of Abbreviations

A acceptor

acac[−] deprotonated acetylacetone

ATRA atom transfer radical addition

bath 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline

BIH benzimidazoline

bISC back-intersystem crossing

bpmp 2,6-bis(2-pyridylmethyl)pyridine

bpop 2,6-bis(pyridine-2-yloxy)pyridine

bptp 2,6-bis(pyridine-2-ylthio)pyridine

bpy 2,2'-bipyridine

bpz 2,2'-bipyrazine

BTP bis (1*H*-1,2,4-triazol-5-yl)pyridine

btz 3,3'-dimethyl-1,1'-bis-(*p*-tolyl)-4,4'-bis(1,2,3-triazol-5-ylidene)

CE cage-escape

CFL compact fluorescent lamp

CNDipp 2,6-diisopropylphenylisocyanide

CT charge-transfer

CV cyclic voltammetry

D donor

DABCO 1,4-diazabicyclo[2.2.2]octane

dap 2,9-di(*p*-anisyl)-1,10-phenanthroline

ddpd *N,N'*-dimethyl-*N,N'*-dipyridin-2-yl-pyridine-2,6-diamine

DFT density functional theory

dgpy 2,6-diguanidylpyridine

dmcbpy 2,2'-bipyridine-4,4'-dicarboxylate
DPA 9,10-diphenylanthracene
dpc[−] deprotonated 3,6-di-*tert*-butyl-1,8-di(pyridine-2-yl)-carbazole
dqp 2,6-di(chinolin-8-yl)pyridine
DTET doublet-triplet energy transfer
en ethylenediamine
EnT energy transfer
ES excited state
Et ethyl
ET electron transfer
fac facial
FRET Förster resonance energy transfer
GCR geminate charge-recombination
GS ground state
IC internal conversion
ⁱPr *iso*-propyl
ISC intersystem crossing
IR infrared
L ligand
LC ligand-centered
LED light emitting diode
LFP laser flash photolysis
LFS ligand field splitting
LMCT ligand-to-metal-charge-transfer
MC metal-centered
Me methyl
MLCT metal-to-ligand-charge-transfer
NHC *N*-heterocyclic carbene

NIR near-infrared

NMR nuclear magnetic resonance

nr non-radiative

P phosphorescence

Pc phthalocyanine

PC photocatalyst

${}^M_e\text{PDP}^{2-}$ deprotonated 2,6-bis(5-methyl-3-phenyl-1*H*-pyrrol-2-yl)pyridine

PDT photodynamic therapy

Ph phenyl

phen 1,10-phenanthroline

phtmeimb[−] deprotonated phenyl[tris(3-methylimidazol-1-ylidene)]borate

ppy[−] deprotonated 2-phenylpyridine

Q quencher

QY quantum yield

r radiative

RDF radial distribution function

SCE saturated calomel electrode

SF spin-flip

SOC spin-orbit coupling

SV Stern-Volmer

TA transient absorption

${}^t\text{Bu}$ *tert*-butyl

TM transition metal

TMC transition metal complex

tpe 1,1,1-tris(pyrid-2-yl)ethane

TPP^{2−} deprotonated 5,10,15,20-tetraphenylporphyrin

tpy 2,2':6',2''-terpyridine

tren(py)₃ tris(2-pyridyl-methylimino-ethyl)amine

TS Tanabe-Sugano

TTA triplet-triplet-annihilation

TTA-UC triplet-triplet-annihilation upconversion

TTET triplet-triplet energy transfer

UHP ultra high power

UC upconversion

UV ultraviolet

vis visible

VC vibrational cooling

Xant 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene

Introduction

1.1 Catalyzing a Sustainable Future

The blue planet is a home to more people than ever before. Further growth in global population is expected for the coming decades.^[1] This development is associated with a panoply of challenges, among these are an ever increasing need for energy and resources.^[2] Since Earth can only provide so much, it is imperative that we utilize the energy sources and materials provided to us efficiently and environmentally sound.

Over the past decades, awareness for these pressing issues has increased. While finite energy sources like fossil fuels are still heavily used, sustainable energies have received a tremendous increase in attention.^[2,3] One of the most prominent representatives of the latter is light energy, which can be transformed into electrical (photovoltaic technology) or chemical energy (photochemistry).^[3–6]

The concept of harvesting and employing light is neither new, nor man-made. In fact, the most skilled photochemists – plants and algae – have been doing it for potentially billions of years as the basis of photosynthesis.^[5,7] They do this by using so-called chromophores: molecules, which are capable of absorbing visible light and utilizing its energy chemically. Human photochemists have developed numerous classes of chromophores themselves, transition metal complexes (TMCs) being one of the most prominent examples.^[8]

TMCs are a highly diverse class of chemicals and consist of one or more central metal atoms coordinated by a variable number of ligands. Together, these parts create new compounds, which display a variety of interesting photophysical and electrochemical properties. Thus, they can serve in a plethora of applications, such as organic light emitting diodes,^[9] dye-sensitized solar cells^[10] or as photocatalysts (PCs) in e.g. organic synthesis or medical procedures like photodynamic therapy.^[6,8,11] A PC can engage in electron transfer (ET) or energy transfer (EnT) after light-absorption, provided its excited-state (ES) is sufficiently long-lived to permit bimolecular reactions (in the absence of pre-organization). Thus, it is possible to access unique reactivities via the generation of organic radicals/triplets under mild conditions.^[6,8] In the realms of photophysics and photocatalysis, noble metal TMCs containing elements like ruthenium or iridium have been the workhorses for a long time. The most prominent complex of this class, $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine), has been called *the fruit fly of photophysics*.^[12]

While these noble metal TMCs often perform well in their respective applications,

they suffer from severe drawbacks with regards to the finite nature of resources discussed previously. Ruthenium and iridium are among the rarest elements on Earth (Tab. 1.1) and are thus problematic for large-scale applications. This issue is further exacerbated by the fact that these metals are mined in but a few countries,^[13] which makes their global availability unreliable in times of geopolitical conflict. Furthermore, the photostability of ruthenium and iridium complexes is often limited, which further increases their effective cost and lowers the sustainability of their use.^[14]

Tab. 1.1: Earth-abundance (crust; mg/kg) of selected transition metals.^[13]

Ru/Ir	Ti	V	Cr	Mn	Fe	Co	Cu	Zr	Mo	W
0.001	5700	120	100	950	56000	25	60	170	1.2	1.3

Over the past decade, there has been a shift within the photochemistry community. Compounds based on more earth-abundant 3d transition metals such as iron, copper, chromium, cobalt, vanadium and manganese, as well as abundant 4/5d metals like molybdenum, zirconium and tungsten, have enjoyed the attention of many research groups (Fig. 1.1).^[15–20] This development has been fueled by both a desire to replace noble metals as part of a more sustainable approach to photochemistry and by curiosity on potential unique reactivities.^[21,22]

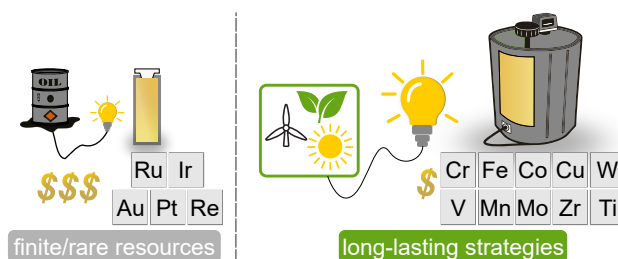


Fig. 1.1: Utilizing cheap, abundant materials and sustainable energy sources is a superior, scalable long-term plan. These approaches can help scale technologies like photocatalysis from cuvettes to reactors.

This work focuses mainly on the application of pseudo-octahedral chromium(III) complexes with long ES lifetimes in photocatalysis. Promises, challenges, as well as photo- and electrochemical particularities of these compounds as PCs are explored and assessed. Furthermore, the tunability of their electrochemical and emissive properties is investigated. The subsequent introduction will elucidate the photophysical properties of these so-called *Molecular Rubies*, comparing them to classic noble metal- and other 3d TMCs. Thereafter, the focus will be shifted towards concepts behind bimolecular reactions and the photocatalytic cycle. Lastly, recent advances in the utilization of earth-abundant metals in photocatalysis as well as future challenges, like upscaling (Fig. 1.1) and creation of a truly sustainable (photo)chemical industry will be illuminated.

1.2 Different Chromophores – Different Excited States

All chromophores have one commonality: they absorb energy in the form of light and are thereby promoted to an ES. However, the nature of the ES varies between different molecules and depends mainly on their electronic structure. In TMCs with electron-rich metal centers and electron-poor ligands, metal-to-ligand charge-transfer (MLCT) states typically dominate. Prominent examples are 4/5d TMCs like $[\text{Ru}(\text{bpy})_3]^{2+}$ (Fig. 1.2a) and *fac*- $\text{Ir}(\text{ppy})_3$ ($[\text{ppy}^-]$ = deprotonated 2-phenylpyridine).^[6,23] In contrast, the low-energy ESs of many 3d TMCs are metal-centered (MC).^[24] The subsequent sections 1.2.1 and 1.2.2 will address underlying photophysical processes in MLCT complexes, challenges associated with MC compounds and how said challenges can be overcome, with a particular focus on so-called *spin-flip* (SF) emitters.

1.2.1 Charge-Transfer Compounds

When an MLCT compound like $[\text{Ru}(\text{bpy})_3]^{2+}$ absorbs visible light ($\lambda_{\text{abs}} = 452 \text{ nm}$), a metal-centered *d* electron is transferred to a vacant, ligand-centered π^* orbital (MLCT; Fig. 1.2b), yielding a formally oxidized ruthenium(III) center and a radical anionic $\text{bpy}^{\bullet-}$ ligand.^[25,26] The initially populated state is of singlet multiplicity ($^1\text{MLCT}$), as the electronic transition upon absorption is spin-allowed. From the $^1\text{MLCT}$ state, ultrafast ($\approx 15 \text{ fs}$) and nearly quantitative intersystem-crossing (ISC) occurs.^[27–29] The heavy atom effect and the thereby induced strong spin-orbit coupling (SOC) allow this formally spin-forbidden transition to proceed. Thus, the vibrationally excited ("hot") $^3\text{MLCT}$ state is populated, from which vibrational energy is dispersed as heat through collision of $^3[\text{Ru}(\text{bpy})_3]^{2+}$ with solvent molecules (*vibrational cooling*, VC). The ES complex thereby reaches the vibrational GS and the relaxed geometry of the $^3\text{MLCT}$ state within 300 fs.^[29] The $^3\text{MLCT}$ state is slightly distorted relative to the ^1GS ^[30] due to the Coulomb attraction resulting from charge separation in the ES and due to the occupation of (nominally ligand-centered) antibonding orbitals.^[31] Said distortion leads to broad, unstructured emission bands as well as considerable vibronic coupling between the ES and GS (strong coupling limit, Fig. 1.5; detailed in section 1.2.2).^[32]

Following population of the $^3\text{MLCT}$ state, relaxation back to the electronic ^1GS can occur via spin-forbidden phosphorescence ($\lambda_{\text{em}} = 620 \text{ nm}$).^[23] The number of photons thus emitted N_{p} divided by the number of initially absorbed photons N_{abs} is referred to as the phosphorescence quantum yield $\Phi_{\text{p},0}$.^{a)}

^{a)} The subscript "0" denotes the absence of an external quencher (section 1.3), outside of potential quenching through solvent molecules via multiphonon-relaxation (section 1.2.2).

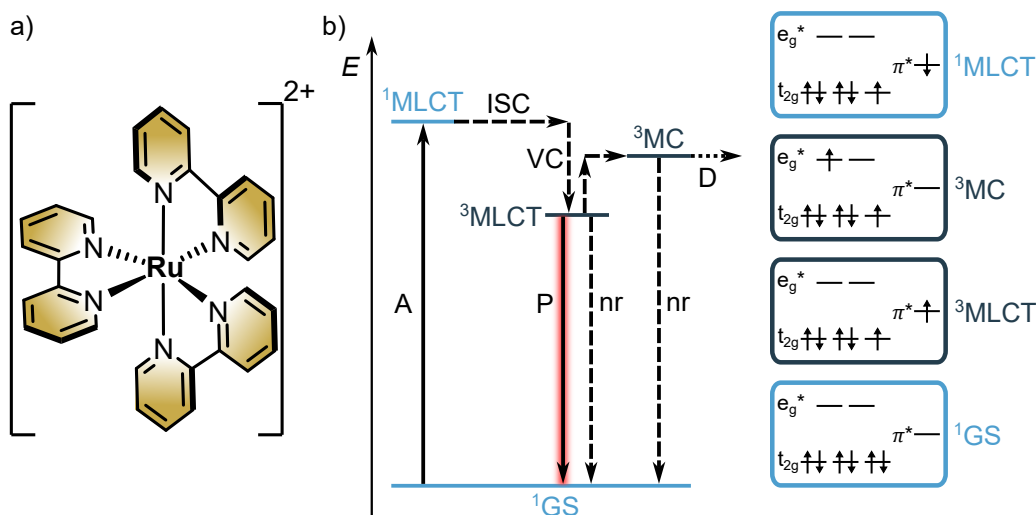


Fig. 1.2: a) Molecular structure of [Ru(bpy)₃]²⁺. b) Simplified Jablonski-type diagram for [Ru(bpy)₃]²⁺, including photophysical processes (A = absorption, ISC = intersystem crossing, VC = vibrational cooling, P = phosphorescence, nr = non-radiative decay, D = dissociation).

$\Phi_{P,0}$ depends on the efficiency of ISC Φ_{ISC} , the radiative rate k_p and the ES lifetime τ_0 (eq. 1.1). The ES lifetime τ_0 is the reciprocal sum of the rate constants of all processes that depopulate the ES (eq. 1.4).^[23,26]

$$\Phi_{P,0} = \frac{N_p}{N_{abs}} = \Phi_{ISC} \cdot k_p \cdot \tau_0 \quad (1.1)$$

$$\tau_0 = \frac{1}{k_r + k_{nr}} \quad (1.2)$$

Owing to the strong SOC in [Ru(bpy)₃]²⁺, Φ_{ISC} is close to unity and fluorescence from the ¹MLCT state is therefore not a relevant competitive mechanism.^[29] Furthermore, the value for k_p is high ($\approx 10^4 \text{ s}^{-1}$),^[33] since CT transitions are not affected by *Laporte's* rule and because they possess a large transition dipole moment.^[34] Due to the spin-forbidden nature of phosphorescence, and despite SOC rendering the spin selection rule less strict, a relatively long ES lifetime ($\tau_0 \approx 1 \mu\text{s}$) is observed for [Ru(bpy)₃]²⁺. These factors combined result in a high $\Phi_{P,0}$ of close to 10% in deaerated acetonitrile.^[25,29]

Apart from phosphorescence, non-radiative decay can depopulate the ³MLCT state, due to its (slight) geometric distortion and the resulting increase in vibronic coupling with the ¹GS (Fig. 1.5). Another major decay pathway is the thermally activated population of energetically higher-lying ³MC states (Fig. 1.2). In these interconfigurational MC states, antibonding e_g^* orbitals are populated, which leads to significant elongation and potential dissociation of the M–L bonds.^[34] Barring the latter, this strong distortion enables efficient non-radiative decay, which decreases $\Phi_{P,0}$ and τ_0 .

Despite the potential detrimental influence of MC states, they play a subordinate role in the photophysics of 4d and especially 5d TMCs, due to their high energies (*vide infra*). The lead is performed by the CT states discussed above. This ES ordering is a result of the large intrinsic ligand field splitting (LFS) caused by the expansive 4/5d orbitals, which allow for good overlap with ligand orbitals (Fig. 1.3a).^[35,36] The strong LFS shifts MC states to higher energies, (initially) preventing their population. In some 5d TMCs like the classic example *fac*-Ir(ppy)₃, the MC states are so high in energy that they become irrelevant, which contributes to a $\Phi_{p,0}$ of almost 100%.^[37,38]

Inherent Challenges of 3d Transition-Metal Complexes

In many 3d TMCs the ES landscape looks rather different. Here, MCs are considerably lower in energy, due to the small spatial expansion of the 3d orbitals. Their small size stems from a lack of a radial node (at $r \neq 0$) for the first new subshell of a given orbital angular momentum quantum number (e.g. 3d; Fig. 1.3).

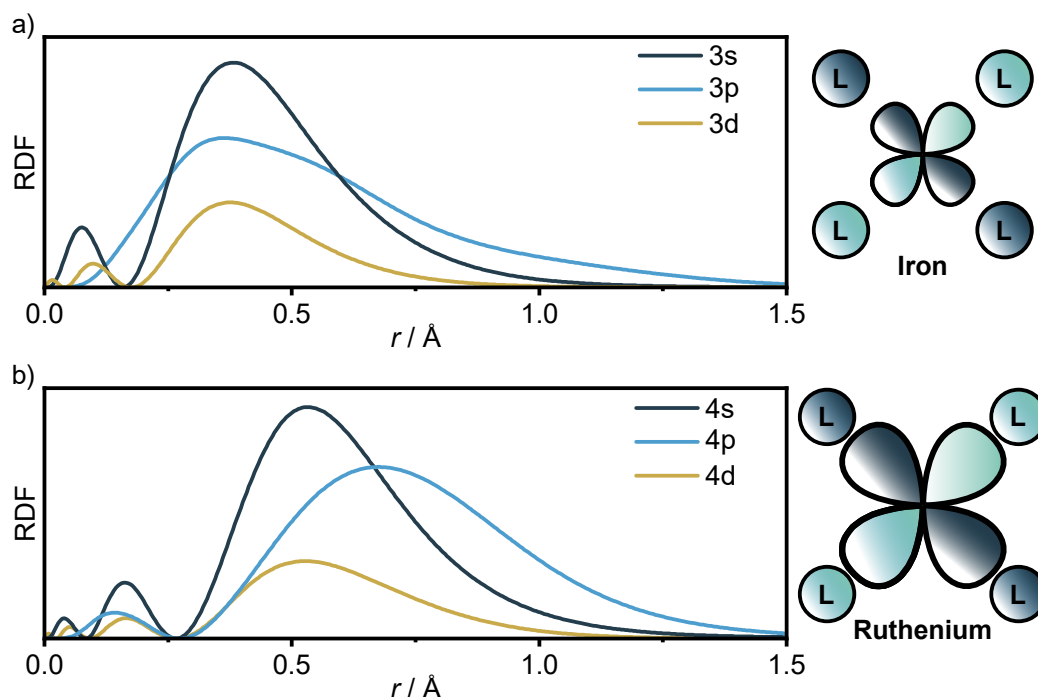


Fig. 1.3: Left side: radial distribution functions (RDFs) for a) the $n = 3$ shell of Fe^{II} and b) the $n = 4$ shell of Ru^{II}. Right side: schematic depiction of the different degrees of 3d/4d metal and ligand (L) orbital overlap resulting from the *primogenic effect*. Figure according to ref. [35].

This so-called *primogenic effect* leads to an increased effective nuclear charge acting on the 3d orbitals, which shifts the maximum value of their radial distribution function closer to the nucleus, resulting in less efficient overlap with ligand orbitals at a fixed distance (Fig. 1.3).^[35,36] The *primogenic effect* translates to 3d TMC

photophysics being typically dominated by MC transitions, which yield short-lived, non-emissive ("dark") states.^[15,39,40] An evident example is the *fruit fly's* lighter, isoelectronic homologue $[\text{Fe}(\text{bpy})_3]^{2+}$, which is non-emissive and possesses an ES lifetime in the sub-nanosecond range.^[41,42]

Strongly emissive iron(II) complexes have been a white whale of the photochemistry community for a long time, as iron is the most abundant transition metal on Earth.^[13,39] However, research into TMCs based on other earth-abundant metals has not been lacking. Multiple strategies for avoiding the population of detrimental MC states have therein been pursued.^[15,16,39,40,43–45] Perhaps the most straightforward approach has been the utilization of metals with completely filled (d^{10} ; e.g. copper(I), zinc(II)) or completely vacant (d^0 ; zirconium(IV)) d subshells, which renders d - d transitions impossible.^[16] A design strategy applied for TMCs with partially filled d -subshells is the utilization of strong field ligands, which are meant to destabilize the MC states. This approach has been implemented e.g. in multiple d^6 complexes of Cr^0 ,^[46] Mn^{I} ^[47,48] and Co^{III} .^[49,50] Representative examples of the presented design strategies will be highlighted in the context of photocatalytic applications (section 1.4).

One approach omitted from the discussion so far takes advantage of a special kind of MC: intraconfigurational *spin-flip* states.

1.2.2 Spin-Flip Compounds

SF compounds get their name from their "trademark" ESs that only differ from the GS by a flipped electron spin (and an electron pairing in the case of $^2\text{T}_{1g}$; Fig. 1.4). In principle, SF states are accessible with d^2 , d^3 , d^4 and d^8 configurations and can therefore be achieved by multiple transition metals, including e.g. vanadium(II/III), manganese(III/IV), nickel(II) or molybdenum(II/III/IV).^[51] However, the most prominent SF emitters are pseudo-octahedral chromium(III) complexes, which possess a d^3 configuration. Their ES dynamics will be discussed in the following section, using $[\text{Cr}(\text{ddpd})_2]^{3+}$, flagship of the so-called *Molecular Rubies*, as an example (ddpd = *N,N'*-dimethyl-*N,N'*-dipyridin-2-yl-pyridine-2,6-diamine; Fig. 1.6, X = NMe).^[52,53] For the sake of simplicity, O_h point group symmetry labels will be assumed.

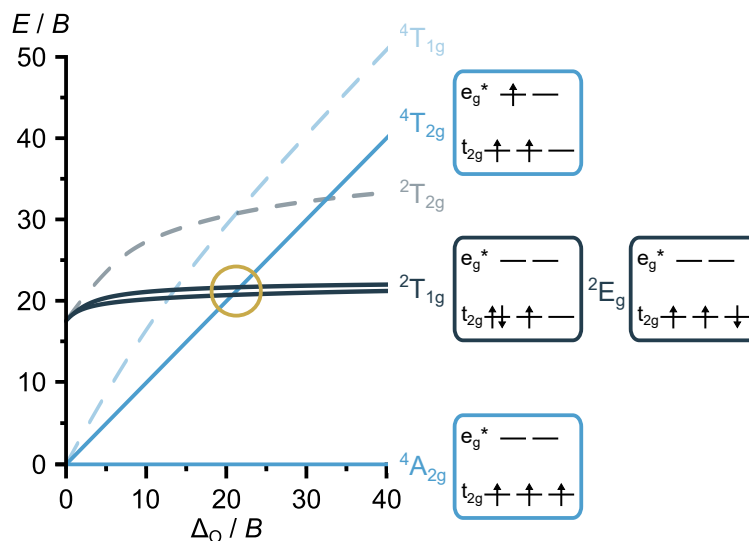


Fig. 1.4: Partial *Tanabe-Sugano* diagram for a d^3 ion in an octahedral ligand field and selected microstates. Past the ${}^4T_{2g}/{}^2E_S$ crossing point (orange circle), SF luminescence becomes possible.^[54,55]

Excited-State Dynamics

Dominated by MC states, the ES landscape of SF emitters like $[\text{Cr}(\text{ddpd})_2]^{3+}$ contrasts that of CT compounds. Therefore, it is sensible to consult the relevant d^3 *Tanabe-Sugano* (TS) diagram (Fig. 1.4). Importantly, potential energetically close-lying CT states are not described by the TS diagram and will not be discussed in detail for the sake of conciseness. Generally speaking, accounting for potentially parasitic or beneficial CT states is important in the successful design of SF emitters.^[51] Looking at the TS diagram, it is immediately apparent that the energetic ordering of the electronic states depends on the LFS Δ_O . While the *interconfigurational* 4E_S s are destabilized upon an increase in Δ_O , the energy of the *intraconfigurational* 2E_S s is nearly unaffected. The strong field ligand ddpd places $[\text{Cr}(\text{ddpd})_2]^{3+}$ at $\Delta_O \approx 32 B$,^[53] which is well past the first ${}^4T_{2g}/{}^2E_S$ crossing point. The significance of this high Δ_O will be discussed in more detail in the section about special features of *Molecular Rubies*.

In the ${}^4A_{2g}$ GS of chromium(III) complexes each orbital of the t_{2g} set is singly occupied (Fig. 1.4). Excitation of the complex with blue light populates the triply orbitally degenerate ${}^4T_{2g}$ state (Fig. 1.7b). Due to the occupation of an antibonding e_g^* orbital and the *Jahn-Teller-Effect*, the ${}^4T_{2g}$ state is strongly distorted and potentially dissociative.^[26,40,56] However, in $[\text{Cr}(\text{ddpd})_2]^{3+}$ rapid ISC (<200 fs) occurs from the quartet to the doublet manifold, despite the relatively light central ion and lack of the heavy-atom effect. The efficient ISC can be explained by a high density of energetically close-lying doublet states ($E({}^4T_{2g}) \approx E({}^2T_{2g})$)^[57] and the change in angular orbital momentum ($e_g^* \rightarrow t_{2g}$), which is in accordance with *El-Sayed's*

rule.^[58] After *internal conversion* (IC) and VC (≈ 3 ps) the lowest-energy doublet states $^2T_{1g}$ and 2E_g are populated. Both states are close in energy and their relative populations follow a *Boltzmann* distribution.^[57] In their $(t_{2g})^3(e_g^*)^0$ configurations no antibonding orbitals are populated. Thus, the 2 ESs are almost undistorted relative to the GS and horizontal displacement of the respective potential well is minimal (nested states; Fig. 1.5). This lack of distortion leads to sharp emission bands and prevents vibronic coupling to the GS (weak coupling limit), thereby impeding non-radiative decay.^[52,53,57] The energy difference between 4 GS and 2 ES mostly arises from the difference in the interelectronic repulsion of the t_{2g} electrons.^[31,51] This results in intrinsically rather low emission energies in the red to NIR-region ($\lambda_{em} = 738, 775$ nm for $[\text{Cr}(\text{ddpd})_2]^{3+}$). The transition back to the 4 GS via phosphorescence is both spin- and *Laporte*-forbidden, resulting in very long ES lifetimes τ_0 in the millisecond-range ($\tau_0([\text{Cr}(\text{ddpd})_2]^{3+}) = 1.1$ ms in MeCN),^[59] which can be exploited for efficient bimolecular reactions (sections 1.3 and 1.4).

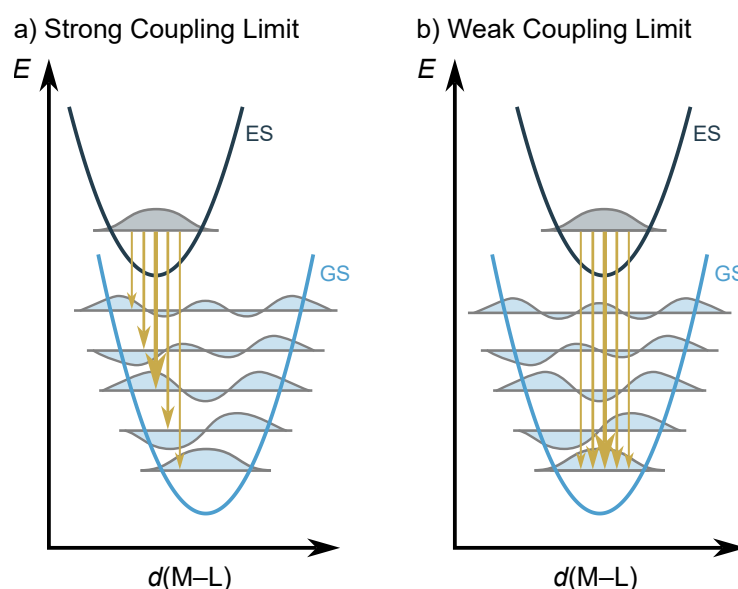


Fig. 1.5: Potential energy wells for ES and GS for a) the strong coupling limit and b) the weak coupling limit.

Molecular Rubies - What Makes Them Special?

A question perhaps even more pressing than the one in the headline above is as to where *Molecular Rubies* get their name from. It is a nod to the red gemstone ruby ($\text{Cr}^{\text{III}}:\text{Al}_2\text{O}_3$), which displays an intense, sharp dual emission ($\lambda_{em} = 692.8, 694.3$ nm; $\Phi_P \approx 90\%$).^[60–63] When $[\text{Cr}(\text{ddpd})_2]^{3+}$ was discovered in 2015, it too displayed dual emission – at an unprecedented intensity for molecular systems.^[52] While "classic" chromium(III) complexes such as $[\text{Cr}(\text{bpy})_3]^{3+}$ or $[\text{Cr}(\text{tpy})_2]^{3+}$ (tpy = 2,2':6',2''-terpyridine; Fig. 1.6), displayed very low QYs and short ES lifetimes, *Molecular Rubies* like $[\text{Cr}(\text{ddpd})_2]^{3+}$ improved these parameters by orders of magnitude.^[52,64–67] In

the following years, more representatives of this class were developed and characterized, such as $[\text{Cr}(\text{bpm})_2]^{3+}$ (bpm = 2,6-bis(2-pyridylmethyl)pyridine; Fig. 1.6, $X = \text{CH}_2$)^[68] and $[\text{Cr}(\text{tpe})_2]^{3+}$ (tpe = 1,1,1-tris(pyrid-2-yl)ethane; Fig. 1.6).^[69]

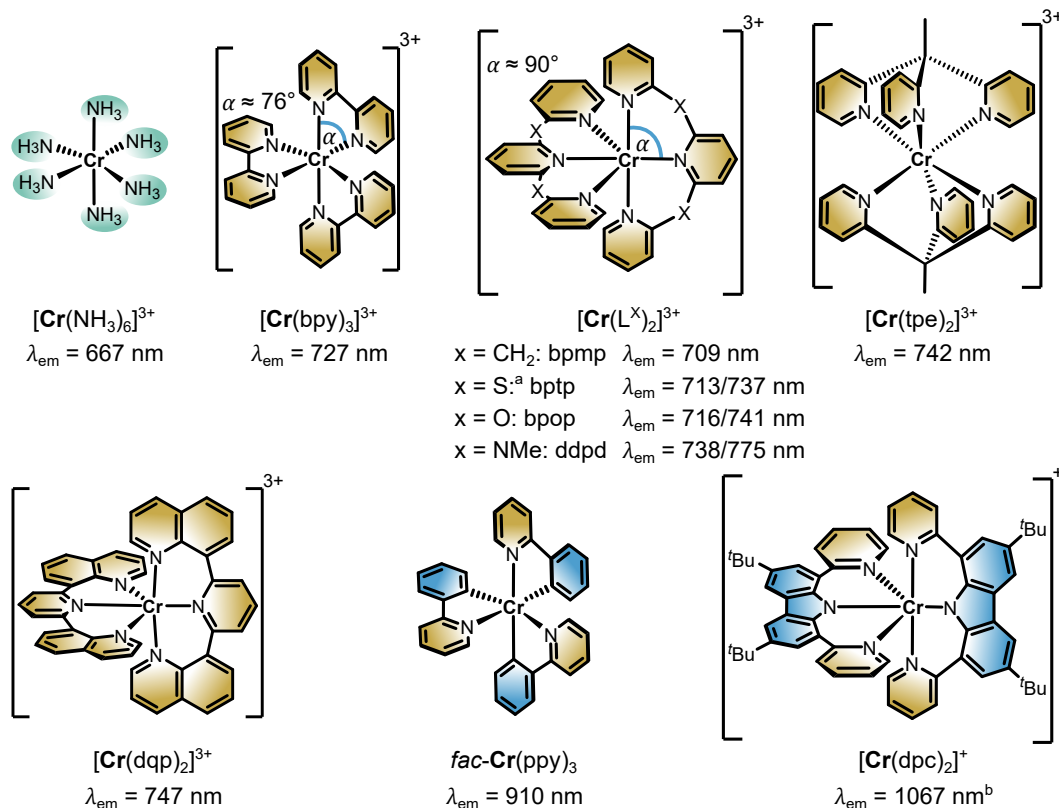


Fig. 1.6: Selected examples of classic chromium(III) complexes, *Molecular Rubies* and their respective emission energies.^[52,64,65,68–73] Green: σ donor; orange: σ donor and π acceptor; blue: σ donor and π donor ligand manifolds. ^a: in the case of $[\text{Cr}(\text{btp})_2]^{3+}$ the N–Cr–N bond angle is closer to 85° .^[70] ^b: measured at 77 K. btp = 2,6-bis(pyridine-2-ylthio)pyridine; bpop = 2,6-bis(pyridine-2-yloxy)pyridine.

Key to the success of these compounds lies in the circumvention of various detrimental processes in their ESs. In $[\text{Cr}(\text{ddpd})_2]^{3+}$, the introduction of the methylamino-bridges allow for an almost ideal N–Cr–N bite angle of close to 90° , as opposed to $<80^\circ$ in $[\text{Cr}(\text{bpy})_3]^{3+}$, which maximizes Cr–N orbital overlap. LFS and the energetic gap between $^4\text{T}_{2g}$ and the ^2ESs is thus increased, preventing detrimental back-ISC (bISC; Fig. 1.7a). Suppressing bISC is critical, as it competes with phosphorescence via depopulation of the desired emissive states. Furthermore, repopulation of the strongly distorted $^4\text{T}_{2g}$ state can potentially result in non-radiative decay and ligand dissociation. Hence, strong ES distortion must be avoided, as it can stabilize the $^4\text{T}_{2g}$ state and facilitate bISC. Therefore, chelating ligands are beneficial, as they partially suppress large-amplitude motions (*Jahn-Teller* distortion).^[53,57] Another undesirable process in the ES of chromium(III) complexes is trigonal distortion (Fig. 1.7c), which lowers the symmetry of the complex and facilitates non-radiative decay. Trigonal distortion is prevalent in complexes with bidentate ligands like $[\text{Cr}(\text{bpy})_3]^{3+}$,^[53]

but it can be addressed by rigidification of the ligand (e.g. $[\text{Cr}(\text{phen})_3]^{3+}$; phen = 1,10-phenanthroline)^[64] or the employment of tridentate ligands like tpy or ddpd. While phen and tpy suppress trigonal distortion, they do not provide efficient orbital overlap, which results in quantum yields and lifetimes that are still far away from $[\text{Cr}(\text{ddpd})_2]^{3+}$.^[59,64,66,67]

A persisting issue that lowers emission QYs and lifetimes even in *Molecular Rubies* is multiphonon-relaxation, in which energy transfer (EnT) occurs from the ES chromium(III) center to vibrational overtones (usually ν^4/ν^5) of X–H oscillators (X = C/N/O).^[51] Energy acceptors can either be solvent molecules that are close to the metal or the X–H oscillators adjacent to the coordinating nitrogen atom. The impact of multiphonon relaxation is evident by the stark increase in QYs and lifetimes in deuterated solvents and/or upon (partial) deuteration of the ligands (e.g. $[\text{Cr}(\text{bpmp})_2]^{3+}$ in $\text{H}_2\text{O}/\text{HClO}_4$: $\Phi_{\text{P}} = 15.8\%$; $[\text{Cr}([\text{D}_2]\text{-bpmp})_2]^{3+}$ in $\text{D}_2\text{O}/\text{DClO}_4$: $\Phi_{\text{P}} = 24.6\%$).^[68,74] The mechanism behind this EnT process and the effect of deuteration is explained in section 1.3.3.

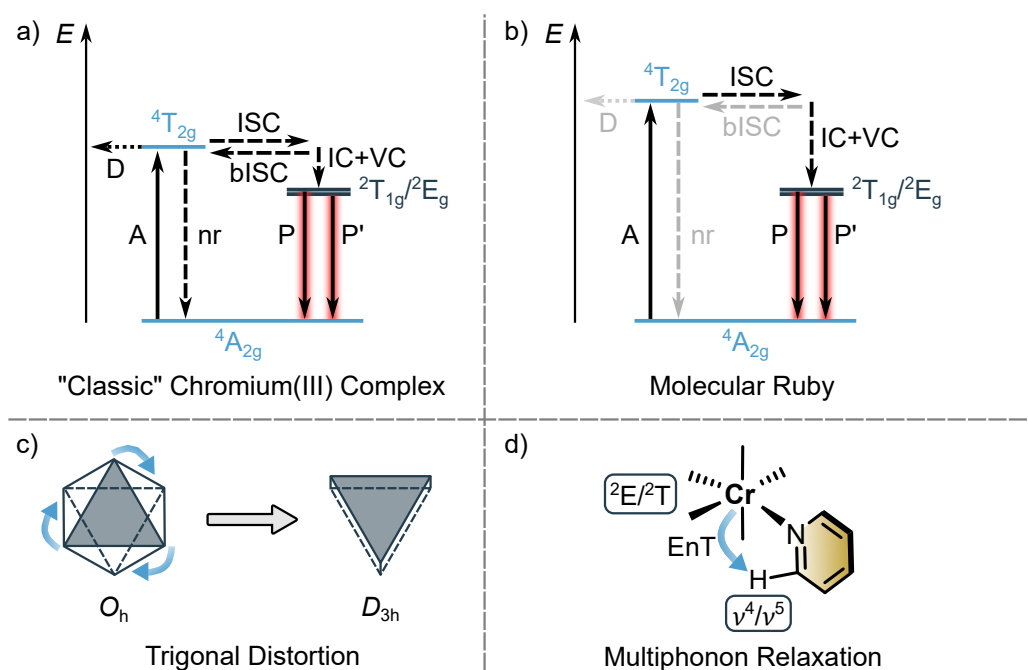


Fig. 1.7: Simplified Jablonski-type diagrams for a) a chromium(III) complex with weak LFS and b) a *Molecular Ruby*, in which bISC is suppressed due to strong LFS. Non-radiative decay can further occur via c) trigonal distortion and d) multiphonon relaxation.

Due to their desirable (photophysical) properties, like their dual emission, long ES lifetimes and high level of stability, *Molecular Rubies* have been utilized in e.g. temperature-, pressure-, pH- and oxygen-sensing.^[52,68,75–77] This work is focused on their application in photocatalysis, which will be discussed separately in section 1.4.1.

Emission Energy Tuning

Seeing how CT and SF emission are rather different in nature, it is evident that different knobs need to be turned to tune their respective energies as well (Fig. 1.8).

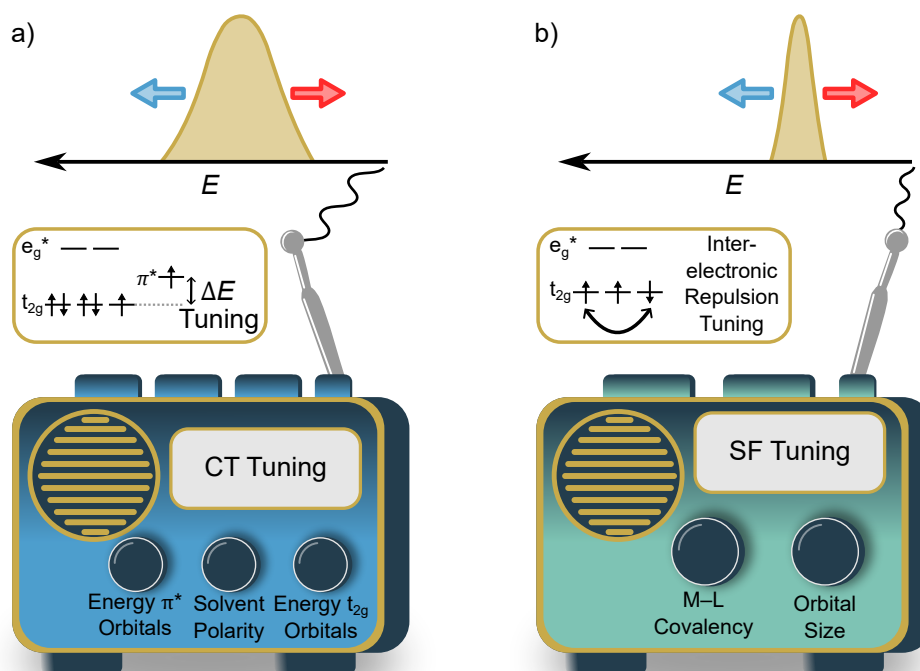


Fig. 1.8: Tuning the emission energy of a) MLCT emitters and b) SF emitters requires the adjustment of different knobs.

The (de)stabilization of MLCT states is easily explained in a one-electron picture. Adjusting the relative energies of donor (t_{2g}) and acceptor (π^*) orbitals modifies the energy gap ΔE and thus the emission wavelength. One way to achieve this is to change the metal ion, e.g. from Ru^{II} to Os^{II} . The latter possesses energetically higher $5d$ orbitals, thereby reducing ΔE and resulting in red-shifted emission (e.g. $\lambda_{\text{em}} = 620 \text{ nm}$ vs. $\lambda_{\text{em}} = 742 \text{ nm}$ for the bpy complexes).^[23,78] Introducing electron-donating or -withdrawing groups into the ligand manifolds is a prevalent approach to adjusting the π^* energies. However, an important caveat is that the donor and acceptor orbitals are not independent of each other, as they are both part of the same π system. This means that if a donating substituent is introduced, destabilization of both the π^* orbitals and of the t_{2g} orbital set occurs. Consequently, while conceptually simple, the tuning of MLCT states via ligand modification is a delicate endeavour and far from trivial.^[79,80] Finally, a simple way of changing the emission energy in CT compounds does not involve manipulating the structure of the emitter itself but rather the surrounding matrix, e.g. different solvents. The charge separation in CT states is stabilized to different extents, depending on the nature (i.e. polarity) of the solvent, the dipole moment of the solute and the resulting interaction between

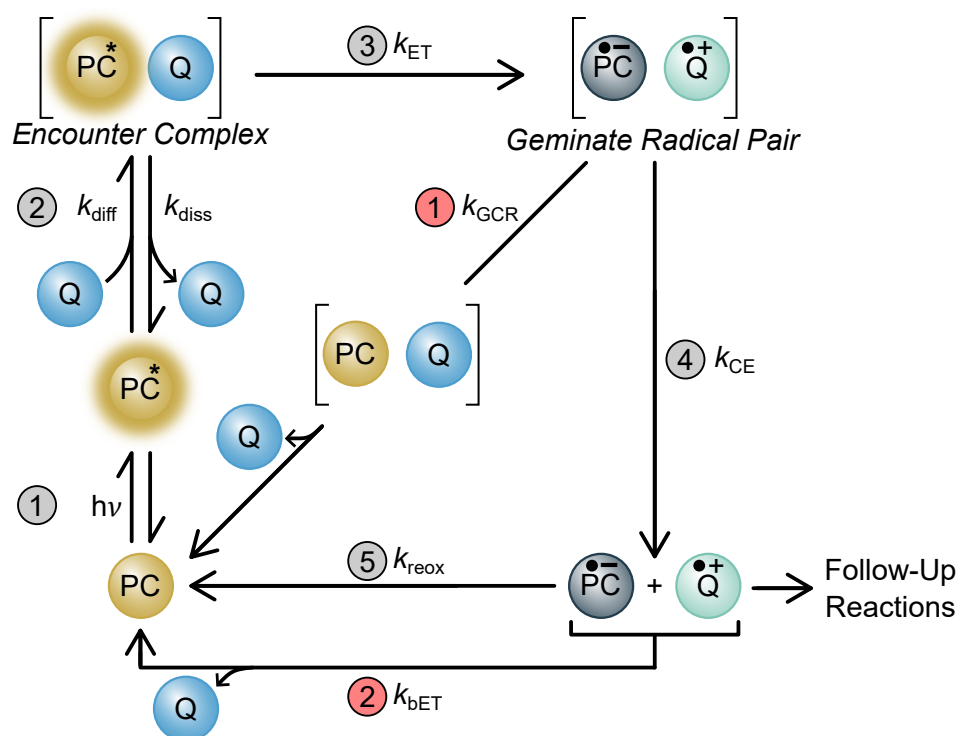
them (solvatochromism).^[81–83] The physical state of the matrix also has a significant influence, such as the rigidochromic shift in frozen/solid environments.^[84]

Tuning the emission energies in SF emitters needs to be approached rather differently. For starters, the aforementioned solvatochromism is virtually unobservable in SF compounds, due to the lack of charge separation in the ES and the low transition dipole moment.^[51] As for modifications to the compounds themselves, energetic manipulation of the metal- or ligand-centered orbitals does not typically yield easily predictable effects on the emission energy. This results from the shared $(t_{2g})^3(e_g^*)^0$ configuration in both the 4GS and 2ES (in the case of Cr^{III}). A facile tuning approach via the introduction of electron-donating or -accepting substituents is therefore less feasible than for CT emitters. Instead, the necessary knob to turn is the degree of covalency of the M–L bonds, thereby adjusting spatial expansion of the respective molecular orbitals. More spacious orbitals permit a higher degree of electron delocalization, which results in a decrease of interelectronic repulsion and the *Racah* parameter B (*nephelauxetic effect*).^[51,85] The doublet states experience a larger drop in repulsion as the covalency increases than the quartet states. This is a result of the spin-paired electrons in the doublet states getting spatially closer to each other, resulting in increased *Coulomb* repulsion compared to unpaired electrons. All in all, this translates to lower emission energies upon higher degrees of covalency and vice versa.^[31,86,87] Some illustrative examples complexes with almost pure σ ligands like $[Cr(NH_3)_6]^{3+}$ ($\lambda_{em} = 667$ nm) or $[Cr(en)_3]^{3+}$ ($\lambda_{em} = 670$ nm) fall on the more "ionic" end of the spectrum,^[65] while compounds with anionic ligands like ppy^- ($\lambda_{em} = 910$ nm) or dpc^- ($\lambda_{em} = 1067$ nm; 77 K) on the other end (en = ethylenediamine; dpc = 3,6-di-*tert*-butyl-1,8-di(pyridine-2-yl)-carbazolato).^[72,73] Chromium(III) complexes with polypyridyl ligands (such as $[Cr(ddpd)_2]^{3+}$, $[Cr(bpmp)_2]^{3+}$ and $[Cr(tpe)_2]^{3+}$) typically emit in the 700 to 800 nm range.^[52,68,69] Similar to CT compounds, SF energies depend on the central ion. Ions with larger orbitals and a lower intrinsic *Racah* parameter B_0 like Mo^{III} or V^{III}/V^{II} yield lower emission energies in the NIR-II region.^[31,88–90]

It is important to point out that the explanation presented above is rather simplified. Recent experimental and high-level theoretical investigations have highlighted that besides electronic effects, the emission energy is influenced by an intricate interplay of bond lengths, precise bond and torsion angles, even in very similar systems.^[70] Such a multitude of factors is difficult to predict in advance, particularly when the structural deviations between compounds are more pronounced. Tuning emission energies in SF emitters via ligand modification thus remains highly complex and their rational design is still a challenging task.

1.3 The Photocatalytic Cycle

The relaxation pathways discussed thus far have been unimolecular in nature, barring solvent interactions. However, provided that an ES species is sufficiently long-lived (detailed in section 1.3.1), it can potentially react with other molecules in solution and thereby reduce its QY (quenching).^[23,26] Photocatalysis is built on this foundation of bimolecular reactivity and a photocatalytic cycle is comprised of numerous elementary steps (Scheme 1.1).^[91] In this example a photoredox cycle is shown, which operates on electron transfer (ET). Specifically, a reductive quenching cycle (referring to initial reduction of PC*) is depicted and will serve as the basis of subsequent elaborations. Oxidative quenching operates in an analogous fashion, with PC* getting oxidized instead. In the following paragraph, a brief overview of the steps involved in photoredox catalysis will be provided. Thereafter, some of the key processes will be illuminated more brightly in sections 1.3.1 and 1.3.2. Aspects specific to EnT mechanisms and catalysis will be discussed separately in section 1.3.3.



Scheme 1.1: Schematic depiction of possible elementary steps in a dynamic reductive ES quenching cycle.

A productive photocatalytic cycle starts off with light excitation of the PC (①).^[23] The thus more reactive PC^* can then form an *encounter complex* with the substrate (or *quencher* Q; ②, k_{diff}). Subsequently, ET can occur (③, k_{ET}), which yields the so-called *geminate* (or *spin-correlated*) radical pair.^[91,92] Said pair can now escape

its solvent cage (*cage escape*, ④, k_{CE}) and the radical cation $\text{Q}^{\bullet+}$ can participate in subsequent reactions. The ability to easily generate organic radicals under mild conditions via "titration" of light is one of the main benefits that photoredox catalysis provides (exemplary reactions in section 1.4).^[6,8,23] To close the catalytic cycle, the reduced PC needs to be re-oxidized by a sacrificial oxidant or an oxidizing intermediate (⑤, k_{reox}).

If the number of absorbed photons N_{abs} led to the formation of an equal number of product molecules N_{prod} , a reaction quantum yield $\Phi_{\text{R}} = 100\%$ would be obtained (eq. 1.3). In reality, this is rarely the case, as unproductive pathways within the catalytic cycle (and the follow-up chemistry, which will not be discussed further) can considerably decrease Φ_{R} .^[91,93–95] In some cases, chain reactions occur, e.g. through oxidation of the substrate by a downstream intermediate, which can lead to $\Phi_{\text{R}} > 100\%$.^[96–100]

$$\Phi_{\text{R}} = \frac{N_{\text{abs}}}{N_{\text{prod}}} \quad (1.3)$$

Undesired processes that will lower the Φ_{R} are geminate charge recombination prior to cage-escape (①, k_{GCR}) as well as *non-geminate* back-ET (②, k_{BET}), both of which will be discussed in section 1.3.2. The reaction quantum yield can be further decreased via competing unimolecular processes like emission (section 1.2). In fact, conducting emission measurements at different substrate concentrations (*Stern-Volmer* experiments) can provide valuable insight into how fast a PC^* reacts with a given substrate and what fraction of PC^* molecules get quenched.

1.3.1 Quantifying Quenching Rate and Efficiency – The Stern-Volmer Equation

When a substrate Q is present in a solution next to an ES photocatalyst, quenching becomes available as an additional decay pathway. This process depends on the quenching rate constant k_{q} and the concentration of the quencher [Q]. The expression for the emission lifetime in the presence of the quencher thus yields eq. 1.4:

$$\tau = \frac{1}{k_{\text{r}} + k_{\text{nr}} + k_{\text{q}}[\text{Q}]} \quad (1.4)$$

Combined with eq. 1.2 for τ_0 , the following relation is obtained:

$$\frac{\tau_0}{\tau} = \frac{k_{\text{r}} + k_{\text{nr}} + k_{\text{q}}[\text{Q}]}{k_{\text{r}} + k_{\text{nr}}} \quad (1.5)$$

Simplification of eq. 1.5 gives the *Stern-Volmer* (SV) equation (eq. 1.6).^[23,101,102] The proportionality of Φ and τ follows from eq. 1.1 (omitting Φ_{ISC} in this more general case).

$$\frac{\Phi_0}{\Phi} = \frac{\tau_0}{\tau} = 1 + k_q\tau_0[Q] = 1 + K_{SV}[Q] \quad (1.6)$$

In practical terms, SV data is usually obtained by measuring the emission lifetime (time-resolved) and/or intensity (steady-state) at different quencher concentrations. A plot of $\frac{\tau_0}{\tau}$ or $\frac{\Phi_0}{\Phi}$ versus $[Q]$ yields the *Stern-Volmer* constant K_{SV} from the slope (in the case of dynamic quenching, Fig. 1.10).^[23] This constant represents the sensitivity of the PC to quenching per unit of a specific substrate ($[K_{SV}] = M^{-1}$) and if $[Q] = K_{SV}^{-1}$, then 50% of the original emission lifetime/intensity is quenched.^[102] The *Stern-Volmer* constant is the product of two critical factors: k_q and τ_0 .

With regards to the latter, a frequently presented rule of thumb calls for an ES lifetime of $\tau_0 \geq 1$ ns for bimolecular reactions to occur.^[26,91,103–105] The underlying idea is clear: if the ES species is too short-lived, it simply will not have enough time to react with a substrate, since the rate of diffusion is limited. Said limit is described by the *Smoluchowski* equation (eq. 1.7),^[106] which gives an expression for the diffusion-controlled bimolecular rate constant k_{diff} ($[k_{diff}] = M^{-1}s^{-1} = Lmol^{-1}s^{-1}$). This depends on the collision radius R (typically the sum of the molecular radii of PC and quencher, given in cm) and the diffusion coefficients D of both species (in cm^2s^{-1}). N_A is *Avogadro's* number (in mol^{-1}) and 1000 is a correction factor to convert cm^3 to L.^[102]

$$k_{diff} = \frac{4\pi N_A}{1000}(R_{PC} + R_Q)(D_{PC} + D_Q) \quad (1.7)$$

In typical solvents like water or acetonitrile values of $k_{diff} \approx 10^9$ to $10^{10} M^{-1}s^{-1}$ are the upper limit.^[91,102,107] The collisional frequency between freely diffusing molecules Z is the product of k_{diff} and $[Q]$ (eq. 1.8).

$$Z = k_{diff}[Q] \quad (1.8)$$

Assuming $k_{diff} = 10^{10} M^{-1}s^{-1}$ and a high substrate concentration of $[Q] = 100$ mM, $Z = 10^9 s^{-1}$ is obtained. This means that on average a molecule of PC* and Q would collide after 1 ns. Therefore, 1 ns is a decent approximation of the fastest possible quenching, assuming diffusion-controlled ($k_q \approx k_{diff}$), high-concentration conditions. In reality, longer ES lifetimes τ_0 are desirable because k_q can often lie considerably below the diffusion limit (*vide infra*).^[107–109] Extending τ_0 permits favorable quenching efficiency η , even at lower substrate loadings and/or k_q values (Fig. 1.9).^[91]

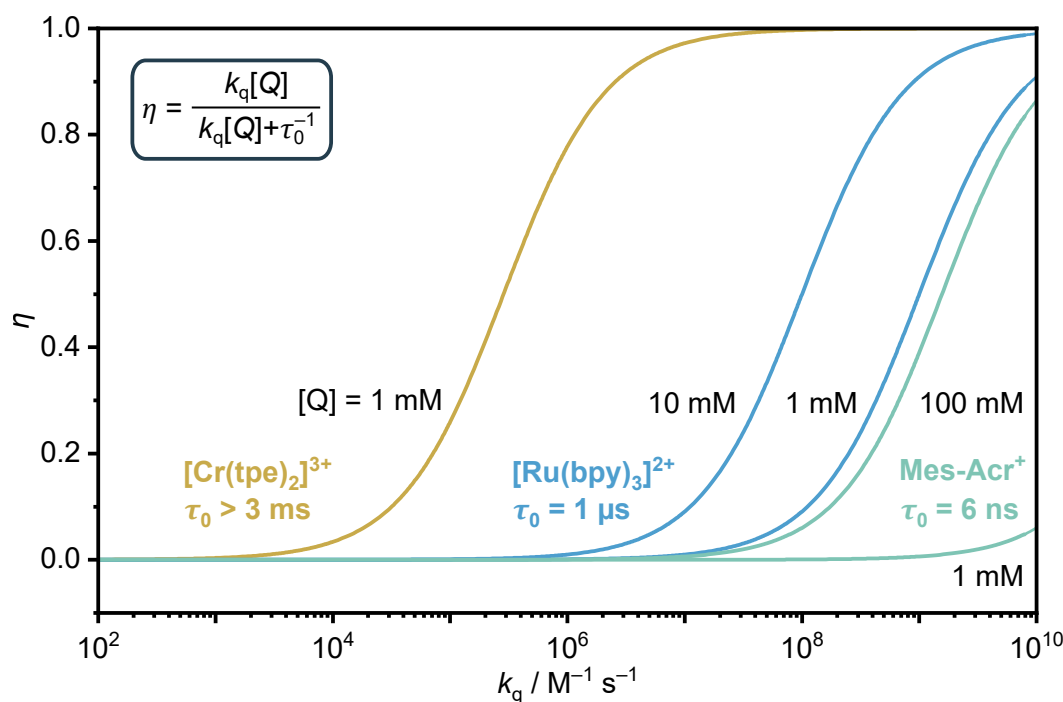


Fig. 1.9: Quenching efficiency η as a function of the bimolecular rate constant k_q at different substrate concentrations (1 mM, 10 mM, 100 mM) for different photocatalysts. The expression for η contains the ratio of quenching to all of the decay processes, with $\tau_0^{-1} = k_r + k_{nr}$ (eq. 1.2). Extremely long ES lifetimes like τ_0 of $[\text{Cr}(\text{tpe})_2]^{3+}$ facilitate highly efficient quenching, even at low substrate loadings and moderate rate constants.^[110] In contrast, the organic photocatalyst 9-mesityl-10-methylacridinium (Mes-Acr^+) suffers from unsatisfactory quenching at dilute conditions even for diffusion-controlled reactions.^[111]

The bimolecular rate constant k_q encompasses the formation of the association complex and the actual ET/EnT step itself.^[91] Thus, k_q is affected by multiple factors, including the thermodynamic driving force ΔG^0 , the reorganization energies λ of both reactants (more details in section 1.3.2) and the accessibility of the ES PC to the quencher, which can be impeded e.g. by steric demands.^[75,102] Furthermore, the rate constants for the formation k_{diff} and dissociation k_{diss} affect k_q ($k_{\text{diff}}k_{\text{diss}}^{-1}$ = the equilibrium constant K of the encounter complex; Scheme 1.1; eq. 1.9). The empirical *Rehm-Weller* equation (eq. 1.9) provides an expression for k_q that links this kinetic parameter to the thermodynamic driving force ΔG^0 .^[91,112–114]

$$k_q = \frac{k_{\text{diff}}}{1 + \frac{k_{\text{diss}}}{Z} \left[\exp\left(\frac{\Delta G^\ddagger}{RT}\right) + \exp\left(\frac{\Delta G^0}{RT}\right) \right]} \quad (1.9)$$

Aside from factors intrinsic to the PC/Q pair, bimolecular quenching rates are sensitive to external variables like temperature, solvent viscosity or ionic strength of the solution for charged reactants (*Brønsted-Bjerrum* theory).^[115–117] In fact, highly charged species can associate prior to light-absorption due to *Coulomb* attraction, which can result in static quenching.^[108,118]

Static quenching generally occurs via the formation of a non-emissive GS adduct.^[119] Unlike dynamic quenching, it is therefore time-*independent* and does not influence the emission lifetime, but merely the intensity (Fig. 1.10b). PC molecules "trapped" in this adduct do not emit at all – it is not a matter of competing between emission and quenching like in the dynamic case. If both types of quenching occur, the plot derived from the time-resolved emission data yields the expected linear behavior, as it is only influenced by the dynamic process. Steady-state emission data is affected by both [Q]-dependent pathways, resulting in a quadratic relationship (Fig. 1.10c).^[23]

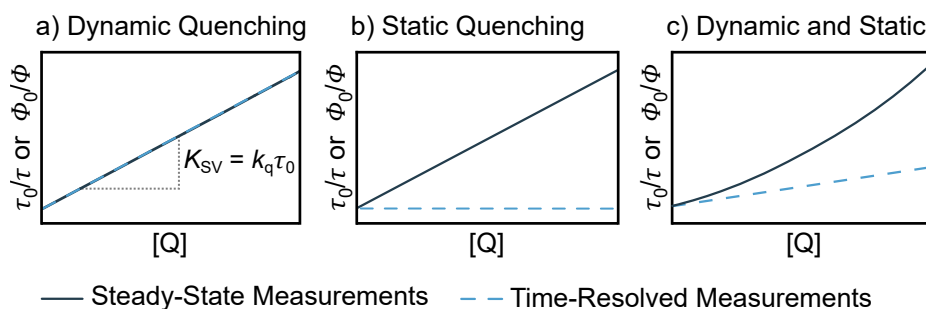


Fig. 1.10: Schematic depiction of *Stern-Volmer* plots based on steady state (dark blue) and time-resolved (light blue, dashed) emission data for a) dynamic, b) static and c) dynamic and static quenching.

SV data is invaluable in determining a) whether/how fast and efficiently a given ES PC reacts with a particular substrate and b) whether this process occurs dynamically and/or statically. Comparing k_q values of individual substrates (e.g. different participants in a photocatalytic reaction) can provide insight into potential mechanistic pathways. However, it is of critical importance to emphasize that SV analyses *do not* provide information on the actual process (i.e. ET vs. EnT) responsible for the ES quenching. Other methods, like the observation of intermediates via (transient) absorption spectroscopy or product analysis are required to distinguish between these mechanisms.^[23] Furthermore, no information on follow-up processes like cage-escape vs. geminate charge recombination is obtained.^[91]

1.3.2 Electron Transfer in Photoredox Catalysis

Electron transfer is one of the defining aspects of photoredox catalysis. It is understood based on the theory crafted by *Rudolph A. Marcus*, which offers an expression for the ET rate constant k_{ET} (eq. 1.10).^[120–122]

$$k_{ET} = \frac{2\pi}{\hbar} \frac{H_{DA}^2}{\sqrt{4\pi\lambda k_B T}} \exp \left[-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right] \quad (1.10)$$

Remarkably, within this model k_{ET} depends on only three variables: the thermodynamic driving force ΔG^0 , the reorganization energy λ and the electronic coupling

between electron donor and acceptor H_{DA} (*vide infra*).

In order to facilitate the discussion of these parameters, it is expedient to look at the frequently employed free energy surfaces (Fig. 1.11), that represent the reactants ($\text{D} + \text{A}$) and products ($\text{D}^{\bullet+} + \text{A}^{\bullet-}$). In these depictions the Gibbs free energy G is shown as a function of the nuclear configuration q . The parabolic shape results from the approximation of the molecular vibrations and changes in polarization of the surrounding solvent as a collective harmonic oscillator.^[122] The minima of these free energy surfaces represent the equilibrium position of the overall system ($\text{D} + \text{A} + \text{solvent}$) prior to and after ET (Fig. 1.11a, ① vs. ③). Movement along the curve represents an increase in energy through bond-length changes and solvent polarization (reorganization). This approximation is significantly simplified since non-linear molecules possess $3N - 6$ vibrational degrees of freedom,^[123] however, it provides a tangible model for understanding the ET process.

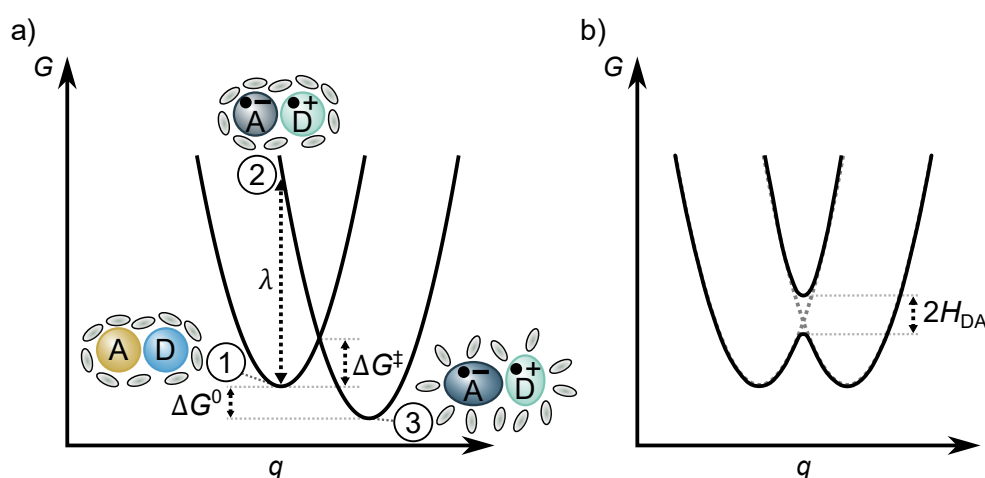


Fig. 1.11: a) Free energy surfaces for an exergonic ET reaction, highlighting the thermodynamic driving force ΔG^0 , activation barrier $\Delta G^\ddagger$ and reorganization energy λ . The structural (re)organization of the donor, acceptor and solvent cage are schematically depicted at different nuclear configurations q along the respective free energy surfaces. b) Electronic coupling H_{DA} results in mixing of potential energy surfaces, leading to partial electron delocalization.

In accordance with the *Born-Oppenheimer* approximation, the geometry of the overall system must not change upon ET. Thus, thermal ET ($\text{①} \rightarrow \text{③}$) can only occur when the energies along the reactant and product surfaces are equal (quantum mechanical tunneling omitted).^[122] This prerequisite is fulfilled at the intersection, where an electron can "hop" from the reactant to the product surface. The free energy required to achieve this necessary change in nuclear configuration is the activation energy $\Delta G^\ddagger$. After the ET process, the products and the surrounding solvent relax into their equilibrium configuration (Fig. 1.11a).^[122] The energetic difference between the relaxed geometries of reactant and product surfaces corresponds to the thermodynamic driving force ΔG^0 . Optical ET ($\text{①} \rightarrow \text{②}$) can occur upon light absorption of the system with $E = h\nu = \lambda$. This generates charge separation at the equilibrium

geometry of the reactants, resulting in the products being high in energy prior to achieving their relaxed geometry ($\textcircled{2} \rightarrow \textcircled{3}$). One important note is that the ET step in photoredox catalysis is a *thermal* process. Light energy is merely required to generate a sufficiently reactive ES photocatalyst, which can then proceed to partake in ET (PC^* and Q in Scheme 1.1 $\hat{=}$ A and D in Fig. 1.11a).

The thermodynamic driving force ΔG^0 is one of the parameters that influence electron transfer rates k_{ET} according to eq. 1.10. It highlights the interconnected nature of thermodynamics and kinetics (similar to eq. 1.9). In the realm of photoredox catalysis, information on the driving force is usually obtained via electrochemical reduction potentials E_{red} .^{b)} For the GS PC and most substrates, these are accessible experimentally via cyclic voltammetry (CV).^[125–127] Since a photoredox catalyst reacts with substrates from its lowest ES, the 0-0 transition energy of the said state E_{00} is added to the GS potential. Thus, the ES reduction potential can be estimated by eq. 1.11 (in the case of oxidative quenching E_{00} is subtracted instead).^[23,124]

$$E_{\text{red}}^* = E_{\text{red}} + E_{00} = E_{\frac{1}{2}}(\text{PC}^{n/(n-1)}) + E_{00} \quad (1.11)$$

The potential difference ΔE_{red} of the ES catalyst (E_{red}^*) and the substrate ($E_{\text{red,Q}}$) can be used to judge the feasibility of ES quenching, since ΔE_{red} is directly linked to ΔG (eq. 1.12; z : number of transferred electrons; F : Faraday constant).^[122]

$$\Delta G = -zF\Delta E_{\text{red}} = -zF(E_{\text{red}}^* - E_{\text{red,Q}}) \quad (1.12)$$

The ES reduction potential E_{red}^* dictates the library of substrates that can or cannot potentially react with PC^* via ET. Within the context of a photocatalytic synthesis, interaction of PC^* with only one of possibly multiple reactants may be desired. Thus, choosing a catalyst with a suitable E_{red}^* is paramount.^[23,126–128] From equations 1.11 and 1.12 it is evident that tuning of the ES potential can be achieved by manipulating either the emission energy (and thereby E_{00} ; section 1.2.2) or the GS potential E_{red} . Adjustment of the GS potential is typically achieved by introducing electron-withdrawing or -donating substituents that facilitate/impede reduction of the catalyst. In the case of TMCs, choosing different types of ligands (e.g. pyrazine- vs. pyridine-based) or using a different metal can drastically alter the reduction potential (section 1.4).^[128–133]

A key point derived from *Marcus* theory is that an increase in ΔG^0 is accompanied by an increase in k_{ET} – until it is not. The maximum value for k_{ET} is reached when $|\Delta G^0|$ equals the reorganization energy λ and the process becomes barrierless ($\Delta G^\ddagger = 0$; Fig. 1.12c). Even higher driving forces will shift the ET into the so-called

^{b)} Reduction potentials describe electrochemical half-reactions written in the direction of $\text{A}^+ + e^- \rightarrow \text{A}$. Oxidation potentials consider the inverse direction and are of opposite sign ($E_{\text{red}} = -E_{\text{ox}}$). In the literature, these terms are often used with a lack of precision, ES potentials and their estimation included. A brief and accurate explanation was provided by *Tucker and Stephenson*.^[124] In this text, only reduction potentials will be used for the sake of clarity and consistency.

inverted region, in which a barrier is re-introduced and the ET process slows down again (Fig. 1.12d).^[122,134]

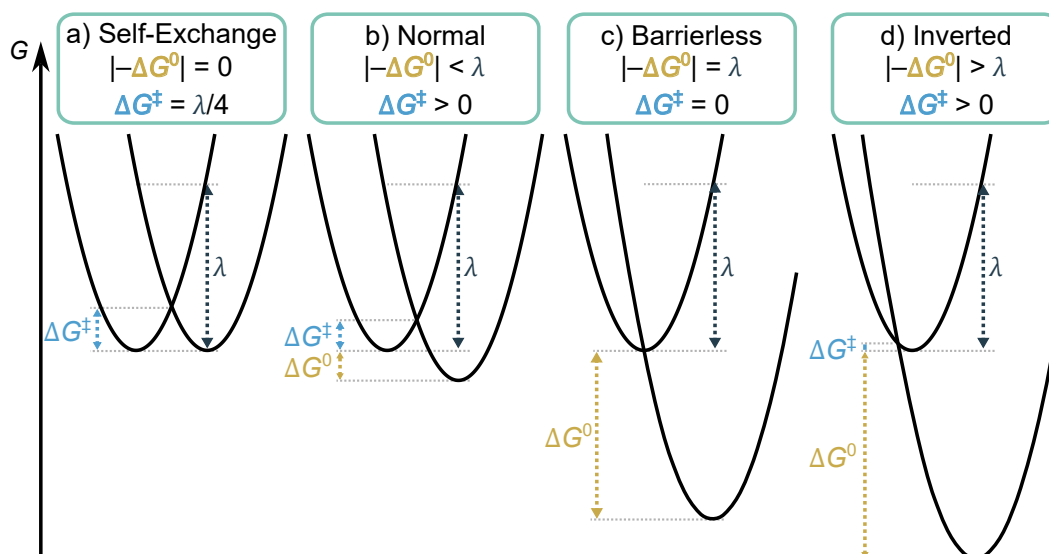


Fig. 1.12: Different *Marcus* regions of ET are defined by the driving force ΔG^0 and the reorganization energy λ .

The reorganization energy λ corresponds to the energetic difference between product and reactant surface in the equilibrium configuration of the reactants (Fig. 1.11, Fig. 1.12). It is the sum of two addends: "outer-sphere" (λ_o) and "inner-sphere" (λ_i) reorganization energy (not to be confused with inner- and outer-sphere ET; *vide infra*).^[122] The outer-sphere component stems from the response of the surrounding dipolar solvent molecules to the new distribution of electron density within the D-A pair. In contrast, the inner-sphere contribution stems directly from bond-length and -angle changes within the reactants/products, which is a result of differently populated orbitals. Combined, the outer- and inner-sphere processes enable the relaxation of the products (and the surrounding solvent cage) to their equilibrium geometry after ET (Fig. 1.11a).^[122,135] Reorganization energy varies drastically between systems and is the main reason k_{ET} differs by orders of magnitude, even in self-exchange ($\Delta G^0 = 0$; Fig. 1.12a) reactions.^[136] Looking at the thermal ET pathway (*vide supra*), it is evident that λ is directly linked to the activation barrier $\Delta G^\ddagger$, as described by eq. 1.13. From this expression, $\Delta G^\ddagger = \frac{\lambda}{4}$ is obtained for self-exchange reactions, while barrierless processes $\Delta G^\ddagger = 0$ can occur when the magnitude of free energy released by ET equals the required reorganization energy ($|\Delta G^0| = \lambda$).^[122,134]

$$\Delta G^\ddagger = \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \quad (1.13)$$

The electronic coupling H_{DA} results from molecular orbital mixing (wave function overlap) of the D-A couple. Delocalization of electrons is thus facilitated and the energy surfaces change (Fig. 1.11b). When the electronic coupling becomes very strong (e.g. in systems with a bridging ligand; *inner-sphere* ET mechanism), complete electron delocalization can occur and the activation barrier disappears.^[122] ET thus occurs continuously, as the system moves along the nuclear configuration (adiabatic ET). Weak electronic coupling preserves largely isolated redox-centers. Here, thermal ET can only occur after partial reorganization by "hopping" from reactant to product surface (non-adiabatic ET). While H_{DA} is usually weak for *outer-sphere* ET reactions typical in photoredox catalysis, it cannot be zero (since $H_{\text{DA}} = 0 \Rightarrow k_{\text{ET}} = 0$; eq. 1.10).^[122,137] However, for the sake of simplicity (and because H_{DA} is unknown in most cases) energy surfaces in non-adiabatic ET are usually portrayed without electronic coupling (Fig. 1.11a; Fig. 1.12). The need for molecular orbital overlap in ET reactions also dictates a strong distance-dependency, due to the exponential decay of wave function amplitudes.^[138]

Cage-Escape

After ET between PC^* and the substrate has occurred, the geminate radical pair is obtained. From here, two roads diverge in a catalytic cycle, leading either to CE or GCR (Scheme 1.1). CE is typically quantified by the cage-escape yield Φ_{CE} , which is defined as the ratio of cage-escaped $\text{Q}^{\bullet+}$ molecules N_{CE} over the number of quenched excited states N_{qES} (eq. 1.14).^[139] Experimental quantification of CE yields hinges on the determination of these parameters. The amount of escaped molecules can be determined by techniques such as nuclear magnetic resonance (NMR) or transient absorption (TA) spectroscopy.^[91,139] NMR methods are advantageous because they are accessible for most research groups. However, the quantification of N_{CE} typically requires "trapping" agents for the radicals $\text{Q}^{\bullet+}$. This is a drawback as a) these agents may not be compatible with the specific substrate of interest or b) can become themselves part of the solvent cage or c) the trapping step itself may not have unity efficiency, thereby delivering erroneous data. TA spectroscopy allows the direct observation of the cage-escaped reaction partners $\text{PC}^{\bullet-}$ and $\text{Q}^{\bullet+}$, provided they exhibit a suitable spectroscopic signature. If the extinction coefficient $\varepsilon(\lambda)$ of one of these species is known, their concentrations c and thus N_{CE} can be directly determined using the *Beer-Lambert* law (eq. 1.15; A : absorbance; d : optical path-length). In order to access N_{qES} , firstly, the concentration of ES PC in the sample needs to be quantified. This is typically achieved via actinometry with a reference compound, such as $^*\text{[Ru(bpy)}_3\text{)]}^{2+}$.^[140] Of these ESs, the fraction that is quenched at the employed substrate concentration can be determined via SV analysis (section 1.3.1). Since the above experimental procedures are rather laborious and require sophisticated equipment, determination of Φ_{CE} is not a standard practice in most photocatalysis research. Thus, the library of investigated PCs and substrates remains

rather limited to this day.^[139]

Kinetic models used to determine Φ_{CE} based on the competition between k_{CE} and k_{GCR} (eq. 1.14) provide very limited predictive value. While k_{GCR} can be estimated through *Marcus* theory, k_{CE} can at best be roughly approximated by the *Eigen* equation. Estimations of k_{CE} are particularly unreliable since numerous simplifications need to be made and many of the variables (like reorganization energy and electronic coupling within the encounter complex) are unknown. Due to these large uncertainties, calculated values of Φ_{CE} fall short of experimentally determined ones.^[139]

$$\Phi_{\text{CE}} = \frac{k_{\text{CE}}}{k_{\text{CE}} + k_{\text{GCR}}} = \frac{N_{\text{CE}}}{N_{\text{qES}}} \quad (1.14)$$

$$A(\lambda) = \varepsilon(\lambda)cd \quad (1.15)$$

At its most basic level, Φ_{CE} is determined by the relative rates of CE and GCR. The latter is a strongly exergonic process, as it (usually) occurs between two reactive radicals. Luckily for photochemists, the driving force is so large that GCR typically falls into the *Marcus* inverted region (Fig. 1.12d).^[93] Thus, a small barrier is introduced and CE becomes competitive.

One important parameter that affects Φ_{CE} is electron spin. Many PCs (be it TMCs or organic molecules) react from a ^3ES , which results in a geminate radical pair of triplet multiplicity as well (*spin-correlated* radical pair). Thus, GCR is a spin-forbidden process because the resulting species are of singlet multiplicity. This forbiddance is usually much stricter in organic PCs, since they do not possess strong SOC from a lack of the heavy-atom effect (section 1.2.1).^[141] Therefore, Φ_{CE} tends to be higher for organic catalysts. Another important variable that influences CE is the charge of the species involved. Opposite charges within the geminate radical pair can inhibit diffusion out of the solvent cage through *Coulomb* attraction, while like charges will promote the separation of ions. These are but a few factors that affect CE. Many more play a role, like different solvents, pH values, ionic strengths, the specific ions present in solution and (de)localization of charges/radicals.^[91,94] To this day factors affecting CE and the interplay between them are poorly understood and many examples fall outside of the correlations presented above. For instance, plenty of organic PCs can exhibit very low Φ_{CE} and some heavy-atom TMCs achieve near-unity CE with certain substrates.^[139]

Despite its elusive nature, CE is one of the most critical parameters within a photocatalytic cycle and low Φ_{CE} values are oftentimes one of the main contributors to poor reaction QYs and an inefficient use of photons.

Catalyst Reoxidation and Back Electron Transfer

After successful cage escape, the solvent separated radicals $PC^{\bullet-}$ and $Q^{\bullet+}$ are obtained. Unproductive (non-geminate) BET between the pair can occur, even after this separation. In order to avoid this process and to regenerate the catalyst, $PC^{\bullet-}$ needs to be oxidized and $Q^{\bullet+}$ has to undergo rapid subsequent transformations.^[91,142] In some cases reoxidation of the reduced PC can be accomplished by a downstream intermediate. However, if the intermediate is too low in concentration or if the reaction is too slow, terminal oxidants like oxygen or persulfates are necessary.^[142] Achieving efficient follow-up reactivity of $Q^{\bullet+}$ is challenging, as the underlying mechanisms can be highly diverse and are often insufficiently understood. A frequently employed strategy is the use of downstream reaction partners at high concentrations, in order to drive the reaction forward kinetically. Alternatively, rapid unimolecular follow-up chemistry such as deprotonation or σ -bond homolysis can occur.^[143]

1.3.3 Energy Transfer Mechanisms

Dexter Energy Transfer

Similar to ET, *Dexter* EnT can occur when an excited donor D^* (often called *photosensitizer*) and an acceptor A collide and orbital overlap is achieved. In fact, the *Dexter* mechanism involves a double ET (Fig. 1.13a).^[144] Due to this mechanistic similarity, the photocatalytic cycles for EnT and ET catalysis are the same up until the formation of the *encounter complex*.^[145] However, the next step is not charge separation, but EnT from D^* to A (PC^* to Q in Scheme 1.1), which yields D and A^* . From here, back-EnT can occur (depending on the relative energies) or A^* can partake in follow-up reactions.^[145] In photocatalysis, *Dexter* EnT is most commonly used to generate triplet states of organic molecules (or 1O_2 from 3O_2) that are otherwise difficult to access (section 1.4).^[146–149] Aspects specific to EnT catalysis with chromium(III) complexes are discussed in section 1.4.1.

Since the *Dexter* mechanism requires orbital overlap, its EnT rate k_{Dex} decays exponentially with the distance between the reaction partners r_{DA} . In addition, spectral overlap J between the normalized emission of the donor (I_D^{norm}) and the normalized absorbance of the acceptor (A_A^{norm}) is a prerequisite for the EnT process (eq. 1.16 and 1.17).^[145]

$$k_{Dex} \propto J \cdot \exp \left[\frac{-2r_{DA}}{(r_D + r_A)} \right] \quad (1.16)$$

$$J = \int_0^\infty I_D^{norm}(\tilde{\nu}) A_A^{norm}(\tilde{\nu}) d\tilde{\nu} \quad (1.17)$$

Due to very low molar absorption coefficients of the corresponding transitions (e.g. $S_1 \rightarrow T_1$ in organic acceptor molecules), experimental determination of the overlap integral J is often impractical. Instead, J is usually approximated with sufficient accuracy by comparing the triplet energies of PC^* and Q^* (assuming triplet-triplet EnT; TTET). Triplet energies are accessible via low-temperature emission measurements or theoretical methods.^[145]

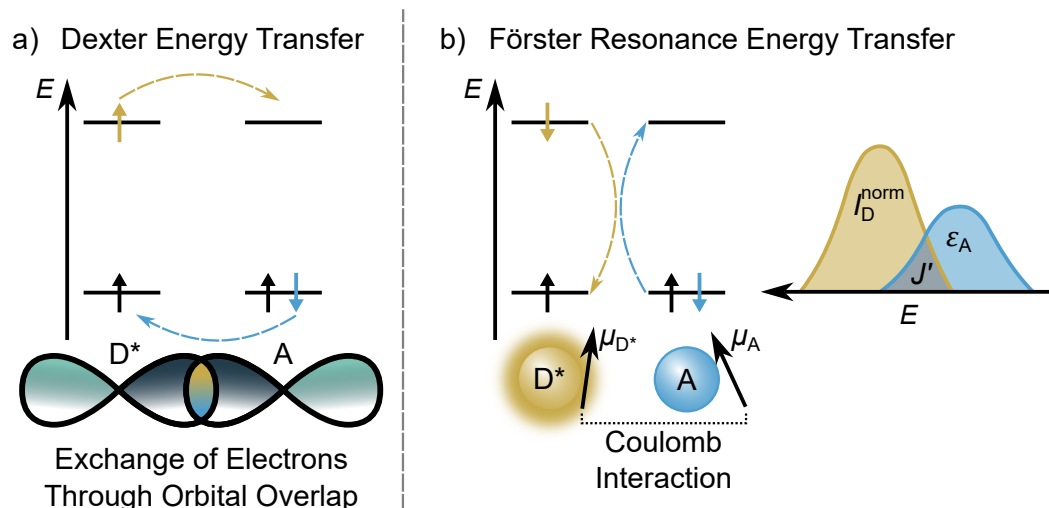


Fig. 1.13: Schematic depiction of energy transfer mechanisms. a) *Dexter* EnT requires orbital overlap, which enables the exchange of two electrons. b) The *Förster* mechanism hinges on the *Coulomb* interaction of oscillating dipoles μ .

Förster Resonance Energy Transfer

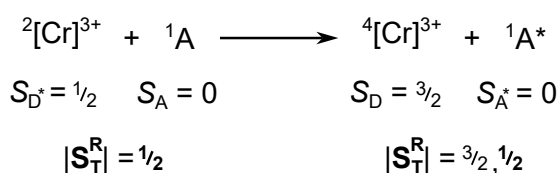
Förster Resonance Energy Transfer (FRET) operates – as the name betrays – on a rather different mechanism than *Dexter* EnT. FRET is based on the *Coulombic* dipole-dipole interactions between an ES donor D^* and an acceptor A (Fig. 1.13b).^[102,150] Thus, the rate constant k_{FRET} depends on the spectral overlap J' (eq. 1.18) between the emission of D and molar absorption of A. In contrast to *Dexter* EnT, the absorption spectrum is *not* normalized, as the molar absorption coefficient of the acceptor ϵ_A dictates what fraction of the energy can be absorbed. This dependency on molar absorptivity necessitates spin conservation within the D and A couple, as ϵ_A is usually very low for spin-forbidden transitions (eq. 1.19; I_D : emission intensity of the donor, normalized to unit area). Furthermore, according to *Wigner's* rules EnT accompanied by a change in multiplicity is forbidden in most cases (*vide infra*).^[145,151,152] FRET proceeds *through-space* (resonance between dipoles) rather than *through-bond* like ET and *Dexter* EnT. Therefore, its distance dependence is less pronounced (r^{-6}) and permits EnT over up to 10 nm. Furthermore, k_{FRET} depends on the relative

orientation of the D* and A dipoles (described by κ^2), as this dictates the efficiency of the resonance.^[102,153,154]

$$k_{\text{FRET}} \propto \kappa^2 J'(\tilde{\nu}) r^{-6} \quad (1.18)$$

$$J' = \int_0^\infty I_{\text{D}}^{\text{norm}}(\tilde{\nu}) \varepsilon_{\text{A}}(\tilde{\nu}) \tilde{\nu}^{-4} d\tilde{\nu} \quad (1.19)$$

FRET is the underlying mechanism behind multiphonon-relaxation, which results from spectral overlap J' between the SF emission and the vibrational overtones of X–H oscillators in the ligand or solvent (usually $\nu_{\text{X-H}}^4/\nu_{\text{X-H}}^5$; section 1.2.2).^[51] This overlap can be decreased by deuteration of potential acceptors. Owing to the higher mass of deuterium, the analogous X–D vibrations appear at lower energies. Therefore, higher overtones (e.g. $\nu_{\text{X-D}}^6$) with much lower extinction coefficients arise in the energetic range of the SF emission.^[74] Spectral overlap J' is thus decreased and k_{FRET} drops, which leads to higher quantum yields and prolonged lifetimes.^[68,74] At first glance, multiphonon relaxation seems to violate the spin-conservation rule, since the multiplicity of the D and A couple changes (Scheme 1.2). However, when assessing whether this type of EnT is spin-allowed, the total spin angular momenta spanned by the reactants $\mathbf{S}_{\text{T}}^{\text{R}}$ and products $\mathbf{S}_{\text{T}}^{\text{P}}$ need to be considered.^[152] Their magnitudes are described according to $|\mathbf{S}_{\text{T}}^{\text{R}}| = |S_{\text{D}^*} + S_{\text{A}}|, |S_{\text{D}^*} + S_{\text{A}} - 1|, \dots, |S_{\text{D}^*} - S_{\text{A}}|$ and $|\mathbf{S}_{\text{T}}^{\text{P}}| = |S_{\text{D}} + S_{\text{A}^*}|, |S_{\text{D}} + S_{\text{A}^*} - 1|, \dots, |S_{\text{D}} - S_{\text{A}^*}|$, respectively. $|S_{\text{D}}|$, $|S_{\text{D}^*}|$, $|S_{\text{A}}|$ and $|S_{\text{A}^*}|$ represent the magnitudes of the spin angular momenta of the GS and ES of the donor and acceptor, respectively. A reaction is considered spin-allowed if there is a common value of $|\mathbf{S}_{\text{T}}^{\text{R}}|$ and $|\mathbf{S}_{\text{T}}^{\text{P}}|$, as the $\Delta S = 0$ condition is then fulfilled. In the case of multiphonon relaxation in chromium(III) complexes, a common value of $|\mathbf{S}_{\text{T}}^{\text{R}}| = \frac{1}{2} = |\mathbf{S}_{\text{T}}^{\text{P}}|$ exists (Scheme 1.2), which permits EnT to proceed.



Scheme 1.2: Scheme for EnT in the case of multiphonon relaxation in chromium(III) complexes. The relevant values of the spin angular momenta and the magnitudes of the the total spin angular momenta are given.

1.4 Photochemistry: From Early Days to Future Challenges

Light-driven chemistry can hardly be considered a recent concept. In fact, Italian photochemistry pioneer *Giacomo Ciamician* was using sunlight to conduct reactions more than a century ago (Fig. 1.14).^[155] Around the same time *Paterno* described the [2+2] photocycloaddition between benzaldehyde and 2-methyl-2-butene, a reaction that was later reinvestigated by *Büchi*.^[156–158] In the 1940s *Schenck* described the photosensitizer-mediated generation of $^1\text{O}_2$ as an early example of EnT catalysis.^[149,159]

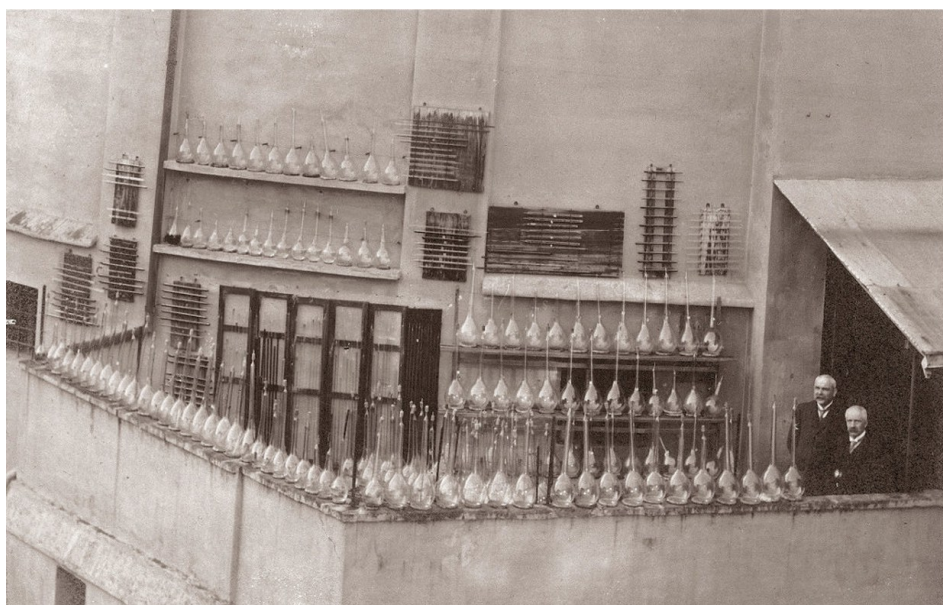


Fig. 1.14: Photochemistry on the roof top – Giacomo Ciamician and Paolo Silber at the University of Bologna, Italy (ca. 1912). Reprinted with permission, courtesy of Alma Mater Studiorum University of Bologna - University Museum System - “Giacomo Ciamician” Chemistry Collection.

Later that same century photoactive compounds like $[\text{Ru}(\text{bpy})_3]^{2+}$ were studied in various contexts, including light-induced water splitting^[160] and several early examples of photoredox catalysis in organic syntheses.^[161] However, the latter never gained much traction until its renaissance around 2008/2009, with three independent publications from the groups of *Yoon*, *MacMillan* and *Stephenson*, using $[\text{Ru}(\text{bpy})_3]^{2+}$ in different photocatalytic transformations (*vide infra*).^[162–164] Ever since these studies were published, research on photoredox catalysis has experienced an explosion in popularity,^[165] which is not surprising, considering the potential this field holds.

Merits and Early Examples of Photocatalysis in Synthetic Chemistry

Generally speaking, utilizing light to drive reactions grants access to reactivity that cannot be achieved with thermal chemistry (e.g. [2+2] cycloadditions).^[166] Often-times, milder reaction conditions can be utilized, as photochemical transformations are usually performed under ambient temperature and pressure, which promotes product purity.^[91,124,145,167] The latter is further favored since light can be viewed as a "reagent" that leaves no traces after the reaction, contrasting e.g. chemical oxidants. Furthermore, the ability to shut down a reaction very quickly by simply removing the light source allows for precise reaction timing and can serve as a desirable safety feature.^[167,168] A drawback of reactions like the *Paterno-Büchi* cycloaddition is the need for ultraviolet (UV) radiation to achieve direct excitation of the substrates. Utilization of UV light poses a potential safety hazard and can reduce selectivity, as it is absorbed by most organic molecules. Photocatalysis circumvents these issues as it allows for the use of visible light in most cases, facilitating the indirect generation of organic radicals or reactive triplet states.^[124,145,146,167] Additionally, the redox/ES energy tunability of PCs can be leveraged to further improve selectivity and to widen potential substrate scopes by enhancing their ES oxidative/reductive power (section 1.3.2).^[128]

In 2008 *Yoon* and co-workers reported a [2+2] cycloaddition between *Michael*-acceptors via visible light mediated photocatalysis using the *fruit fly* $[\text{Ru}(\text{bpy})_3]^{2+}$. Within the catalytic cycle, PC^* does not directly react with the main substrate itself. Instead, a sacrificial reductant ($^i\text{Pr}_2\text{NEt}$) quenches $^*\text{[Ru(bpy)}_3\text{]}^{2+}$ and the reduced $[\text{Ru}(\text{bpy})_3]^+$ transfers an electron to the substrate, which subsequently engages in the cycloaddition process.^[162] This type of mechanistic "detour" is frequently employed, when a strong reducing agent such as the $[\text{Ru}]^+$ complex is required ($E_{\text{red}} = -1.33 \text{ V vs. SCE}$).^{c),[8]} *Nicewicz* and *MacMillan* published work on the asymmetric alkylation of aldehydes via coupled organo- and photocatalytic cycles, which demonstrated the successful integration of photoredox catalysis into an already complex mechanism.^[163] Shortly after, *Stephenson* and co-workers described the tin-free dehalogenation of several substrates.^[164] Similarly to the cycloaddition reported by *Yoon*, $[\text{Ru}(\text{bpy})_3]^+$ is the species acting as the reducing agent for the halogenated substrate. Access to dehalogenation reactions that omit toxic tin compounds is highly valuable, as the removal of halogen substituents is highly relevant to this day (e.g. as part of synthetic routes or from contaminants in waste water). In the following years, a panoply of photocatalytic transformations were described, including the functionalization of amines, C-C/C-N/C-S couplings and many more,

^{c)} There is currently no convention on which potential-ranges correspond to terms like "strong" or "very strong" when discussing (photo)oxidants or -reductants, though recommendations have been made.^[128] Hence, values for $E_{\text{red}}/E_{\text{red}}^*$ will be provided, which permit a more objective categorization. Reduction potentials will be referenced versus the *Saturated Calomel Electrode* (SCE). Potentials referenced differently in original publications were converted according to *Pavlishchuk* and *Addison*.^[169]

usually catalyzed by noble metal TMCs.^[6,8,170]

Today, examples of photocatalytic reactions can quite literally fill books.^[25,171–173] Thus, a comprehensive literature review cannot be provided here. Instead, the focus will be on the more recent paradigm shift within the community: the utilization of more earth abundant materials to explore new reactivities and to achieve more sustainable photocatalysis (Fig. 1.15).^[15,16,44,174,175] In particular, examples of non-noble metal TMCs will be selected, their underlying photophysics and reactivity explained briefly and exemplary photocatalytic transformations will be showcased. First off, the main star of this work, chromium(III) complexes, will take the spotlight. Thereafter, other TMCs with photoactive MC/CT or LC states will be highlighted. A brief discussion on current and future challenges for the photocatalysis research community, such as reaction scaling and the creation of truly sustainable photochemistry, will round out this introduction.

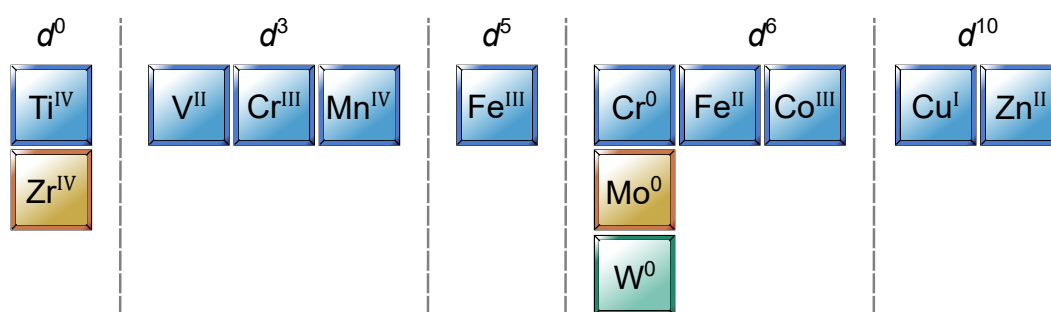


Fig. 1.15: Earth-abundant transition metals for photocatalysis discussed in this section. Their respective d electron configurations are highlighted.

1.4.1 Chromium(III) Complexes in Photocatalysis

Electron Transfer Catalysis – Catalyst Design and Applications

After photoexcitation, pseudo-octahedral chromium(III) complexes react from long-lived ^2MC states (section 1.2.2). They are usually confined to reductive quenching, as their oxidation is inaccessible unless they possess especially electron-rich ligands.^[52,68,69,73]

The viability of a given chromium(III) complex in photoredox catalysis is largely determined by its ES reduction potential E_{red}^* and the localization of the reduction in the $^*\text{[Cr]}^{\text{III}}/\text{[Cr]}^{\text{II}}$ half-reaction. Undesirable metal-centered reduction is typically observed in compounds with electron-rich ligands like $[\text{Cr}(\text{ddpd})_2]^{3+}$. Upon reduction a high-spin Cr^{II} species ($S = 2$) is obtained, which is kinetically labile and decomposes easily.^[15,52,176] Furthermore, electron-rich ligands lead to low E_{red} and thus E_{red}^* , resulting in a sparse substrate scope. Since tunability of the ES energy in chromium(III) complexes is limited barring severe changes to the ligand manifold (section 1.2.2), adjustments of E_{red}^* mainly rely on changes in

E_{red} (Tab. 1.2).^[15] Thus, chromium(III) photoredox catalysts with electron-poor polypyridyl/phenanthroline ligands are preferable (Tab. 1.2), as they possess higher E_{red} values and facilitate ligand- over metal-centered reduction.^[71,177–179] In cases like $[\text{Cr}(\text{bpy})_3]^{3+}$ and $[\text{Cr}(\text{tpy})_2]^{3+}$, the reduced complexes have been described as Cr^{III} centers with a ligand radical anion $\text{L}^{\bullet-}$ respectively.^[177,178] For $[\text{Cr}(\text{tpe})_2]^{2+}$ and $[\text{Cr}(\text{bpmp})_2]^{2+}$ the situation is more intricate. These reduced complexes (with $S = 1$) can be approximated as a resonance of a low-spin Cr^{II} center and a Cr^{III} with an antiferromagnetically coupled $\text{L}^{\bullet-}$, according to density functional theory (DFT) calculations.^[68,69]

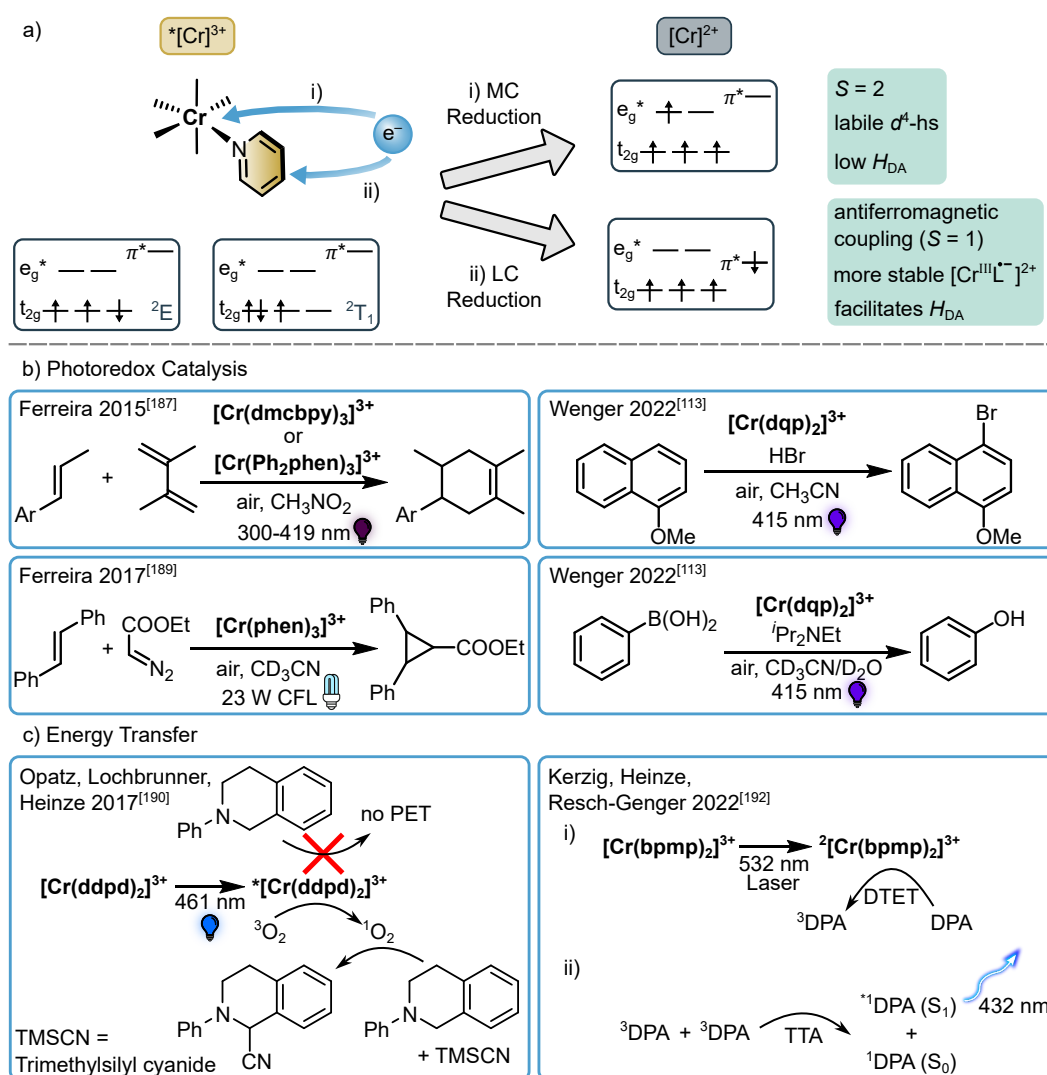
The (at least partial) localization of the reduction on the ligand leads to improved stability of the reduced complex, since the formation of labile high-spin Cr^{II} is avoided. Furthermore, LC reductions should permit increased electronic coupling H_{DA} between the ES Cr^{III} species and the substrate, thus aiding in the ET process (section 1.3.2).^[15]

Tab. 1.2: Electrochemical and photophysical data of selected chromium(III) complexes. Values measured in acetonitrile unless otherwise noted. ^a Measured in 1 M $\text{HCl}_{(\text{aq})}$, ^b Determined from E_{00} , ^c measured in H_2O , ^d measured in $\text{H}_2\text{O}/\text{HClO}_4$.

Complex	E_{red}/V	$E^*_{\text{red}}/\text{V}$	$\lambda_{\text{em}}/\text{nm}$	$E(^2\text{ES})/\text{eV}$	$\tau_0/\mu\text{s}$
$[\text{Cr}(\text{dmcbpy})_3]^{3+}$ [180,181]	+0.12	+1.82	733 ^a	1.70 ^{a,b}	7.7 ^a /25
$[\text{Cr}(\text{tpy})_2]^{3+}$ [66,67]	−0.15	+1.46	770	1.61	0.14
$[\text{Cr}(\text{bpy})_3]^{3+}$ [180]	−0.25	+1.46	729 ^a	1.71 ^{a,b}	69 ^a
$[\text{Cr}(\text{phen})_3]^{3+}$ [180]	−0.27	+1.43	730 ^a	1.70 ^{a,b}	304 ^a
$[\text{Cr}(\text{Ph}_2\text{phen})_3]^{3+}$ [180]	−0.29	+1.38	744 ^a	1.67 ^{a,b}	425 ^a
$[\text{Cr}(\text{dqp})_2]^{3+}$ [71]	−0.42	+1.24	724/747	1.66	2140 ^c
$[\text{Cr}(\text{bpmp})_2]^{3+}$ [68]	−0.43	+1.32	709 ^d	1.75 ^d	1550 ^d
$[\text{Cr}(\text{tpe})_2]^{3+}$ [69,110]	−0.50	+1.25	742	1.75 ^b	3500
$[\text{Cr}(\text{ddpd})_2]^{3+}$ [52,181]	−0.73	+0.87	738/775	1.60	1136
$[\text{Cr}(\text{CF}_3\text{BTP})_2]^-$ [182]	−1.00	+0.59	850	1.59	5
$[\text{Cr}(^t\text{BuPhBTP})_2]^-$ [182]	−1.21	+0.29	905	1.50	23

In 2015 *Ferreira* and co-workers reported radical cation [4+2] cycloadditions with several Cr^{III} complexes, including $[\text{Cr}(\text{Ph}_2\text{phen})_3]^{3+}$ and $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ (Scheme 1.3; dmcbpy = 2,2'-bipyridine-4,4'-dicarboxylate).^[183,184] The mechanism of this reaction, especially the role of oxygen, has been investigated in several studies and is still ambiguous.^[98,181,185,186] Even though the mechanism is not fully resolved, this cycloaddition is an illustrative example of reactivity that is accessible via photoredox catalysis, but not thermally. The employed electron-rich dienophiles and electron-deficient dienes are mismatched for a thermal *Diels-Alder* reaction. However, after photocatalytic oxidation of the dienophile, the electronic demands are reversed, which allows the reaction to proceed. Photocatalyzed [4+2] cycloadditions with

electron-poor dienophiles were also reported and several mechanistic pathways were suggested.^[187] In addition to *Diels-Alder*-type reactions, [3+2] cycloadditions with vinyl diazo species as well as cyclopropanations were described (Scheme 1.3).^[188,189] Wenger and co-workers have reported several photocatalytic transformations with $[\text{Cr}(\text{dqp})_2]^{3+}$, including the oxidative bromination of methoxy-arenes, the generation of phenols from boronic acids as well as the vinylation of an *N*-aryl amine (Scheme 1.3).^[113] The same group recently reported reductive transformations (such as the light-induced debromination of phenacylbromide) using the anionic complexes $[\text{Cr}(\text{R}^{\text{BTP}})_2]^-$ ($\text{R} = \text{CF}_3, ^t\text{BuPh}$), which possess comparatively negative reduction potentials ($E_{\text{red}} = -1.00 \text{ V}$ and -1.21 V ; BTP = bis (1*H*-1,2,4-triazol-5-yl)pyridine; Tab. 1.2). Therefore, the one-electron reduced species $[\text{Cr}(^t\text{BuPhBTP})_2]^{2-}$ is capable of reducing the substrate, after initial quenching of $^*[\text{Cr}(^t\text{BuPhBTP})_2]^-$ with $i\text{Pr}_2\text{NEt}$.^[182]



Scheme 1.3: a) Metal- vs. ligand-centered reduction in chromium(III) complexes, b) schematic examples of photoredox catalysis and c) applications based on energy transfer. CFL = compact fluorescent lamp.

Energy Transfer Catalysis and Upconversion

The *Molecular Ruby* $[\text{Cr}(\text{ddpd})_2]^{3+}$ has been employed in EnT catalysis, specifically for the efficient sensitization of singlet oxygen ($\Phi(^1\text{O}_2) = 61\%$). The generated $^1\text{O}_2$ served in the α -cyanation of aliphatic amines (Scheme 1.3).^[190] $[\text{Cr}(\text{ddpd})_2]^{3+}$ is particularly well-suited for photosensitization, as its E_{red} and E_{red}^* are rather low in comparison to similar complexes (Tab. 1.2), which therefore perform better as photoredox catalysts. Generally speaking, the substrate scope for EnT catalysis is fairly limited for chromium(III) complexes, owing to their low doublet energies. Additionally, the *Dexter* mechanism necessitates orbital overlap with the shielded metal center. While ET can be facilitated by (partial) LC reduction, this is not possible for EnT.^[15] However, its ability to generate $^1\text{O}_2$ while not being conducive to direct substrate oxidation could make $[\text{Cr}(\text{ddpd})_2]^{3+}$ viable for applications such as photodynamic therapy.^[191]

$[\text{Cr}(\text{bpm})_2]^{3+}$ has been used in sensitized triplet-triplet annihilation-upconversion (sTTA-UC) of 9,10-diphenyl anthracene (DPA), in which two green photons yield one blue photon.^[192] Owing to its ability to absorb green light and its comparably high doublet energy, $[\text{Cr}(\text{bpm})_2]^{3+}$ can engage in doublet-triplet EnT (DTET) to DPA and is thus able to generate ^3DPA . Subsequently, TTA can occur between two ^3DPA molecules, yielding one ^1GS and one emissive ^1ES (Scheme 1.3).

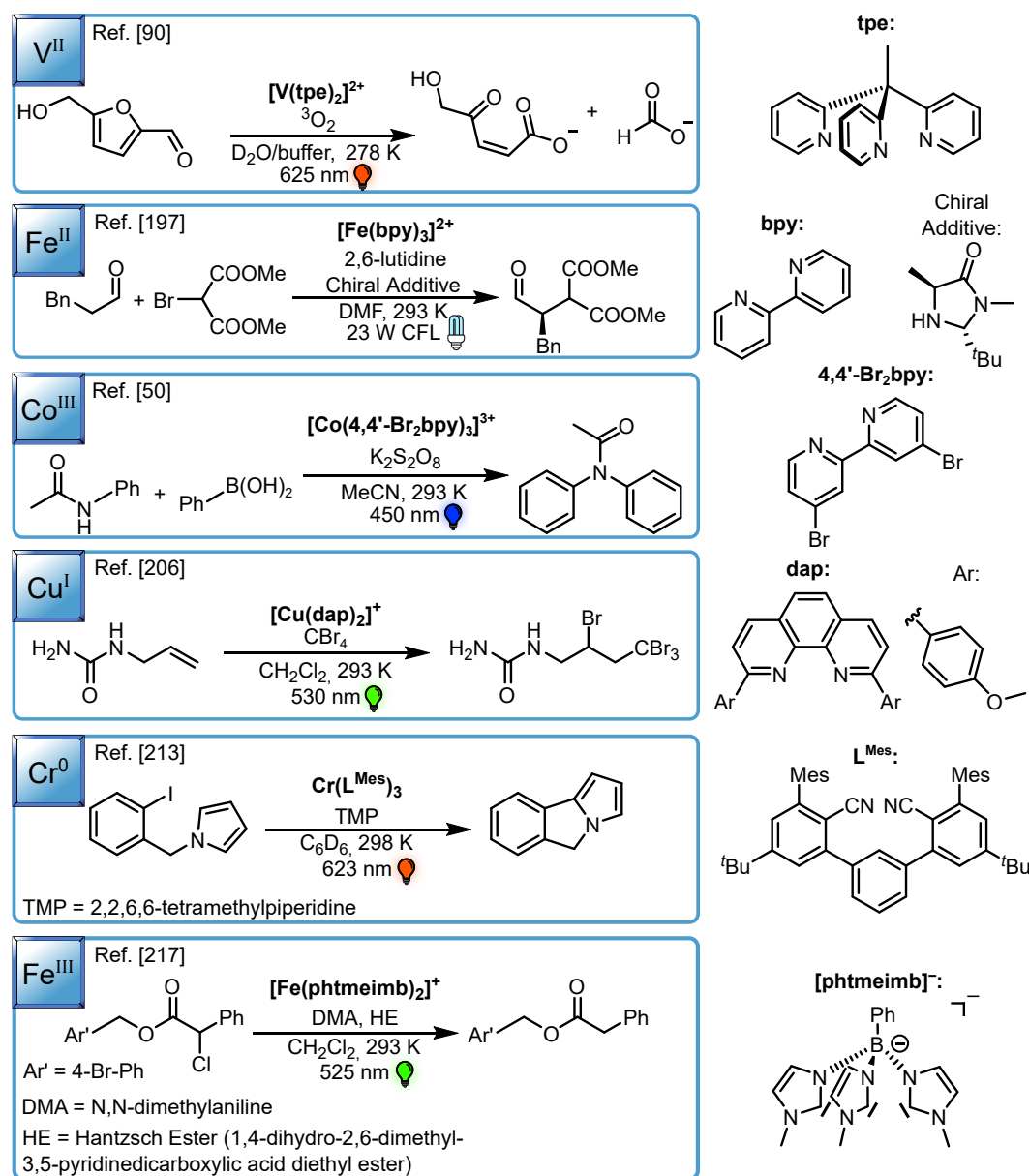
1.4.2 Photocatalysis with Other Earth Abundant Metals

TMCs with Photocatalytically Active MC States

Bimolecular reactivity from MC states is not limited to chromium(III) complexes. Sticking with the d^3 configuration, the recently reported **vanadium(II) compound** $[\text{V}(\text{tpe})_2]^{2+}$ possesses emissive, long-lived ($\tau_0 = 760$ ns) ^2ES s, which have been described as an admixture of $^2\text{MLCT}$ and ^2MC . Despite its low doublet energy ($\lambda_{\text{em}} > 1300$ nm; ≈ 0.95 eV), $[\text{V}(\text{tpe})_2]^{2+}$ was successfully used in the orange-red (625 nm) light-mediated $^1\text{O}_2$ generation for the oxidation of 5-(hydroxymethyl)furfural in water (Scheme 1.4) and for a *Schenck-Ene* reaction with 1-methylcyclohexene in acetonitrile.^[90]

Moving to the right in the $3d^3$ series, the highly charged **manganese(IV) complex** $[\text{Mn}(\text{dgpy})_2]^{4+}$ exhibits an interesting "two-state" photoreactivity (dgpy = 2,6-diguanidylpyridine).^[193,194] Similar to $[\text{V}(\text{tpe})_2]^{2+}$, the lowest-energy ^2ES of $[\text{Mn}(\text{dgpy})_2]^{4+}$ is of mixed character, in this case of $^2\text{LMCT}/^2\text{MC}$ and has a lifetime in the nanosecond range. The high ES reduction potential $E_{\text{red}}^* = +1.80$ V enables the photooxidation of naphthalene by dynamic quenching.^[194] Unexpectedly, $^*\text{[Mn}(\text{dgpy})_2]^{4+}$ also manages to oxidize solvents like acetonitrile and benzene, which was attributed to static reactivity from the initially populated $^4\text{LMCT}$ state

($E_{\text{red}}^* > +2.40$ V). Since a large share of this oxidative power stems from the complexes' high GS potential ($E_{\text{red}} = +0.94$ V), its reoxidation is highly challenging. Thus, this compound has been limited to non-catalytic photooxidation. Photocatalytic activity was recently achieved using a manganese complex with the *N*-heterocyclic carbene (NHC) ligand phtmeimb[−] and two substituted derivatives (phtmeimb[−] = deprotonated phenyltris(3-methylimidazol-2-ylidene)borate; Scheme 1.4).^[195] Interestingly, both partners of the [Mn]^{IV}/[Mn]^{III} pair display long-lived ESs and a mixture of the redox couple was used in a multitude of photoinduced arene-couplings. Multiple potential mechanistic pathways were proposed, including a consecutive excitation of both the [Mn]^{IV} and [Mn]^{III} species, which then serve as photooxidant and photoreductant, respectively.



Scheme 1.4: Selected examples of photocatalysis with earth-abundant metal TMCs.

Iron(II) complexes possess a d^6 configuration and low-lying MC states that are rapidly populated after initial MLCT excitation (section 1.2.1). While these MC states tend to be short-lived (picosecond range) due to their typically strongly distorted geometry, some examples of iron(II) photocatalysis have been reported.^[15,16,19] For instance, the lowest-energy ES of $[\text{Fe}(\text{bpy})_3]^{2+}$ ($^5\text{T}_2$) approaches a lifetime of close to a nanosecond, which barely permits bimolecular reactivity (1.3.1).^[196] Thus, $[\text{Fe}(\text{bpy})_3]^{2+}$ has been utilized in the asymmetric alkylation of aldehydes, which had been similarly described with ruthenium- and iridium-based catalysts (Scheme 1.4).^[197,198] Importantly, control experiments showed continuation of the respective reactions after removal of the light source. These findings indicate that the ES iron(II) compound serves mainly as an initiator. The complex $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ ($\text{tren}(\text{py})_3$ = tris(2-pyridyl-methylimino-ethyl)amine) is able to absorb yellow light (580 nm) and very quickly (≈ 200 fs) reaches a comparatively long-lived $^5\text{T}_2$ state ($\tau_0 = 55$ ns).^[199] $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ was employed as a mild photoreductant ($E_{\text{red}}^* = +0.03$ V) for a series of differently substituted benzoquinones. Observation of the oxidative quenching rates within this row via transient absorption (TA) spectroscopy permitted an estimation of the ES reduction potential and the ES energy.^[199] While some examples of Fe^{II} photoredox catalysis have been reported, many mechanistic aspects like the orbitals and spin-states involved in ET are still ambiguous and require further investigation.^[16]

Cobalt(III) complexes are isoelectronic to their iron(II) counterparts. However, the increased charge results in an intrinsically higher LFS, which can be amplified via the introduction of strong ligands like NHCs, guanidines or pyridines.^[49,50,200] For MCs sufficiently high in energy, the transition back to the GS falls into the *Marcus*-inverted region and is thus decelerated. This behaviour was recently demonstrated for a series of $[\text{Co}(\text{bpy})_3]^{3+}$ derivatives, in which stronger driving forces for the $^3\text{MC} \rightarrow ^1\text{GS}$ transition led to longer ES lifetimes (up to 6.5 ns). The bromine-substituted complex $[\text{Co}(4,4'\text{-Br}_2\text{bpy})_3]^{3+}$ was utilized as a strongly oxidizing photocatalyst ($E_{\text{red}}^* = +1.65$ V) in the cross-coupling of aryl amides with aryl boronic acids (Scheme 1.4).^[50]

Not Exclusive to Noble Metals – Photocatalytically Active CT/LC States

Through molecular design, long-lived, photoactive CT states can be realized in 3d TMCs. In d^{10} **copper(I) complexes** excited MC states are avoided by default and MLCT transitions dominate the ES landscape. In terms of photocatalytic applications, Cu^{I} is probably the most researched 3d metal and many examples have been published thus far.^[16,175,201–204] Tetracoordinated copper(I) complexes, such as the phenanthroline compound $[\text{Cu}(\text{dap})_2]^+$, usually react as reductants from their photoactive $^3\text{MLCT}$ state ($E_{\text{red}}^* = -1.43$ V; $\text{dap} = 2,9\text{-di}(p\text{-anisyl})\text{-}1,10\text{-phenanthroline}$). In $[\text{Cu}(\text{dap})_2]^+$ and similar pseudo-tetrahedral Cu^{I} compounds, this ES is rather long-lived ($\tau_0 = 270$ ns), despite the tendency of the formally oxidized d^9 metal cen-

ter ($[\text{Cu}^{\text{II}}\text{L}^{\bullet-}]$) to undergo *Jahn-Teller* distortion. This so-called *flattening distortion*, is less severe due to the introduction of bulky substituents in the phenanthroline moiety.^[201] $[\text{Cu}(\text{dap})_2]^+$ and related compounds have been used in numerous examples of photoredox catalysis, including activation of benzylic halides or formation of C-C bonds via atom transfer radical addition (ATRA) reactions (Scheme 1.4).^[204–206] A mechanistic peculiarity of copper-catalyzed ATRA reactions is the potential coordination of intermediates to the Cu^{II} species. The transfer of this coordinated functionality to organic radicals is thus facilitated. In some cases, this reactivity gives access to products that cannot be obtained with other PCs, e.g. in the chlorosulfonylation of alkenes with $[\text{Cu}(\text{dap})_2]^+$, whereas utilization of $[\text{Ru}(\text{bpy})_3]^{2+}$ merely leads to chlorination.^[21,202,207] While oxidative quenching is the more common mechanistic pathway, copper(I) complexes can be quenched reductively. For example, $[\text{Cu}(\text{bath})(\text{Xant})]^+$ has been utilized in the cobalt-cocatalyzed reduction of aldehydes and ketones (bath = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; Xant = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene). Even though the overall transformation is reductive, $^*[\text{Cu}(\text{bath})(\text{Xant})]^+$ oxidizes an electron donor in the first step of the mechanism ($E_{\text{red}}^* = +1.52 \text{ V}$). Subsequently, the generated $[\text{Cu}(\text{bath})(\text{Xant})]^0$ acts as a reducing agent ($E_{\text{red}} = -1.67 \text{ V}$) for the cobalt-cocatalyst.^[208]

Zinc(II) compounds share the $3d^{10}$ configuration of their copper(I) counterparts, however, they are confined to LC transitions, due to the redox-inert nature of the central ion. So far, only few examples of zinc(II) photocatalysis have been described. The porphyrinato complex $\text{Zn}(\text{TPP})$ ($E_{\text{red}}^* = +0.96 \text{ V}$) succeeded in the photooxidative activation of trithiocarbonates, which subsequently engaged in polymerization of styrene, acrylates and acrylamides ($\text{TPP}^{2-} = \text{deprotonated 5,10,15,20-tetraphenylporphyrin}$).^[209] The structurally similar complex $\text{Zn}(\text{Pc})$ is able to sensitize $^1\text{O}_2$ upon near-infrared (NIR) irradiation, which was demonstrated by the successful α -cyanation of tertiary amines, taking advantage of the sensitizers high absorptivity in the low-energy spectral range ($\text{Pc} = \text{phtalocyanine}$).^[210]

From completely full to fully vacant orbitals: d^0 complexes of **titanium(IV)** and the rather abundant $4d$ metal **zirconium(IV)** can possess photoactive LMCT states. So far, applications of either metal in photocatalysis have remained scarce, but some examples have been reported. Just recently, *Kagan's complex* (a chiral, menthyl-substituted titanocene) was used as a PC in the regio- and enantioselective ring opening of protected, enantiomerically pure epoxides.^[211] The photoexcited zirconium(IV) complex $^*\text{Zr}(\text{MePDP})_2$ can act as a mild oxidant ($E_{\text{red}}^* = +0.31 \text{ V}$) and is easily reduced with benzimidazoline (BIH) derivatives ($\text{MePDP}^{2-} = \text{deprotonated 2,6-bis(5-methyl-3-phenyl-1H-pyrrol-2-yl)pyridine}$). The resulting $[\text{Zr}^{\text{III}}]$ compound subsequently acts as a strong reducing agent ($E_{\text{red}} = -1.78 \text{ V}$) and has been employed in photocatalytic dehalogenations of acyl-species and reductive benzylic coupling reactions.^[212]

Complexes of the **zero-valent group 6 metals chromium(0), molybdenum(0) and tungsten(0)** possess a d^6 configuration. They exhibit low-lying MLCT excited states, due to their electron-rich metal center and electron-poor strong-field ligands (e.g. arylisocyanide ligands) and can act as very strong photoreductants.^[175] For example, the Cr^0 complex $\text{Cr}(\text{L}^{\text{Mes}})_3$ possesses an ES reduction potential of $E_{\text{red}}^* = -2.32$ V and is able to reduce a variety of aryl halides upon irradiation with red light (Scheme 1.4).^[213] Moving down group 6, the ES molybdenum(0) complex $^*\text{Mo}(\text{CNAr}_3\text{NC})_3$ ($E_{\text{red}}^* = -2.22$ V) succeeded in the challenging reduction of acyl cyclopropane, permitting the formation of a substituted 2,3-dihydrofuran.^[214] In a very recent example, "Mo-2" was reported as part of a series with tridentate arylisocyanide ligands. This exceptional photoreductant ($E_{\text{red}}^* = -2.38$ V; $\tau_0 = 2.8$ μs) successfully catalyzed the reduction of several acyl oximes, some of which proved to be outside the scope of the noble metal complex *fac*-Ir(ppy)₃ ($E_{\text{red}}^* = -1.72$ V).^[45] A challenge associated with complexes containing sophisticated arylisocyanide ligands is their often difficult and time-consuming synthesis. In contrast, the recently reported carbonyl compound $\text{Mo}(\text{tpe})(\text{CO})_3$ is easily accessible and serves as a strong photoreductant ($E_{\text{red}}^* = -1.68$ V) in the green-light mediated dehalogenation of chloropyrazine.^[14] Like their lighter homologues, arylisocyanide complexes of tungsten(0) can serve as strong photoreductants. For example, $\text{W}(\text{CNDipp})_6$ ($E_{\text{red}}^* = -2.46$ V) and several derivatives have been employed in the dehalogenation of aryl iodides with subsequent cyclization. This reaction was achieved either by blue-light (445 nm) or pulsed NIR irradiation (810 nm), with the latter operating via a two-photon mechanism (CNDipp = 2,6-diisopropylphenylisocyanide).^[215] While progress has been limited for iron(II) compounds, research on **iron(III)-based photocatalysis** has been rather fruitful in recent years.^[19] These catalysts exhibit large ligand field splitting induced by the highly charged Fe^{III} , which is typically stabilized by electron-rich, strongly donating ligands, such as NHCs. In the resulting low-spin complexes, MC states are shifted to higher energies. Photoexcitation yields $^2\text{LMCT}$ states, from which ISC does not occur. Hence, ES lifetimes for these complexes usually do not surpass the low nanosecond-range. However, they are sufficiently long-lived to achieve bimolecular reactivity.^[216,217] One recently described example of photoredox catalysis was conducted with the carbene iron(III) complex $[\text{Fe}(\text{btz})_3]^{3+}$, which served in the oxidation of alkenes for radical cation [4+2] cycloadditions after absorption of green light ($E_{\text{red}}^* = 1.94$ V; $\tau_0 = 0.10$ ns, btz = 3,3'-dimethyl-1,1'-bis-(*p*-tolyl)-4,4'-bis(1,2,3-triazol-5-ylidene)).^[216] The same complex has been utilized in the addition of alkyl halides to alkenes and alkynes in ATRA reactions.^[218] Reductive dehalogenations of α -halocarbonyles were successfully carried out with $[\text{Fe}(\text{phtmeimb})_2]^+$, in which the ES NHC complex is quenched by a sacrificial donor and the reductive power of the obtained iron(II) complex is subsequently harnessed ($E_{\text{red}} = -0.78$ V; Scheme 1.4).^[217] The well-known neutral complex $\text{Fe}(\text{acac})_3$ is capable of oxidative ring-opening of cyclic carboxylic acids in the presence of air (acac^- = deprotonated acetylacetone).^[219] Due to the much

weaker ligand field induced by the π -donor acac^- , the potential participation of MC states in this bimolecular reactivity cannot be disregarded. Overall, similar to iron(II) photocatalysis, mechanistic understanding of this system is still incomplete.^[19]

When talking about sustainable (photo)chemistry, **uranium** is not the first thing that comes to mind for most people. Usually associated with environmental disasters and warfare, this element has not enjoyed the best of reputations. However, the non-fissile isotope ^{238}U makes up over 99% of the naturally occurring element, which happens to be more abundant than e.g. molybdenum.^[16] **The uranyl cation $[\text{UO}_2]^{2+}$** is a very strong photooxidant ($E_{\text{red}}^* = +2.35 \text{ V}$), capable of oxygenating unsubstituted hydrocarbons like cyclopentane under aerated conditions via hydrogen atom transfer.^[16,220,221] This capability has been utilized for the creation of C-C bonds in completely unactivated substrates.^[222]

Undoubtedly, the replacement of noble metal catalysts by more abundant materials is a key item in the quest for widespread application and increased sustainability of photocatalysis. Yet, there are plenty more hurdles to overcome that will require the ingenuity of current and future researchers.

1.4.3 Challenges of Today and Tomorrow

Photocatalysis has transformed into a bustling research field over the past 15 years. Today, innumerable examples of light-driven reactions and photocatalysts are known. The latter span a broad range of ES energies and redox potentials, thereby gaining access to huge substrate scopes.^[128] However, despite the progress made so far, large-scale applications of photocatalysis remain scarce and its potential positive impact on sustainability is thus limited.^[223–227]

One of the most critical aspects in the establishment of economically and ecologically viable large-scale photochemical processes, is a **fundamental mechanistic understanding**. Although these detailed studies are complex and often require sophisticated equipment, rational reaction design and optimization can only occur when the elementary steps of a particular photocatalytic cycle are well understood (section 1.3). Closely related issues are differences in light sources and reactors between laboratories as well as insufficient documentation of experimental conditions, which frequently lead to **lacking reproducibility**.^[168,228–231] Poorly optimized and irreproducible reaction conditions are unacceptable at larger scales, as they lead to an **inefficient use of photons**. This results in longer reaction times as well as higher cost in terms of both opportunity and energy. The latter is an important factor at an industrial scale despite availability of efficient blue LEDs, due to the electricity required.^[232] Partial mitigation of this issue is achieved by red-light-mediated catalysis, which aims to directly populate the low-lying excited-states of the PCs, thus limiting energy loss. While it may seem appealing to abandon artificial light sources altogether, the utilization of sunlight to power photocatalytic synthesis suffers from major drawbacks: rather low irradiance ($\approx 0.1 \text{ W/cm}^2$) and a considerable share of UV radiation.^[228,229,233–235] The latter can result in diminished selectivity, while the former impedes reaction speed and is closely intertwined with the aforementioned **importance of reactor design**. The construction of suitable photochemical reactors demands a favorable arrangement of the light source(s), as to permit homogenous and intense irradiation of the reactants (this is particularly difficult to achieve for sunlight, as it illuminates large areas with low irradiance). This issue is further amplified by the high molar extinction coefficients of many PCs. These necessitate short optical pathlengths to avoid inhomogenous light absorption, which can limit reactor design options. Additionally, large-scale reactors need to provide efficient mass- and heat transfer as well as appropriate cooling. Through interdisciplinary efforts from chemists, engineers and other technical experts, progress has been made in the development of batch- as well as flow-reactors.^[167,228,233,236–239]

Assuming the above challenges can be overcome in the future, an interesting question remains: **what can be the impact of photocatalysis and light-driven chemistry on sustainability within the chemical industry?** While this topic is multifaceted and nuanced, some brief considerations are provided below (Fig. 1.16).

Direct irradiation with sunlight may not be ideal for photochemical syntheses, however, solar energy can serve as a "green" source of electricity to power intense, artificial light-sources. Furthermore, it holds a lot of potential for the photocatalytic treatment of polluted (waste) water, e.g. via deconstruction of various polymers or reduction of halocarbons. Alongside improved treatment of waste, limiting its production is critical. Thus, the optimization of atom economy of any given (photo)chemical process is paramount.^[94,228] Furthermore, utilized substances (e.g. catalysts) should be recycled and reused, if possible. While waste needs to be minimized and materials recycled, it is just as important to consider the sourcing of chemical building blocks. In the future, photochemical degradation of feedstock materials (e.g. lignin and cellulose) could help to reduce the demand for bulk chemicals derived from oil.^[229,240–242]



Fig. 1.16: Sustainable (photo)chemistry requires more long-term oriented approaches within the industry. Increased use of feedstock materials (orange), renewable/infinite energies (dark blue), improved treatment and potential recycling of waste (green) and high atom-economy (light blue) are parts of the puzzle.

So, is light-driven chemistry the silver bullet for sustainability? No. However, it can certainly be a *piece* of the puzzle that is a long-term-oriented chemical industry. It is important to recognize the potential photochemical transformations hold – unique reactivities and the generation of highly reactive species under mild conditions. However, the key to success is not a singular piece. Rethinking the way resources and energy are obtained, processes are conducted and waste is handled, could potentially create a complete picture.

Molecular Rubies possess extremely long-lived excited states and often high excited-state reduction potentials.^[15] These properties point to their viability for applications in photoredox catalysis, making them interesting prospects for the potential replacement of established, noble-metal TMCs in this field. Particularly, the tripodal compound $[\text{Cr}(\text{tpe})_2]^{3+}$ will be explored for photocatalytic applications. In a separate effort, the new chromium(III) complex $[\text{Cr}(\text{dgpy})_2]^{3+}$ will be synthesized and characterized. The ligand dgpy possesses two saturated, cyclic guanidine moieties. It thus varies from more typical polypyridine ligands like ddpd and tpe utilized in *Molecular Rubies*.^[52,68–70] Investigation of this novel complex aims to achieve deeper insight into the photophysics of chromium(III) compounds.

Establishment of a Molecular Ruby in Photoredox Catalysis

Most TMCs used as photocatalysts contain rare and expensive noble metals. Only few examples of chromium(III) complexes in photoredox catalysis have been described, so far (section 1.4.1). $[\text{Cr}(\text{tpe})_2]^{3+}$ possesses an extremely long ES lifetime and a high ES reduction potential ($\tau_0 = 3.5 \text{ ms}$; $E_{\text{red}}^* = +1.25 \text{ V vs. SCE}$),^[69,110] which should enable bimolecular reactivity from its excited state. Thus, the first aim of this work is the successful utilization of this *Molecular Ruby* as a photoredox catalyst (Fig. 2.1a; section 3.2 and 3.3). During these first applications, strengths and weaknesses of this potential new catalyst are to be assessed. As part of this evaluation, the chromium(III) complex will be compared to a noble metal TMC that will serve as a benchmark. If possible, potential particularities of this *Molecular Ruby* in photoredox catalysis will be investigated via mechanistic studies.

Reduction Potential Tuning

The photophysics of $[\text{Cr}(\text{tpe})_2]^{3+}$ are almost completely confined to the metal-center.^[69] Reduction of the complex occurs mostly on the electron-poor ligand. This spatial separation should permit tuning of the reduction potential while leaving the ES energy untouched (Fig. 2.1b). To this end, one or two trifluoromethyl-substituted tpe ligands will be introduced into the parent complex (section 3.4). The introduction of electron-poor ligands to a small, highly charged metal-center like Cr^{III} can be challenging.^[67,68,243] Thus, an appropriate synthetic approach will have to be developed. The target complexes will be characterized using spectroscopic and electrochemical methods as well as quantum chemical calculations. The goal of

this research is the development of a series of complexes that differ merely by their reduction potentials and can thus perspectively serve as useful tools in mechanistic studies.

Scaling Photocatalysis from the Cuvette to the Flask

Even though countless photocatalytic transformations have been described over the years, they are usually confined to the cuvette-scale in proof-of-concept studies (section 1.4.3). Bottlenecks such as the high cost of noble-metal catalysts impede scalability/widespread synthetic application of photocatalysis. Furthermore, the typically used CT complexes necessitate the use of very short optical paths (e.g. flow reactors) to avoid inhomogenous light-absorption and local temperature spikes, due to their high extinction coefficients (section 1.4.3). Factors such as these limit accessibility for most laboratories. This research aims to tackle these challenges using $[\text{Cr}(\text{tpe})_2]^{3+}$ (Fig. 2.1c; section 3.5). The chromium(III) complex is based on a much cheaper and more abundant metal, which keeps its cost low – assuming the target compound is easily accessible. Therefore, the first goal in this endeavour will be to develop cheap and scalable syntheses of both the ligand and complex. Furthermore, the inversion-symmetric $[\text{Cr}(\text{tpe})_2]^{3+}$ possesses low absorptivity, due to its metal-centered optical transitions (*Laporte's rule*).^[69] Thus, photocatalytic reactions utilizing this compound could benefit from long optical paths, which can be easily achieved in ubiquitous standard glassware. Of course, a prerequisite for these plans is the successful application of $[\text{Cr}(\text{tpe})_2]^{3+}$ as a photocatalyst in the first part of this work. The research outlined here should contribute to a more widespread implementation of photocatalysis in synthetic laboratories and potentially larger scales in the future.

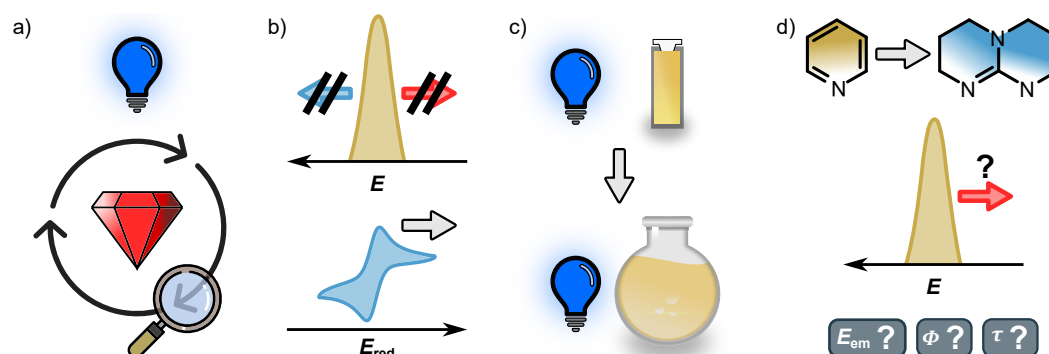


Fig. 2.1: Depictions of the aims pursued in this work. a) Implementation of a *Molecular Ruby* in photoredox catalysis and investigation of mechanistic aspects, b) independent reduction potential tuning c) scaling of photocatalysis from a cuvette- to a laboratory-scale, d) emission energy tuning and photophysical characterization.

A New Type of Ligand – Fundamental Photophysical Investigations

Most *Molecular Rubies* possess σ -donating and π -accepting polypyridyl ligands. Emission energies of these complexes typically fall into a narrow range, due to a similar *nephelauxetic effect* (section 1.2.2). This research aims to achieve a bathochromic shift of the emission energy via the introduction of the dgpy-ligand containing two σ - and π -donating guanidine units (Fig. 2.1d; section 3.6). The optical properties of this novel compound will be assessed, aiming to gain deeper understanding on the photophysics of chromium(III) complexes. The results obtained from this study could help to inform future decisions in the development of new *Molecular Rubies*.

Overall, two main goals will be pursued in this work: the application of *Molecular Rubies* as photocatalysts and an improved understanding of their underlying photophysics. The first objective is motivated by the desire to contribute to the increased and widespread utilization of photocatalysts based on earth-abundant materials in organic synthesis. The motivation behind the second main part of this research is to deepen our understanding of *Molecular Rubies* and to inform future design decisions. The knowledge gained could aid in the development of more abundant, cheaper yet high-performing alternatives to noble-metal TMCs in optical applications.

Results and Discussion

3.1 Overview

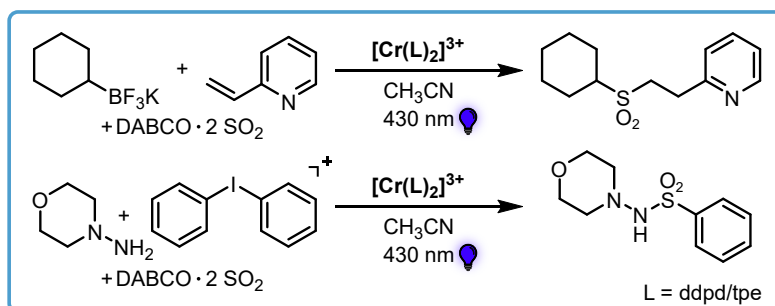
The results of the research conducted for this work have been published in, or submitted to peer-reviewed journals.^[110,181,244–246] In the following sections, these publications are reprinted.

Prior to the first study presented here, called *Molecular Rubies in Photoredox Catalysis* (section 3.2), very few examples of chromium(III) complexes in photocatalytic applications had been reported.^[183,187–190] The only prior example of a *Molecular Ruby* in this context had been the photosensitization of $^1\text{O}_2$ by $[\text{Cr}(\text{ddpd})_2]^{3+}$ from its long-lived doublet states.^[190] However, utilization of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in photoredox catalysis did not appear viable, due to its low (excited-state) reduction potential and the labile nature of its reduced high-spin Cr^{II} counterpart (section 1.4.1). In contrast, the electron-poor $[\text{Cr}(\text{tpe})_2]^{3+}$ (Scheme 3.2) a) possesses strongly oxidizing and even longer-lived doublet excited states ($E_{\text{red}}^* = 1.25 \text{ V}$; $\tau_0 = 3.5 \text{ ms}$)^{d)} and b) its reduction is (partially) localized on the tpe ligands (section 1.4.1). Thus, the formation of a labile Cr^{II} species is avoided, which recommends this complex for electron transfer catalysis. Within this study, a literature-known photocatalytic radical-cation $[4+2]$ cycloaddition^[183,184] between *trans*-anethole and 2,3-dimethylbutadiene was chosen, to assess the feasibility of $[\text{Cr}(\text{tpe})_2]^{3+}$ as a catalyst. Under the experimental conditions, the *Molecular Ruby* proved to be superior to the established noble metal complex $[\text{Ru}(\text{bpz})_3]^{2+}$ regarding catalytic productivity, due to its high level of (photo)stability (bpz = 2,2'-bipyrazine). As a result of this high stability, $[\text{Cr}(\text{tpe})_2]^{3+}$ displayed unaltered catalytic activity upon multiple cycles of substrate addition. Besides photocatalytic experiments, a mechanistic investigation of the cycloaddition was conducted, particularly regarding the role of oxygen. Despite the net redox-neutral nature of the transformation, it scarcely proceeds under deaerated conditions.^[183,185] Laser flash photolysis (LFP) measurements revealed the accumulation of the reduced complex $[\text{Cr}(\text{tpe})_2]^{2+}$ in the absence of oxygen, indicating an insufficient rate of catalyst reoxidation by potential organic intermediates (such as the radical cation of the cycloaddition product). The increasing concentration of

^{d)} Due to its high reactivity and extremely long excited-state lifetime, the emission of $[\text{Cr}(\text{tpe})_2]^{3+}$ is very easily quenched by trace impurities. For an efficient quencher with $k_q = 10^8 \text{ M}^{-1}\text{s}^{-1}$, a micromolar concentration is sufficient to cut the observed emission lifetime τ in half (*Stern-Volmer* equation; section 1.3.1). Thus, deviating numbers for τ_0 appear throughout the projects presented here. The highest value of $\tau_0 = 3.5 \text{ ms}$ was obtained during the study called *Gram-Scale Photocatalysis with a Stable and Recyclable Chromium(III) Photocatalyst in Acetonitrile and in Water* (section 3.5).^[110]

$[\text{Cr}(\text{tpe})_2]^{2+}$ promotes non-geminate back-ET to the radical cation of the substrate *trans*-anethole, thereby impeding downstream reactivity. Reoxidation experiments confirmed that air is capable of regenerating the catalyst from its reduced form. Thus, oxygen was identified as a redox-mediator in the catalytic cycle, required to prevent detrimental back-ET. Over the course of this study, $[\text{Cr}(\text{tpe})_2]^{3+}$ was identified as a strongly oxidizing, highly stable photocatalyst that can operate effectively under aerated conditions.

In the second project on *Visible-Light Induced Fixation of SO_2 into Organic Molecules with Polypyridine Chromium(III) Complexes* $[\text{Cr}(\text{ddpd})_2]^{3+}$, $[\text{Cr}(\text{bpmp})_2]^{3+}$ and $[\text{Cr}(\text{tpe})_2]^{3+}$ were tested for the photocatalytic syntheses of sulfones and sulfonamides in two multi-component reactions (Scheme 3.1; section 3.3). This research was conducted in collaboration with the groups of [REDACTED] (Johannes Gutenberg-Universität Mainz) and [REDACTED] (Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau).



Scheme 3.1: Visible-light mediated fixation of SO_2 in two separate three-component reactions with *Molecular Rubies* as photocatalysts.

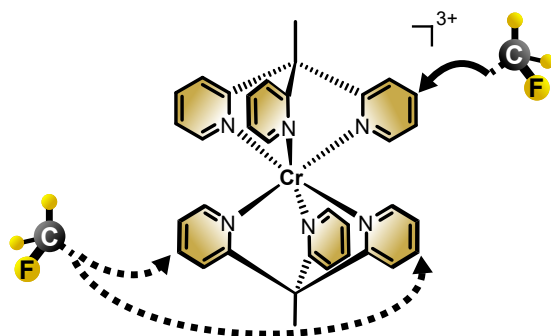
No catalytic activity was observed for $[\text{Cr}(\text{bpmp})_2]^{3+}$, as the complex proved susceptible to deprotonation by some of the basic substrates.^[68] In contrast, successful SO_2 -fixation was achieved with both $[\text{Cr}(\text{tpe})_2]^{3+}$ and even the weak photooxidant $[\text{Cr}(\text{ddpd})_2]^{3+}$. Consistent with the findings of the previous study, catalyst reoxidation was slow in these photoreactions and accumulation of the respective $[\text{Cr}]^{2+}$ -species was observed. These reduced complexes are strongly colored and therefore impeded the reactions due to an inner filter effect (presumably more pronounced for $[\text{Cr}(\text{tpe})_2]^{3+}$, due to its low extinction coefficient).^[69,176,244] While $[\text{Cr}(\text{ddpd})_2]^{3+}$ displayed photocatalytic activity under the reaction conditions, it lacked stability compared to $[\text{Cr}(\text{tpe})_2]^{3+}$ (formation of a labile Cr^{II} -species; section 1.4.1). This was demonstrated in photolysis experiments in the presence of substrates. Owing to its superior stability, $[\text{Cr}(\text{tpe})_2]^{3+}$ was again employed for mechanistic investigations by *Stern-Volmer* analyses and determination of cage-escape yields Φ_{CE} via LFP. Four substrates were compared and the obtained values for Φ_{CE} varied greatly. Two similar components, the cyclic tertiary amines 1,4-diazabicyclo[2.2.2]octane (DABCO; released from its SO_2 adduct DABSO) and 4-aminomorpholine (4-AM), gave values of <7% for and 73%, respectively. These differences between cage-escape yields

were crucial for the success of this multi-component reaction. Both amines reacted with $^*[\text{Cr}(\text{tpe})_2]^{3+}$, which was undesired in the case of DABCO. Since quenching by DABCO was largely unproductive, this side-reaction did not inhibit the desired reaction completely. While they were advantageous in this particular case, the widely different Φ_{CE} values for the two substrates are not easily explained. These results underline the inherent difficulty of predicting cage-escape yields and highlight the need for further research on this aspect of the photocatalytic cycle. In the subsequently conducted third study, groundwork for future investigations on parameters like cage-escape yields was laid out.

In most photocatalysts, the excited-state energy and the reduction potential are closely intertwined. Both parameters usually depend on the energies of the same frontier orbitals and thus cannot be tuned independently.^[31,128,247] Decoupling of these properties may be achieved if the lowest-energy excited states and the reduction process were largely confined to two different parts of the molecule. This exact condition is fulfilled in $[\text{Cr}(\text{tpe})_2]^{3+}$, which displays almost completely metal-centered photophysics and a largely ligand-centered reduction.^[69] Thus, the introduction of electron-withdrawing substituents on the polypyridyl ligand should permit an anodic shift of the reduction potential without affecting the emission energy. In the study *Decoupling Redox Potentials and Excited State Energies in Substituted Chromium(III) Chromophores*, one or two trifluoromethyl groups were introduced into the parent complex $[\text{Cr}(\text{tpe})_2]^{3+}$ (section 3.4). The substituted complexes $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ and *cis-/trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (Scheme 3.2) were obtained through a microwave-assisted approach. Access to these electron-poor chromium(III) compounds required high temperatures (200 °C) and the use of a solvent-mixture from which the respective target-complex precipitated upon formation. Each CF_3 group shifts the reduction potential anodically by 100 mV relative to $[\text{Cr}(\text{tpe})_2]^{3+}$, while the emission energies remain unchanged. Quantum chemical calculations were congruent with these experimental findings and furthermore predicted essentially unchanged coordination geometries. The successful decoupling of excited-state energies and reduction potentials in these complexes provides a valuable tool for future mechanistic studies (e.g. on reoxidation/back ET rates or cage-escape yields). Comparing Φ_{CE} of a given substrate for the complexes of this series could grant access to a unique possibility: assessing cage-escape yields while adjusting only the thermodynamic driving force. The ability to individually address a single variable is critical in a multifactorial problem like cage-escape, as only then can its isolated influence be evaluated.

In the fourth project of this work, the focus was largely shifted away from mechanistic considerations and fundamental understanding of *Molecular Rubies* as photocatalysts. Instead, desirable traits a photocatalyst should possess to promote the more widespread implementation of photocatalysis into synthetic laboratories (and perspective larger scales) were addressed. These include an accessible and scalable synthesis of the photocatalyst from abundant starting materials, concomitant with low cost. Furthermore, the catalyst should be highly photostable, usable in organic

solvents and in water, recyclable, and permit simple irradiation setups. $[\text{Cr}(\text{tpe})_2]^{3+}$ fulfills the aforementioned requirements, which was highlighted in the study *Gram-Scale Photocatalysis with a Stable and Recyclable Chromium(III) Photocatalyst in Acetonitrile and in Water* (section 3.5).^[110] Using a new synthetic approach, both ligand and complex were obtained on a double-digit gram-scale in high yields, from cheap and abundant building blocks. The previously discussed high photostability of $[\text{Cr}(\text{tpe})_2]^{3+}$ was demonstrated in photolysis experiments with ultra-high power (UHP) LEDs and via recycling of up to >90% of the starting material after photocatalytic transformations. In total, the chromium(III) complex was used in five photoreactions, including one example of energy transfer and two examples of electron transfer in acetonitrile and in water, respectively. The utilization of photocatalysts in water is often problematic, due to insufficient solubility and/or short ES lifetimes.^[103,248,249] However, the easily accessible $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ is highly soluble in water and exhibits an ES lifetime of $\tau_0 \approx 2.5$ ms. Additionally, for one of the transformations in water, ammonium persulfate $[\text{NH}_4]_2[\text{S}_2\text{O}_8]$ was identified as a cheap sacrificial oxidant for $[\text{Cr}(\text{tpe})_2]^{2+}$. This addresses the challenge of slow catalyst reoxidation for this solvent. The reactions in acetonitrile were in part conducted on a gram-scale, using a simple round-bottom flask as the reaction vessel. Due to the low molar extinction coefficient of $[\text{Cr}(\text{tpe})_2]^{3+}$ ($\epsilon(431 \text{ nm}) = 35 \text{ M}^{-1}\text{cm}^{-1}$),^[69] light is absorbed over the entire length of the reactor. A reaction setup with a long optical path thus becomes viable and local temperature spikes or potentially detrimental high concentrations of organic radicals are avoided. The need for specialized equipment like flow-reactors is thus circumvented.

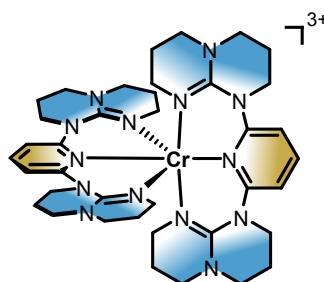


Scheme 3.2: Molecular structure of $[\text{Cr}(\text{tpe})_2]^{3+}$. Modification of the complex with one or two trifluoromethyl groups gives $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ or *cis/trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$, respectively.

In the first four studies the *Molecular Ruby* $[\text{Cr}(\text{tpe})_2]^{3+}$ was identified as a highly promising photocatalyst. It displays strong oxidative power, an extremely long ES lifetime, outstanding photostability and accessibility. Furthermore, it is usable in multiple solvents, including water, and its low molar extinction coefficient allows for easy irradiation setups on laboratory scales, as the complex benefits from longer optical pathlengths. Despite its many benefits, some limitations of $[\text{Cr}(\text{tpe})_2]^{3+}$

were identified as well, most prominently its slow reoxidation, which necessitates the use of a redox shuttle or a sacrificial oxidant. $[\text{Cr}(\text{tpe})_2]^{3+}$ served as the parent complex in a newly developed series of compounds in which the reduction potential is decoupled from the excited-state energy and was therefore tuned independently.

Most molecular rubies, like $[\text{Cr}(\text{ddpd})_2]^{3+}$, $[\text{Cr}(\text{bpmp})_2]^{3+}$ and $[\text{Cr}(\text{tpe})_2]^{3+}$ contain polypyridyl ligands that impose a strong ligand field via their σ -donor and π -acceptor character as well as favorable symmetry (section 1.2.2).^[52,68,69] However, utilization of very similar ligands greatly limits tunability of the emission energy in spin-flip emitters (section 1.2.2). In the final study of this work *Thermally Activated and Non-activated Excited State Decay of $[\text{Cr}(\text{dgpy})_2]^{3+}$* (section 3.6), four of the six pyridines were exchanged for cyclic guanidines, in the complex $[\text{Cr}(\text{dgpy})_2]^{3+}$ (Scheme 3.3). Investigation of its emission properties uncovered a bathochromic shift of around 930 cm^{-1} compared to $[\text{Cr}(\text{ddpd})_2]^{3+}$,^[52] which indicates a more pronounced *nephelauxetic effect* caused by the σ - and π -donating guanidines. This is consistent with shifts seen in complexes containing other types of strongly donating ligands, like carbanions (e.g. $\text{Cr}(\text{ppy})_3$).^[72] In contrast to many of the *Molecular Rubies* with polypyridine ligands, a low quantum yield ($\Phi_{\text{PL},0} = 0.5\%$) and short excited-state lifetime ($\tau_0 = 63\text{ }\mu\text{s}$) were observed for $[\text{Cr}(\text{dgpy})_2]^{3+}$. Through theoretical and experimental methods, two main pathways were identified that facilitate non-radiative decay and decrease $\Phi_{\text{P},0}$ and τ_0 . Comparison of the complex's emission spectrum and the overtone absorption spectra ($\nu_{\text{C-H}}^4/\nu_{\text{C-H}}^5$) of the guanidine ligand precursor 1,5,7-triazabicyclo[4.4.0]dec-5-ene revealed significant spectral overlap, which permits intramolecular energy transfer (multiphonon-relaxation; section 1.3.3). This process is enhanced by the increased number of C–H oscillators in the saturated ligand moiety compared to the more common pyridine units. Temperature-dependent emission measurements of $[\text{Cr}(\text{dgpy})_2]^{3+}$ revealed an energy-barrier (2850 cm^{-1}), separate from the effectively activationless multiphonon-relaxation. This barrier was attributed to bISC from the ^2ES to the strongly distorted $^4\text{T}_2$, which had been similarly described for polypyridyl chromium(III) complexes.^[70] In $[\text{Cr}(\text{dgpy})_2]^{3+}$ this barrier is ca. 15 – 35% lower, which was attributed to more pronounced distortion of the more flexible, partially saturated ligand in the $^4\text{T}_2$ state.

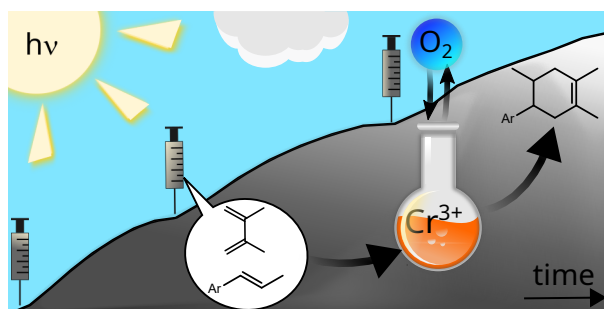


Scheme 3.3: a) Molecular structure of $[\text{Cr}(\text{dgpy})_2]^{3+}$.

3.2 Molecular Rubies in Photoredox Catalysis

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Front Chem. **2022**, *10*, 887439. DOI: 10.3389/fchem.2022.887439.



The *Molecular Ruby* $[\text{Cr}(\text{tpe})_2]^{3+}$ displays an extremely long $^2\text{E}/^2\text{T}_1$ excited-state lifetime ($\tau_0 = 3.5$ ms) and a high excited-state reduction potential ($E_{\text{red}}^* = 1.25$ V vs. SCE). The chromium(III) complex was successfully utilized as a highly stable photoredox catalyst in a visible light-induced radical cation [4+2] cycloaddition. Spectroscopic investigations revealed new insights into the mechanism of the catalyzed reaction, particularly regarding the role of oxygen.

Author Contributions

Steven Sittel conducted the *Stern-Volmer* quenching, the catalytic experiments and the UV/vis/NIR absorption spectroscopy. [REDACTED] performed and analyzed all laser flash photolysis and many luminescence experiments. [REDACTED] conceptualized and supervised the study and wrote the manuscript. All authors discussed the scientific results and wrote parts of the manuscript.

Supporting Information

for this article can be found on pp. 133.

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Molecular Rubies in Photoredox Catalysis

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The molecular ruby $[\text{Cr}(\text{tpe})_2]^{3+}$ and the tris(bipyridine) chromium(III) complex $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ as well as the tris(bipyrazine)ruthenium(II) complex $[\text{Ru}(\text{bpz})_3]^{2+}$ were employed in the visible light-induced radical cation [4+2] cycloaddition (tpe = 1,1,1-tris(pyrid-2-yl)ethane, dmcbpy = 4,4'-dimethoxycarbonyl-2,2'-bipyridine, bpz = 2,2'-bipyrazine), while $[\text{Cr}(\text{ddpd})_2]^{3+}$ serves as a control system (ddpd = *N,N'*-dimethyl-*N,N'*-dipyridin-2-ylpyridine-2,6-diamine). Along with an updated mechanistic proposal for the Cr^{III} driven catalytic cycle based on redox chemistry, Stern-Volmer analyses, UV/Vis/NIR spectroscopic and nanosecond laser flash photolysis studies, we demonstrate that the very weakly absorbing photocatalyst $[\text{Cr}(\text{tpe})_2]^{3+}$ outcompetes $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ and even $[\text{Ru}(\text{bpz})_3]^{2+}$ in particular at low catalyst loadings, which appears contradictory at first sight. The high photostability, the reversible redoxchemistry and the very long excited state lifetime account for the exceptional performance and even reusability of $[\text{Cr}(\text{tpe})_2]^{3+}$ in this photoredox catalytic system.

Keywords: chromium, radical cation, Diels-Alder reaction, [4+2] cycloaddition, photoredox catalysis, singlet oxygen

INTRODUCTION

Complexes with long-lived luminescent metal-to-ligand charge transfer (MLCT) excited states, namely Ru^{II} , Ir^{III} , Os^{II} , or Re^{I} complexes with polypyridine ligands, are the workhorses of many photoredox catalytic cycles, luminescent devices, sensing applications and solar energy conversion processes (Twilton, et al., 2017; Yoon, et al., 2010; Magnuson, et al., 2009; Costa, et al., 2012; Baldo, et al., 2020 Hagfeld, et al., 2010; Heinemann et al., 2017; Mari, et al., 2015; Li, et al., 2018; Yam, et al., 2020). A huge interest exists in replacing the precious metal ions by cheaper, Earth-abundant metal ions such as chromium, iron and copper and considerable progress has been achieved in the last years (Wenger, 2018; Hockin, et al., 2019; Förster and Heinze, 2020; Büldt and Wenger, 2017; Otto, et al., 2018a; Scattergood, 2020; Lindh, et al., 2020; Wenger, 2021; Hossain, et al., 2019). Reductively initiated processes were successfully employed in several instances, e.g. using Mn^{I} , Fe^{II} and Cu^{I} photocatalysts (Herr, et al., 2021; Leis, et al., 2022; Hossain, et al., 2019). Oxidative processes photoinduced by first row transition metal complexes are comparably scarce and have been reported with iron(III) and cobalt(III) (Aydogan, et al., 2021; Pal, et al., 2018) and in particular with chromium(III) photocatalysts (Stevenson, et al., 2015; Higgins, et al., 2016). Oxidatively induced photocatalytic processes, e.g. radical cation [4+2] cycloadditions, have been described by Yoon and coworkers using photooxidizing ruthenium(II) photocatalysts (Lin, et al., 2011; Farney, et al., 2019) and by Shores and others using highly photooxidizing Cr^{III} complexes with 2,2'-bipyridine or 9,10-phenanthroline ligands as photocatalysts PC^{3+} (Scheme 1A) (Stevenson, et al., 2015; Higgins, et al., 2016; Stevenson, et al., 2017; Higgins, et al., 2018). For example, the highly oxidizing complex $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ (1 mol%, CH_3NO_2 , 300–419 nm light, 24–48 h, dmcbpy = 4,4'-

Specialty section:

This article was submitted to
Physical Chemistry and Chemical
Physics,
a section of the journal
Frontiers in Chemistry

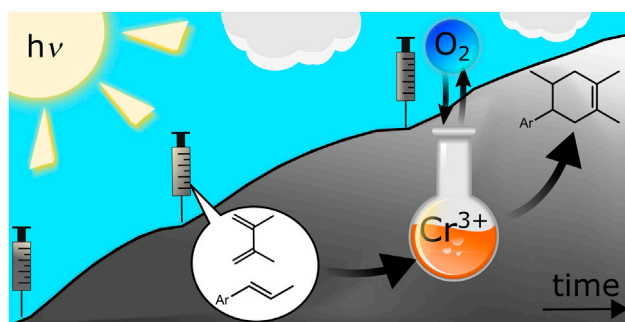
Received: 01 March 2022

Accepted: 17 March 2022

Published: 07 April 2022

Citation:

Sittel 
(2022) Molecular Rubies in
Photoredox Catalysis.
Front. Chem. 10:887439.
doi: 10.3389/fchem.2022.887439



GRAPHICAL ABSTRACT | The molecular ruby $[\text{Cr}(\text{tpe})_2]^{3+}$ catalyzes the visible light-induced radical cation [4+2] cycloaddition with unprecedented photostability and recyclability. Detailed mechanistic studies reveal that reductive quenching of $[\text{Cr}(\text{tpe})_2]^{3+}$ is fast while the first C-C formation is the slowest step and triplet oxygen is required to rapidly regenerate $[\text{Cr}(\text{tpe})_2]^{3+}$ and prevent detrimental back-electron transfer.

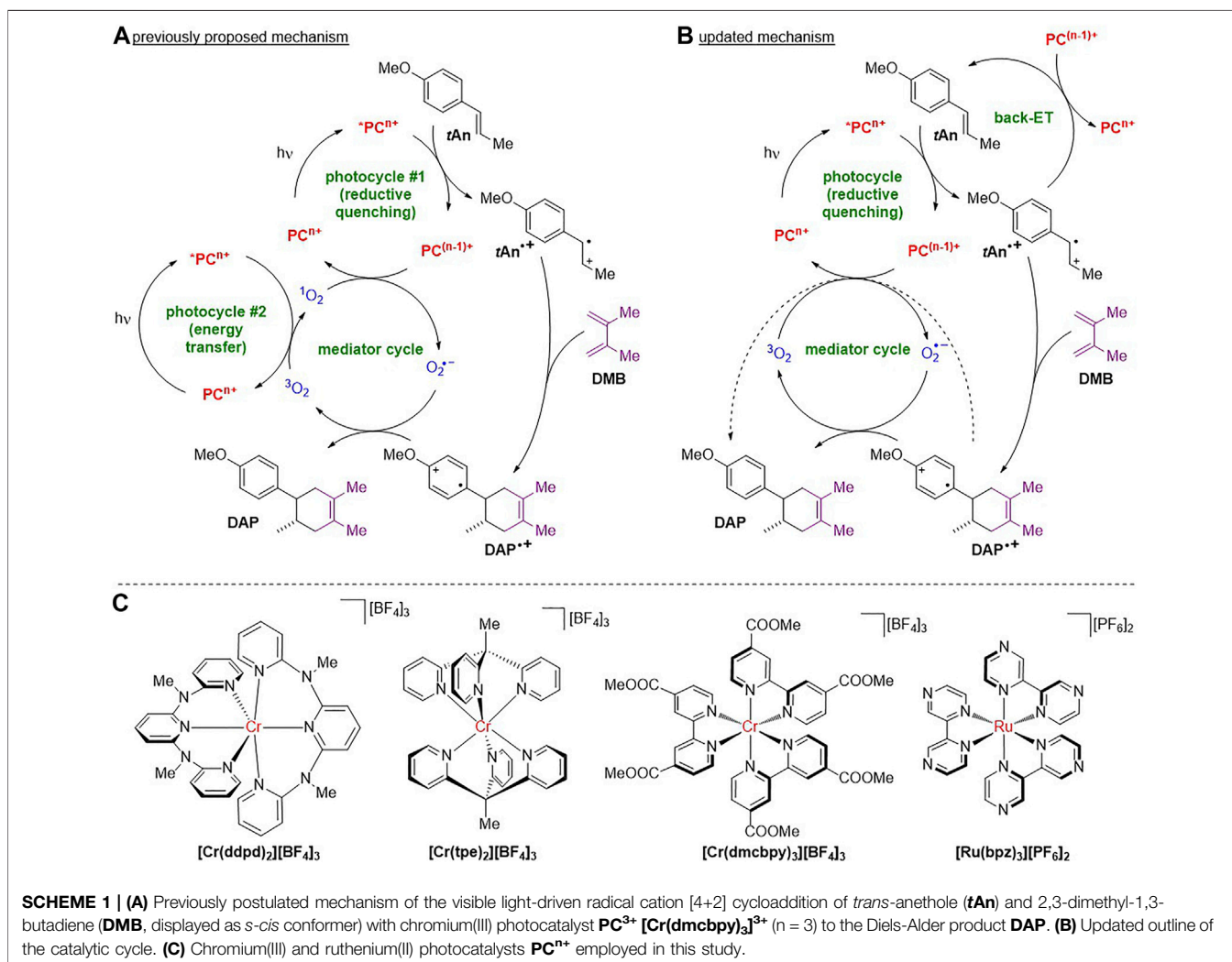
dimethoxycarbonyl-2,2'-bipyridine) catalyzes the Diels-Alder reaction of various dienes such as 2,3-dimethyl-1,3-butadiene (DMB) with styrenes such as *trans*-anethole (*tAn*) to the Diels-Alder product DAP (Scheme 1A) (Stevenson, et al., 2015). $\text{TiO}_2/\text{LiClO}_4$ also catalyzed this reaction using UV light (365 nm, Nakayama, et al., 2019). Radical cations $t\text{An}^{\bullet+}$ and $\text{DAP}^{\bullet+}$ are the proposed key intermediates in this radical cation [4+2] cycloaddition, but they were never observed in this context (Scheme 1A). The $t\text{An}$ radical cation $t\text{An}^{\bullet+}$ had been independently generated by UV light excitation through a biphotonic photoionization. The radical cation $t\text{An}^{\bullet+}$ was observed by nanosecond laser flash photolysis (LFP, 308 nm or 266 nm excitation) by its excited state absorptions at 320–390 nm and 520–660 nm (Murphy, et al., 2000; Johnston and Schepp, 1993). The radical cation $t\text{An}^{\bullet+}$ stabilized with $[\text{FeCl}_4]^-$ had even been isolated and an absorption band at 580 nm had been reported (Horibe, et al., 2019). Other methoxy-substituted aromatic radical cations prepared by oxidation with MoCl_5 were successfully characterized by EPR spectroscopy (Leppin, et al., 2015; Schubert, et al., 2016). In the Cr^{III} or Ru^{II} photocatalyzed reactions, the radical cations $t\text{An}^{\bullet+}/\text{DAP}^{\bullet+}$ were not yet identified spectroscopically (Stevenson, et al., 2015; Higgins, et al., 2016; Lin, et al., 2011; Farney, et al., 2019).

For Cr^{III} photocatalysts and organic thioxanthylum and benzothiadiazole photocatalysts (Tanaka, et al., 2020; Huber, et al., 2020), oxygen is required for the regeneration of the reduced photocatalyst $\text{PC}^{(n-1)+}$ (Scheme 1A, mediator cycle). Interestingly, Rappé and Shores suggested that singlet oxygen $^1\text{O}_2$ is required to regenerate the chromium(III)-based PC^{3+} forming superoxide $\text{O}_2^{\bullet-}$, which in turn reduces the cyclohexenyl radical $\text{DAP}^{\bullet+}$ (Scheme 1A) (Higgins, et al., 2016). According to the suggested mechanism, $^1\text{O}_2$ forms in a separate energy transfer photocycle (Scheme 1A, photocycle #2) so that two photons would be required for a single turnover. The requirement for the $\text{O}_2^{\bullet-}/^1\text{O}_2$ couple instead of the conventional redoxcouple $\text{O}_2^{\bullet-}/^3\text{O}_2$ was invoked by the negative redox potential of the latter ($E_{1/2} = -1.29$ V vs. ferrocene in CH_3CN) (Singh and Evans, 2006), which would be insufficient for photocatalyst regeneration (Higgins, et al., 2016). In contrast to Cr^{III} photocatalysts requiring O_2 , ruthenium(II)-based

photocatalysts seem to operate via a chain mechanism without the need for invoking $^1\text{O}_2$ (Lin, et al., 2011) and even in the absence of oxygen (Farney, et al., 2019).

Under photolysis conditions, Cr^{III} and Ru^{II} complexes of bipyridine-type ligands are photolabile (Maestri, et al., 1976; Jamieson, et al., 1979; Constable, et al., 2014; Soupart, et al., 2020; Limburg, et al., 2016). Ligand loss is observed under irradiation, forming e.g., $[(\mu\text{-OH})_2(\text{Cr}(\text{bpy})_2)_2]^{4+}$ (bpy = 2,2'-bipyridine) (Otto, et al., 2015; Otto, et al., 2018). Reduced complexes such as $[\text{Cr}(\text{Ph}_2\text{phen})_3]^{2+}$ furthermore were reported to decompose in the presence of O_2 to $\text{Cr}=\text{O}$ species (Ph_2phen = 4,7-diphenyl-1,10-phenanthroline) (Higgins, et al., 2016). In contrast, Cr^{III} complexes with tridentate ligands, in particular those inducing a very strong ligand field by large bite angles, are highly photostable, often strongly luminescent with very high excited state lifetimes, and are hence called “molecular rubies” (Otto, et al., 2015; Otto, et al., 2018b; Jiménez, et al., 2019; Treiling, et al., 2019; Reichenauer, et al., 2021). The long-lived excited states of the molecular rubies are metal-centered spin-flip states (doublet states, $^2\text{E}/^2\text{T}_1$) in contrast to the typically exploited triplet MLCT excited states of Ru^{II} or Ir^{III} complexes (Kitzmann, et al., 2022). Important prerequisites for the high lifetime and the photostability of molecular rubies are the large ligand field splitting resulting in dissociative metal-centered quartet states ($^4\text{T}_2$) being shifted to high energy and fast intersystem crossing (ISC) processes that rapidly depopulate the $^4\text{T}_2$ states to arrive at the long-lived $^2\text{E}/^2\text{T}_1$ states with high efficiency and without detrimental back-ISC processes (Otto, et al., 2018a; Kitzmann, et al., 2022). Potential disadvantages of the molecular rubies for photoredox applications are their comparably small extinction coefficients in the visible spectral region due to the Laporte-forbidden nature of the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ excitation and the comparably low excited state energies (1.6–1.75 eV) (Otto, et al., 2018b; Kitzmann, et al., 2022).

In the present study we explore the Cr^{III} photocatalysts $[\text{Cr}(\text{ddpd})_2]^{3+}$ and $[\text{Cr}(\text{tpe})_2]^{3+}$ (Scheme 1B, ddpd = *N,N'*-dimethyl-*N,N'*-dipyridin-2-ylpyridine-2,6-diamine, tpe = 1,1,1-tris(pyrid-2-yl)ethane; Otto, et al., 2015; Treiling, et al., 2019) with the strong field ligands ddpd and tpe, respectively, as potential photostable photocatalysts PC^{3+} for the visible light-



driven radical cation [4+2] cycloaddition of *tAn* and *DMB* (460 nm). We compare the performance with the reported optimized photocatalysts [$\text{Cr}(\text{dmcbpy})_3$] $^{3+}$ and [$\text{Ru}(\text{bpz})_3$] $^{2+}$ ($\text{bpz} = 2,2'$ -bipyrazine; Crutchley, et al., 1980; Schultz, et al., 2015) and we investigate the role of oxygen for the regeneration of the Cr^{III} photocatalysts PC^{3+} using nanosecond LFP studies to arrive at an updated mechanistic picture of the Cr^{III} photocatalyzed radical cation Diels-Alder cycloaddition (Scheme 1B). Finally, we discuss the relevance and importance of extinction coefficients and photostability of the photocatalysts PC^{3+} and detrimental back-electron transfer processes laying the foundation for exploiting stable molecular rubies in forthcoming efficient photoredox reactions.

EXPERIMENTAL DETAILS

General. The photocatalysts [$\text{Cr}(\text{ddd})_2$] $[\text{BF}_4]_3$ (Otto, et al., 2015; Wang, et al., 2022), [$\text{Cr}(\text{tpe})_2$] $[\text{BF}_4]_3$ (Treiling, et al., 2019) and [$\text{Cr}(\text{dmcbpy})_3$] $[\text{BF}_4]_3$ (McDaniel, et al., 2010) were prepared according to literature procedures. 2,3-Dimethyl-1,3-butadiene

(*DMB*, 98%, Sigma-Aldrich with 100 ppm 3,5-di-*tert*-butyl-4-hydroxytoluene as stabilizer) was distilled prior to use. [$\text{Ru}(\text{bpz})_3$] $[\text{PF}_6]_2$ ($\geq 95\%$, Sigma-Aldrich), *trans*-anethole (*tAn*, 99%, Sigma), naphthalene (99%, Acros), CH_3CN for photoreactions (VWR Chemicals, HPLC grade), CH_3CN for spectroscopy (Supelco, hypergrade) and CD_3CN (98.5% D, Deutero) were commercially available and used as received.

UV/Vis absorption spectra were recorded on a Jasco V770 spectrometer using conventional 1.0 cm quartz cells for studies under air and 1.0 cm quartz cells with a Schott valve for studies under inert atmosphere. Emission spectra and luminescence decay curves were recorded with a FLS1000 spectrometer from Edinburgh Instruments equipped with the cooled red and NIR sensitive photomultiplier detectors PMT-980 and N-G09 PMT-1700, together covering the spectral range between 200 and 1700 nm. A xenon arc lamp Xe2 (450 W) was used for excitation in steady-state measurements. Time-resolved luminescence experiments on microsecond to millisecond timescale were performed in the multi-channel scaling mode employing the μs -xenon-flashlamp $\mu\text{F}2$ (pulse width ca. 2 μs) as excitation source. Measurements on the nanosecond timescale

were conducted in the TCSPC mode using a SUPERK FIANUM laser FIU-6 from NKT Photonics as excitation source. Absolute luminescence quantum yields Φ were determined using an integrating sphere from Edinburgh Instruments. Relative uncertainty of Φ is estimated to be $\pm 10\%$. Stern-Volmer studies with oxygen were performed in a long-neck quartz cuvette sealed with a septum. After purging the sample solutions for about 30 min with Argon using a cannula, the emission decay was measured and the resulting lifetime was used as starting point for the Stern-Volmer analysis. To increase the oxygen partial pressures p_{O_2} stepwise, air was added successively to the cuvette via a syringe until air-saturation is reached. After each addition, the solution was shaken for about 2 min. The corresponding p_{O_2} has been determined employing the fiber-optic oxygen meter FireSting-O2 equipped with the solvent resistant probe tip OXSOLV-PT from pyroscience. The fiber of the probe is covered with a 150 mm cannula allowing it to pierce the septum without damaging the sensor. The sensor has been calibrated with deaerated and air-saturated solution. To assure that the p_{O_2} is identical during the oxygen addition and the corresponding emission decay measurement, the emission decay was always recorded after the determination of p_{O_2} as small amounts of air are brought into the cuvette with the cannula and are dissolved in the solution. Transient absorption spectroscopy experiments were conducted using a LP980KS setup from Edinburgh Instruments equipped with a Nano LG 300-10 Nd:YAG laser from Litron (ca. 5 ns pulse width). The frequency-tripled output with a wavelength of 355 nm was employed for the excitation (30 mJ pulse energy). To ensure homogeneous excitation of the whole observation volume (10 mm $\times$ 10 mm quartz cuvette) the beam was brought to a diameter of 1.2 cm using a beam expander. A pulsed Xe-lamp from Hamamatsu (150 W, XBO) was used as probe light source. The transient absorption spectra were recorded with an integration time of 100 ns using an iCCD camera from Andor. For the detection of the decay traces at single wavelengths a photomultiplier tube was employed. All transient absorption experiments were performed at 293 K. 1H NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 400.13 MHz. All resonances are reported in ppm versus the solvent signal as an internal standard ($\delta = 1.94$, CD_3CN) (Fulmer, et al., 2010).

General Procedure for the light-driven radical cation [4+2] cycloaddition. A solution of *trans*-anethole **tAn** (100 mM), 2,3-dimethyl-1,3-butadiene **DMB** (500 mM) and the photocatalyst (0.2–5 mM) in acetonitrile with a total volume of 2 ml was prepared in a 4 ml vial. The vial was capped with a septum, pierced with a needle to allow air contact, equipped with a stir bar and placed in an Aldrich® Micro Photochemical Reactor (16 vial places) equipped with blue LEDs (for the LED emission spectrum in combination with the UV/Vis absorption spectra of the photocatalysts see **Supplementary Figures S1–S4**). The vials were irradiated at 294 K. The progress of the reaction was monitored by 1H NMR spectroscopy. To this end an aliquot of the reaction mixture was taken and added to a solution of an internal standard (naphthalene) in CD_3CN . The yield was determined via

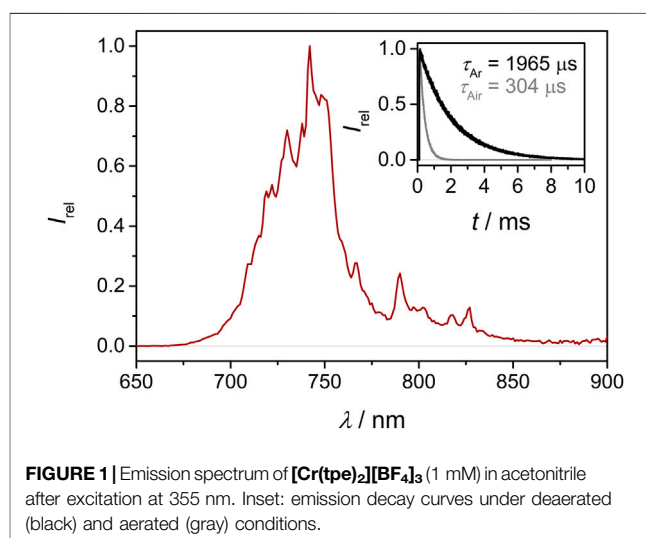


FIGURE 1 | Emission spectrum of $[Cr(tpe)_2][BF_4]_3$ (1 mM) in acetonitrile after excitation at 355 nm. Inset: emission decay curves under deaerated (black) and aerated (gray) conditions.

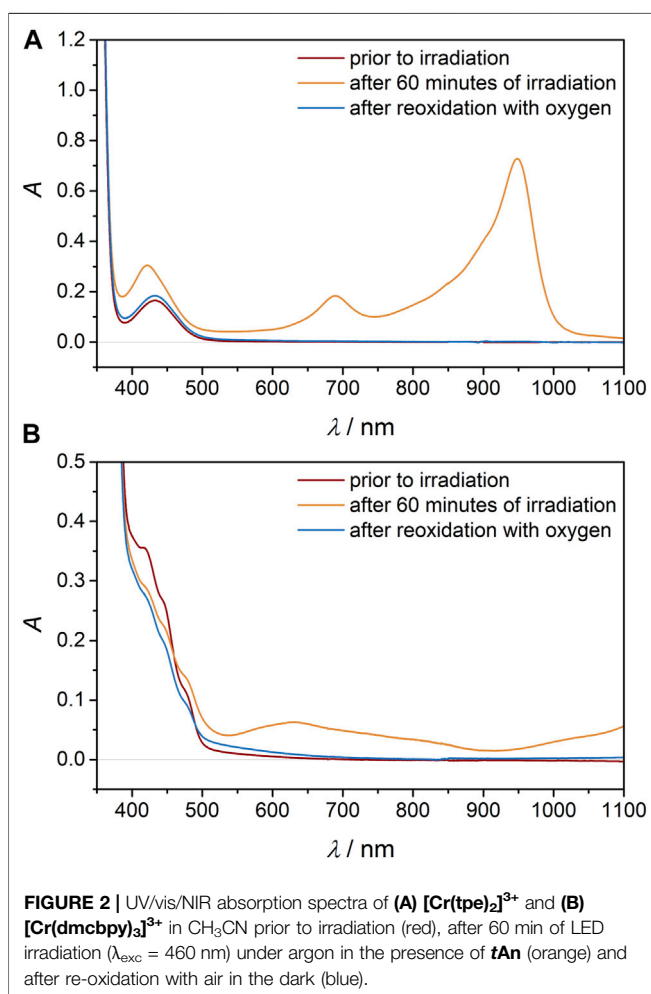
integration of the product and starting material resonances versus the internal standard.

Isolation of the product DAP. In order to isolate the **DAP** product, water (2 ml) was added to the reaction mixture and the solution was extracted with diethylether (2 $\times$ 2 ml). The organic phase was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by filtration through a silica-filled glass pipette using cyclohexane. The solvent was removed under reduced pressure to give the product as a colorless oil.

RESULTS AND DISCUSSION

The photocatalysts $[Cr(ddpd)_2]^{3+}$, $[Cr(tpe)_2]^{3+}$, $[Cr(dmcbpy)_3]^{3+}$ and $[Ru(bpz)_3]^{2+}$ (PC^{n+}) employed in this study are depicted in **Scheme 1C** (Otto, et al., 2015; Treiling, et al., 2019; Crutchley and Lever, 1980). All complexes absorb blue light with absorption maxima at 436, 431, 448 and 440 nm in CH_3CN , albeit with very different extinction coefficients of $\epsilon_{max} = 3770$, 30, 714 and $14,100 M^{-1} cm^{-1}$, respectively. Excitation with blue light leads to phosphorescence emission maxima at 776, 748, 733 and 607 nm, respectively. Under inert atmosphere, the corresponding excited state lifetimes amount to 1136, 1965, 25 and 0.762 μs (**Figure 1**; **Supplementary Figures S5–S7**) and the photoluminescence quantum yields to 12.1, 4.0, 0.14 and 6.5%, respectively.

Thermodynamically, all chromium(III) complexes $[Cr(ddpd)_2]^{3+}$, $[Cr(tpe)_2]^{3+}$ and $[Cr(dmcbpy)_3]^{3+}$ as well as $[Ru(bpz)_3]^{2+}$ can sensitize triplet oxygen (3O_2) to give singlet oxygen (1O_2) due to their excited state energies (1.6–2.16 eV; Otto, et al., 2015; Treiling, et al., 2019; Stevenson, et al., 2015; Vleck, et al., 1995) exceeding the energy of 1O_2 (0.97 eV). In aerated CH_3CN solution, the luminescence lifetimes decrease to 48, 304, 19 and 0.561 μs for $[Cr(ddpd)_2]^{3+}$, $[Cr(tpe)_2]^{3+}$, $[Cr(dmcbpy)_3]^{3+}$ and $[Ru(bpz)_3]^{2+}$, respectively (**Figure 1**; **Supplementary Figures S5–S7**). $[Cr(ddpd)_2]^{3+}$ had been employed for 1O_2 generation for the α -cyanation of aliphatic amines and in biological environments (Otto, et al., 2015; Otto,



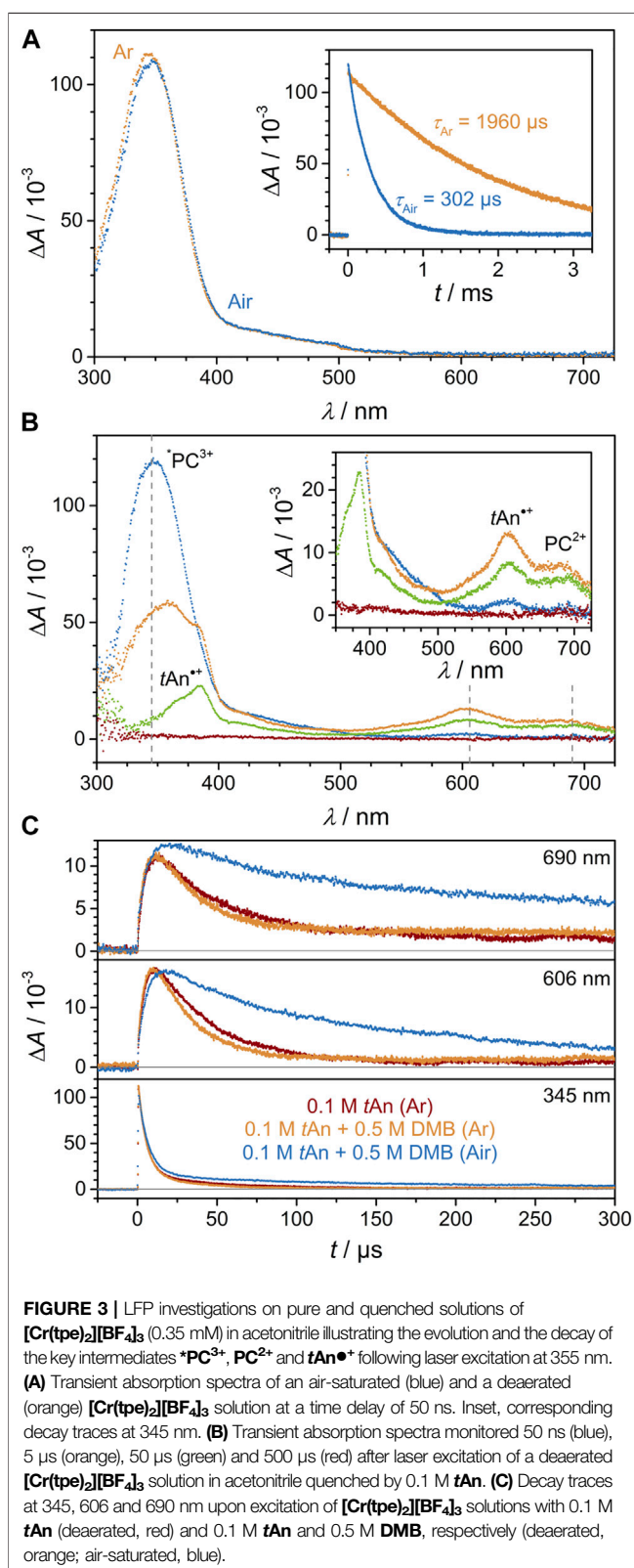
et al., 2017; Basu, et al., 2019). The spin-flip phosphorescence of $[\text{Cr}(\text{tpe})_2]^{3+}$ is likewise quenched by O_2 (Treiling, et al., 2019). Stern-Volmer studies of $[\text{Cr}(\text{ddpd})_2]^{3+}$, $[\text{Cr}(\text{tpe})_2]^{3+}$, $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ and $[\text{Ru}(\text{bpz})_3]^{2+}$ with O_2 in CH_3CN yield $K_{\text{SV}} = 130 \times 10^{-3}$, 34×10^{-3} , 1.8×10^{-3} and $2.3 \times 10^{-3} \text{ hPa}^{-1}$ and $k_q = 115$, 17.3 , 73.3 and $3010 \text{ hPa}^{-1} \text{ s}^{-1}$, respectively (Supplementary Figures S8–S11). The concentration of $^3\text{O}_2$ in air-saturated CH_3CN solution has been reported as 1.9 mM (Montalti, et al., 2006). The formation of $^1\text{O}_2$ was confirmed by its characteristic emission band at 1275 nm (Supplementary Figure S12). Its experimental formation and decay was excellently reproduced by a kinetic model shown in the Supplementary Material (Supplementary Figure S12). As $^1\text{O}_2$ is formed and sufficiently long-lived, it might play a role in the catalytic cycle as proposed by Rappé and Shores (Scheme 1A), although its concentration would be quite low (Higgins, et al., 2016). Even in the presence of oxygen, the excited state lifetimes of $[\text{Cr}(\text{ddpd})_2]^{3+}$, $[\text{Cr}(\text{tpe})_2]^{3+}$, $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ and $[\text{Ru}(\text{bpz})_3]^{2+}$ remain high (Figure 1; Supplementary Figures S5–S7) enabling efficient quenching with other substrates in parallel processes such as photoinduced redox processes.

Indeed, the chromium(III) complexes $[\text{Cr}(\text{ddpd})_2]^{3+}$, $[\text{Cr}(\text{tpe})_2]^{3+}$ and $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ can be reduced to the

corresponding dications at -1.11 , -0.88 and -0.26 V vs. ferrocene, respectively (Otto, et al., 2015; Treiling, et al., 2019; McDaniel, et al., 2010). The ruthenium(II) complex $[\text{Ru}(\text{bpz})_3]^{2+}$ can be reduced at -1.11 V whereby the additional electron occupies a ligand-centered π^* orbital (Campagna, et al., 2007; Balzani, et al., 1978). Reduced chromium(III) complexes are either genuine chromium(II) complexes for electron-rich ddpd ligands (Becker, et al., 2020) or ligand centered radicals for electron-deficient tpe, bpmp or bpy-type ligands (bpmp = 2,6-bis(2-pyridylmethyl)pyridine; Treiling, et al., 2019; Reichenauer, et al., 2020; Scarborough, et al., 2011). While metal-centered reduction to Cr^{II} can labilize ligands, ligand-centered radicals appear comparably stable similar to ligand-reduced ruthenium(II) complexes such as $[\text{Ru}(\text{bpz})_3]^+$ (Campagna, et al., 2007; Balzani, et al., 1978; Lin, et al., 2011).

$[\text{Cr}(\text{bpy})_3]^{3+}$, $[\text{Cr}(\text{tpy})_2]^{3+}$ and related derivatives photooxidize DNA via initial guanine base oxidation (tpy = 2,2', 6',2''-terpyridine) while $[\text{Cr}(\text{ddpd})_2]^{3+}$ does not oxidize guanine bases due to its low excited state redox potential $E_{1/2}([\text{Cr}(\text{ddpd})_2]^{3+}/[\text{Cr}(\text{ddpd})_2]^{2+}) = 0.49 \text{ V}$ (Baptista, et al., 2021; Watson, et al., 1999; Vaidyanathan, et al., 2004; Otto, et al., 2015). We will exploit the selectivity of $[\text{Cr}(\text{ddpd})_2]^{3+}$ for energy transfer over electron transfer later in mechanistic studies (Otto, et al., 2015). On the other hand, the excited state potentials of $[\text{Cr}(\text{tpe})_2]^{3+}$ and $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ of 0.87 and 1.44 V approach or even exceed that of $[\text{Ru}(\text{bpz})_3]^{2+}$ with 0.99 V . Hence, $[\text{Cr}(\text{tpe})_2]^{3+}$, $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ and $[\text{Ru}(\text{bpz})_3]^{2+}$ are strong photooxidants capable of oxidizing $t\text{An}$ to $t\text{An}^{\bullet+}$ ($E_{1/2} = 0.78 \text{ V}$; Higgins, et al., 2016), while $[\text{Cr}(\text{ddpd})_2]^{3+}$ is thermodynamically incompetent for this photoredox reaction. Consequently, $t\text{An}$ reductively quenches the emission of $[\text{Cr}(\text{tpe})_2]^{3+}$, $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ and $[\text{Ru}(\text{bpz})_3]^{2+}$ but not that of $[\text{Cr}(\text{ddpd})_2]^{3+}$. Stern-Volmer and quenching rate constants of $[\text{Cr}(\text{tpe})_2]^{3+}$, $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ and $[\text{Ru}(\text{bpz})_3]^{2+}$ with $t\text{An}$ were determined as $K_{\text{SV}} = 4500$, $75,000$ and 740 M^{-1} and $k_q = 2.3 \times 10^6$, 3000×10^6 and $970 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Supplementary Figures S13–S15). The different rates reflect the different driving forces for the electron transfer from $t\text{An}$ to the excited photocatalyst $^*\text{PC}^{\text{n}+}$ (Marcus, 1993). $[\text{Cr}(\text{tpe})_2]^{2+}$ forms by reduction of $[\text{Cr}(\text{tpe})_2]^{3+}$ with $t\text{An}$ under light irradiation in the photo reactor as confirmed by UV/Vis spectroscopy and comparison with an authentic spectrum (Figure 2A) (Treiling, et al., 2019). Similarly $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ is reduced to $[\text{Cr}(\text{dmcbpy})_3]^{2+}$ (Figure 2B) by reference to spectra of $[\text{CrL}_3]^{2+}$ complexes with bpy-type ligands (Scarborough, et al., 2011; Higgins, et al., 2016).

Interestingly, addition of O_2 to the $[\text{Cr}(\text{tpe})_2]^{2+}$ solution in the dark restores the UV/vis/NIR absorption spectrum of $[\text{Cr}(\text{tpe})_2]^{3+}$ quantitatively demonstrating that $^3\text{O}_2$ can oxidize $[\text{Cr}(\text{tpe})_2]^{2+}$ to $[\text{Cr}(\text{tpe})_2]^{3+}$ (Figure 2A). Similarly, the UV/vis/NIR absorption spectrum of $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ is recovered by addition of O_2 to the $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ solution in the dark at least to a large extent (Figure 2B). This points to some instability either of $[\text{Cr}(\text{dmcbpy})_3]^{2+}$ or the photoexcited complex $^*[\text{Cr}(\text{dmcbpy})_3]^{3+}$. In fact, $[\text{Cr}(\text{tpe})_2]^{3+}$ is photostable in CH_3CN over several days of irradiation while $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ and $[\text{Ru}(\text{bpz})_3]^{2+}$ partially decompose over time



irrespective of the presence or absence of O_2 (Supplementary Figures S16–S21). The recovery of $[\text{Cr}(\text{tpe})_2]^{3+}$ and $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ by oxygen in the absence of light clearly demonstrates that in

contradiction to the previously proposed mechanism no $^1\text{O}_2$ is needed to reoxidize the catalyst. This surprising finding motivated us to perform LFP investigations on $[\text{Cr}(\text{tpe})_2]^{3+}$ to unravel the mechanism and importantly to elucidate the role of oxygen in this photoredox catalytic cycle.

A solution of $[\text{Cr}(\text{tpe})_2]^{3+}$ in deaerated acetonitrile was excited at 355 nm. Figure 3A illustrates the resulting transient absorption spectrum, which is dominated by a strong positive absorption band centered at 345 nm. According to time-dependent Density Functional Theory calculations, this absorption band covers spin-allowed transitions with doublet ligand-to-metal and intraligand character calculated at 345 and 373 nm (Supplementary Tables S1, S2). Analogous quartet transitions are calculated at 325 nm for the quartet ground state. The assignments fit to the observed experimental band maxima of 329 nm (Supplementary Figure S3) and 345 nm for $^4[\text{Cr}(\text{tpe})_2]^{3+}$ and $^2[\text{Cr}(\text{tpe})_2]^{3+}$, respectively. The decay trace observed at 345 nm for $^2[\text{Cr}(\text{tpe})_2]^{3+}$ shows a first order decay with a time constant of 1960 μs . In air-saturated solution the absorption spectrum remains unaltered, but the lifetime substantially decreases to 302 μs , compared to the deaerated solution. Both lifetimes excellently agree with the emission lifetimes determined via time-resolved emission (Figures 1, 3A).

Excitation of a deaerated solution of $[\text{Cr}(\text{tpe})_2]^{3+}$ in the presence of 0.1 M $t\text{An}$ initially yields the same absorption spectrum as the photocatalyst alone showing that no observable intermediates are formed due to direct excitation of $t\text{An}$ (Figure 3B). The $^*\text{PC}^{3+}$ absorption (345 nm) rapidly decays with a lifetime of ca. 5 μs (Figure 3C), which agrees with the time constant found for the emission quenching (Supplementary Figure S14, $\tau_0 = 1965 \mu\text{s}$, $K_{\text{SV}} = 4520 \text{ M}^{-1}$, 0.1 M $t\text{An}$). Two new bands appear at 385 and 606 nm (Figure 3B) that coincide with the absorption maxima reported for $t\text{An}^{\bullet+}$ by Johnston and Schepp (Johnston and Schepp, 1993) confirming the formation of the radical cation by reductive quenching of $^*\text{PC}^{3+}$. An additional weak band was observed at 690 nm that can be assigned to PC^{2+} by comparison with an authentic spectrum (Figure 2A; Treiling, et al., 2019), albeit $t\text{An}^{\bullet+}$ also significantly contributes to the absorption at this wavelength. Figure 3C (red curves) displays the decay traces at the absorption maxima 345, 606 and 690 nm, corresponding to $^*\text{PC}^{3+}$, $t\text{An}^{\bullet+}$ and PC^{2+} , respectively. Interestingly, the kinetic traces at 606 and 690 nm show a first-order decay with a lifetime of ca. 45 μs (first measurement with a fresh sample) after an initial rise period of approximately 20 μs . This finding is unexpected for two reasons: the radical cation $t\text{An}^{\bullet+}$ is much more long-lived than described by Johnston and Schepp (Johnston and Schepp, 1993) and the unproductive non-geminate back-electron transfer (back-ET) from PC^{2+} to $t\text{An}^{\bullet+}$ should be the dominant deactivation process in the absence of oxygen or DMB, which would yield a second-order decay. This deviation from the expected second-order rate law can be rationalized by a build-up of PC^{2+} during the LFP experiment, which can lead to pseudo-first order kinetics. Although PC^{2+} and $t\text{An}^{\bullet+}$ are initially formed in equal amounts, PC^{2+} can accumulate by removing a fraction of $t\text{An}^{\bullet+}$ via a side reaction. In fact, $t\text{An}^{\bullet+}$ is known to undergo a variety of reactions besides back electron transfer, e.g. addition to

tAn, nucleophilic addition and dimerization (Johnston and Schepp, 1993; Johnston and Schepp 1995). In principle, the addition of ***tAn*^{•+}** to ***tAn*** alone could also explain the observed pseudo first-order rate law. However, only traces of side products were observed upon irradiation with a LED, which reveals that only a small fraction of ***tAn*^{•+}** follows this reaction path. Yet this small amount of removed ***tAn*^{•+}** would suffice to explain the accumulation of **PC²⁺** as the ***tAn*** concentration exceeds the concentration of **[Cr(tpe)₂]³⁺** by approximately two orders of magnitude. The substantial residual signal at 690 nm provides further evidence for this incomplete reoxidation of **PC²⁺** to **PC³⁺**. In order to test whether **PC²⁺** accumulates during the LFP experiments, we performed repeated measurements of the decay trace at 606 nm (eight iterations) with the same sample. In this series of experiments the lifetime successively decreases to a limiting value of 23 μs (Supplementary Figure S22). Moreover, the static UV/vis/NIR spectrum recorded after the LFP measurement clearly shows the characteristic spectral signature of **PC²⁺** (Supplementary Figure S23).

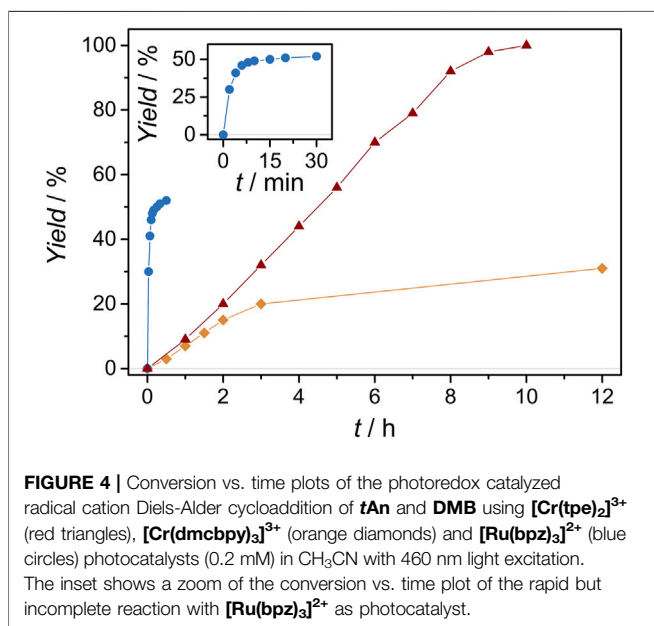
In order to observe the [4+2] cycloaddition step of ***tAn*^{•+}** to **DMB** to give **DAP^{•+}** (Scheme 1B), LFP measurements were conducted with additional 0.5 M **DMB**. However, the obtained transient absorption spectra in the presence and absence of **DMB** are basically identical (Supplementary Figure S24). Consequently, the formation of **DAP^{•+}** cannot be monitored under these conditions. Figure 3C (orange curve) illustrates the corresponding decay traces. Despite of the large excess of **DMB**, the decay rate observed at 606 nm (***tAn*^{•+}**) and 690 nm (**PC²⁺**) is only slightly increased. The very slow kinetics might be explained by the preferred *s-trans* conformation (by 8.3 kJ mol⁻¹; Squillacote and Liang, 2005) of **DMB** and the steric demands of the diene **DMB** and the dienophile ***tAn*^{•+}** posing a barrier for the addition/cyclization step to **DAP^{•+}**. This argument also rationalizes the missing accumulation of **DAP^{•+}**. Hence, the slow [4+2] cycloaddition of **DMB** with ***tAn*^{•+}** is probably the bottleneck of the reaction sequence. In agreement with this interpretation, the first C–C bond formation of the asynchronous radical cation [4+2] cycloaddition has been identified computationally to be the most demanding step (Young, et al., 2017).

Finally, LFP measurements were performed on an air-saturated solution of **[Cr(tpe)₂]³⁺**, 0.1 M ***tAn*** and 0.5 M **DMB**. The shape of the absorption spectra remains unaffected by the presence of oxygen (Supplementary Figure S25). Surprisingly, the presence of oxygen strongly *prolongs* the lifetime of ***tAn*^{•+}** (Figure 3C, blue curves). This contrasts the reported reaction of ***tAn*^{•+}** (prepared by direct photoionization at 308 or 266 nm) with O₂ (Johnston and Schepp, 1993), which *shortens* the lifetime significantly (*k*_{O₂} = 2.3 × 10⁷ M⁻¹s⁻¹). The decay of ***tAn*^{•+}** (prepared by photoinduced electron transfer to **PC³⁺**) in the presence of O₂ can be reasonably well described with second order kinetics (Supplementary Figure S26) in contrast to the first order decay found for the Ar-saturated samples. We surmise that ³O₂ oxidizes **PC²⁺** recovering the catalyst in its initial form, which prevents the accumulation of **PC²⁺** during the LFP measurement and also during the continuous irradiation in the laboratory scale

experiments. Consequently, the non-geminate back-ET from **PC²⁺** to ***tAn*^{•+}** is slowed down by the removal of **PC²⁺** with O₂, which enhances the lifetime of ***tAn*^{•+}**. Interestingly, the lifetime of ***tAn*^{•+}** further increases, when the decay trace at 606 nm is repeatedly recorded with the same sample but stays constant after the sixth iteration (Supplementary Figure S26). This observation might be explained by photochemical self-cleaning, which removes trace impurities in the catalyst solution.

In summary, the collected data support the simplified productive mechanistic picture outlined in Scheme 1B. This scheme includes a non-productive back-ET pathway, but lacks a second photocycle proposed in Scheme 1A involving ¹O₂. Excitation of the Cr^{III} photocatalyst initially yields a quartet excited state (⁴T₂ or ⁴CT states), which evolve to the productive doublet states via ISC. While **[Cr(dmcby)₃]³⁺** suffers from occasional photodissociation, **[Cr(tpe)₂]³⁺** is stable towards photodissociation and photosubstitution. Both complexes can form ¹O₂ from ³O₂ in their long-lived excited doublet states but with comparably low efficiency. In fact, our studies clearly demonstrate that ¹O₂ is unnecessary to regenerate **PC³⁺** from **PC²⁺** as ³O₂ is already competent in spite of its formal reduction potential being very negative (Singh, et al., 2006). Hydrogen-bond forming water has been reported to shift the O₂^{•-}/³O₂ potential to less negative values and protonation of O₂^{•-} to HO₂[•] might even drive the redox reaction due to O₂^{•-} consumption, which might explain the **PCⁿ⁺** regeneration competency of the O₂^{•-}/³O₂ pair in non-dried CH₃CN (Singh, et al., 2006). Consequently, ¹O₂ as proposed in Scheme 1A is not mandatory for the productive catalytic cycle (Scheme 1B). Reductive quenching of the long-lived excited doublet states of **PC³⁺** by the styrene ***tAn*** is highly efficient forming the reduced photocatalyst **PC²⁺** and the radical cation ***tAn*^{•+}**. In the absence of O₂, **PC²⁺** can recombine with ***tAn*^{•+}** in a non-productive back-ET due to the microsecond lifetime of ***tAn*^{•+}** in the absence of substrates. Even in the presence of excess **DMB**, the lifetime of ***tAn*^{•+}** exceeds microseconds suggesting that the addition of ***tAn*^{•+}** to **DMB** is the rate-determining step for the catalytic cycle. Shores and others also noticed that the cycloaddition step is slow with terminally substituted dienes but is positively influenced by the presence of O₂ (Higgins, et al., 2016). In the presence of O₂, **PC²⁺** is re-oxidized sufficiently fast by ³O₂ to give **PC³⁺** and O₂^{•-}. The removal of **PC²⁺** prolongs the lifetime of ***tAn*^{•+}** increasing the probability for the radical addition step. Both **PC²⁺** and O₂^{•-} are thermodynamically capable to reduce the product cyclohexene radical cation **DAP^{•+}** to the final product. The radical cation **DAP^{•+}** is not observed by LFP neither in the presence nor absence of O₂ suggesting that its reduction by **PC²⁺** is faster than its formation (Scheme 1B). Consequently, the main task of O₂ is to rapidly remove **PC²⁺** to prevent non-geminate back-ET from **PC²⁺** to ***tAn*^{•+}** and thus to enable the slow addition reaction of ***tAn*^{•+}** to **DMB**, while O₂^{•-} is not necessarily required to reduce **DAP^{•+}**. Furthermore, rapid regeneration of **PC³⁺** prevents accumulation of the highly absorptive one-electron reduced photocatalyst **PC²⁺** **[Cr(tpe)₂]²⁺** (Figure 2A) which would absorb a significant amount of the incoming photons.

The competent photocatalysts **[Cr(tpe)₂]³⁺**, **[Cr(dmcby)₃]³⁺** and **[Ru(bpz)₃]²⁺** were employed in catalytic experiments with ***tAn***



and DMB substrates in air-saturated CH₃CN under visible light excitation (460 nm). The overlap of the absorption spectra of PCⁿ⁺ and the emission of the LEDs employed reveal that photon absorption in this spectral region increases in the series [Cr(tpe)₂]³⁺, [Cr(dmcbpy)₃]³⁺ and [Ru(bpz)₃]²⁺ due to the weak Laporte-forbidden absorption bands of the Cr^{III} photocatalysts in the visible spectral region. This is particularly concerning for the centrosymmetric complex [Cr(tpe)₂]³⁺ with an extinction coefficient at its absorption maximum of only $\epsilon_{431} = 30 \text{ M}^{-1} \text{ cm}^{-1}$ as compared to the much higher extinction coefficients of [Cr(dmcbpy)₃]³⁺ ($\epsilon_{448} = 714 \text{ M}^{-1} \text{ cm}^{-1}$) and [Ru(bpz)₃]²⁺ ($\epsilon_{440} = 14,100 \text{ M}^{-1} \text{ cm}^{-1}$). Consequently, we employed a loading of 5 mM [Cr(tpe)₂]³⁺ in initial catalytic tests. According to ¹H NMR spectroscopic reaction monitoring (Supplementary Figures S27–S31), full conversion to the Diels-Alder product DAP is achieved with [Cr(tpe)₂]³⁺ within ca. 80 min (Supplementary Figure S32). In the absence of O₂ only traces of DAP were observed after 4 h irradiation (Supplementary Figure S33). Introduction of O₂ to this pretreated reaction mixture initiates the catalytic turnover and the reaction proceeds quantitatively. This confirms that the unproductive back-ET efficiently prevents the formation of DAP^{•+}. In the absence of light (24 h) or [Cr(tpe)₂]³⁺ (24 h) DAP formation is not observed (Supplementary Figures S34, S35). In the latter case, traces of 4-anisaldehyde and other byproducts are formed (Supplementary Figure S35). Reducing the catalyst loading to 1 and 0.2 mM prolongs the reaction time to reach full conversion to ca. 5–6 and 9–10 h, respectively (Figure 4; Supplementary Figure S36). Notably, full conversion is achieved with [Cr(tpe)₂]³⁺ in all cases. The solutions remain only weakly colored during the photolysis experiments suggesting a high stability of [Cr(tpe)₂]³⁺, ^{*}[Cr(tpe)₂]³⁺ and [Cr(tpe)₂]²⁺. In fact, addition of new tAn and DMB substrates to the catalysis solution after full conversion, resumes the catalytic activity without noticeable degradation as demonstrated two times (Supplementary Figure S37). The high photo and redoxstability of

[Cr(tpe)₂]³⁺ (Supplementary Figure S38) and the resulting recyclability (Supplementary Figure S37) are unique to [Cr(tpe)₂]³⁺ (Figure 4).

[Ru(bpz)₃]²⁺ reacts initially much faster than the Cr^{III} photocatalysts [Cr(dmcbpy)₃]³⁺ and [Cr(tpe)₂]³⁺ with initial rates being 300×10^{-4} , 2.5×10^{-4} and $4.3 \times 10^{-4} \text{ mM min}^{-1}$ and turnover frequencies being TOF = 75, 0.6 and 1.1 min⁻¹, respectively (loading 0.2 mM; Figure 4). Importantly, [Cr(dmcbpy)₃]³⁺ and [Ru(bpz)₃]²⁺ do not achieve full conversion under these conditions (loading 0.2 mM) but the catalytic activity levels off at ca. 30 and 50% conversion after 720 and 6 min, respectively. Photodecomposition of the [Cr(dmcbpy)₃]³⁺ and [Ru(bpz)₃]²⁺ with ligand loss is likely responsible for this behavior. Indeed, the UV/Vis spectra of the solutions after the catalysis changed for [Cr(dmcbpy)₃]³⁺ and [Ru(bpz)₃]²⁺, but not for [Cr(tpe)₂]³⁺ (Supplementary Figures S38–S40). Although conditions for chromium(III) and ruthenium(II) complexes with bidentate ligands can be optimized to achieve full conversion, re-using these photocatalysts has not yet been reported (Lin, et al., 2011; Stevenson, et al., 2015; Farney, et al., 2019).

Only traces of byproducts form during the reaction with [Cr(tpe)₂]³⁺ as photocatalyst. Discernible ¹H NMR resonances at $\delta = 9.84$, 7.82, 6.87 and 3.86 ppm suggest the formation of 4-anisaldehyde arising from the reaction of tAn^{•+} with oxygen (<< 1%; Supplementary Figure S41) (Lewis and Kijima, 1988). A further byproduct with ¹H NMR resonances around 8.8 ppm also likely arises from a tAn^{•+} derived species but could not be definitely assigned, yet various dimers and other oxygenated products are conceivable (Nozaki, et al., 1968). Side reactions of tAn with ¹O₂ are excluded as a photocatalytic control reaction using [Cr(ddpd)₂]³⁺ as PC³⁺ which is merely capable to form ¹O₂ but not tAn^{•+} does not yield any products.

At first glance, molecular rubies seem to be rather unattractive in the context of photochemical applications, such as photoredox catalysis, due to their low absorbance in the visible part of the spectrum, which appears to imply an inefficient use of the incident photons. This seems especially true for [Cr(tpe)₂]³⁺, which has an extinction coefficient as low as $30 \text{ M}^{-1} \text{ cm}^{-1}$ at the maximum of the band in the visible region. However, for one-photon processes and a reasonable reactor design, this turns out to be not the case, especially when the photocatalyst is as stable (reusable) and easy to access as [Cr(tpe)₂]³⁺. Laboratory scale applications typically go hand in hand with a moderate upscaling compared to the mechanistic studies that are typically conducted in a cuvette or vial. On a preparative laboratory scale it is convenient to conduct the reaction in a round bottom flask or a larger cuvette, such an optical path of 10 cm or more is likely achieved. In this case, [Cr(tpe)₂]³⁺ photocatalyst loadings of 1 and 5 mM give absorbances of 0.3 and 1.5, respectively. According to the Lambert-Beer law 50 and 97% of the incident photons are absorbed, which is a fairly efficient use of light. In fact, the low extinction coefficient of [Cr(tpe)₂]³⁺ and other molecular rubies might be even beneficial in some reactions as byproduct formation can be decreased by mitigating high local concentrations of radical intermediates as opposed to reactions with strongly absorbing catalysts.

CONCLUSION

The chromium(III)-based photocatalysts PC^{3+} [$\text{Cr}(\text{dmcbpy})_3$] $^{3+}$ and [$\text{Cr}(\text{tpe})_2$] $^{3+}$ catalyze the visible light-driven radical cation [4+2] cycloaddition of *trans*-anethole **tAn** and 2,3-dimethyl-1,3-butadiene **DMB** using visible light similar to the highly oxidative ruthenium(II) photocatalyst [$\text{Ru}(\text{bpz})_3$] $^{2+}$. The chromium(III) photocatalysts PC^{3+} are quenched reductively by **tAn** to give PC^{2+} and **tAn** $^{\bullet+}$. The reaction of **tAn** $^{\bullet+}$ with **DMB** to the **DAP** $^{\bullet+}$ product radical cation is the slowest step of the catalytic cycle. Therefore, oxygen is required for efficient performance to retard unproductive non-geminate back-electron transfer from PC^{2+} to the long-lived radical cation **tAn** $^{\bullet+}$ by rapid oxidative regeneration of the photocatalyst. The concomitantly formed superoxide and the reduced photocatalyst PC^{2+} reduce the product radical cation **DAP** $^{\bullet+}$ to the Diels-Alder product **DAP** so that **DAP** $^{\bullet+}$ does not accumulate. In contrast to [$\text{Cr}(\text{dmcbpy})_3$] $^{3+}$ and [$\text{Ru}(\text{bpz})_3$] $^{2+}$ the molecular ruby [$\text{Cr}(\text{tpe})_2$] $^{3+}$ is exceptionally photo and redoxstable and possesses an ultralong excited state lifetime in the millisecond range. Quantitative conversion is achieved contrary to the photolabile photocatalysts [$\text{Cr}(\text{dmcbpy})_3$] $^{3+}$ and [$\text{Ru}(\text{bpz})_3$] $^{2+}$. Furthermore, recycling of [$\text{Cr}(\text{tpe})_2$] $^{3+}$ is successful without significant loss of activity. This mechanistic and exploratory study of the photoredox properties of a molecular ruby paves the way for an efficient and sustainable utilization of photocatalysts based on Earth-abundant chromium ions, in particular photo- and redoxstable molecular rubies, in oxidative photoredox catalysis.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding authors.

REFERENCE

- Aydogan, A., Bangle, R. E., Cadranal, A., Turlington, M. D., Conroy, D. T., Cauët, E., et al. (2021). Accessing Photoredox Transformations with an Iron(III) Photosensitizer and Green Light. *J. Am. Chem. Soc.* 143, 15661–15673. doi:10.1021/jacs.1c06081
- Baldo, M. A., Thompson, M. E., and Forrest, S. R. (2000). High-Efficiency Fluorescent Organic Light-Emitting Devices Using a Phosphorescent Sensitizer. *Nature* 403, 750–753. doi:10.1038/35001541
- Balzani, V., Bolletta, F., Gandolfi, M. T., and Maestri, M. (1978). Bimolecular Electron Transfer Reactions of the Excited States of Transition Metal Complexes. *Org. Chem. Theor.* 75, 1–64. doi:10.1007/BFb0048835
- Baptista, F. A., Krizsan, D., Stitch, M., Sazanovich, I. V., Clark, I. P., Towrie, M., et al. (2021). Adenine Radical Cation Formation by a Ligand-Centered Excited State of an Intercalated Chromium Polypyridyl Complex Leads to Enhanced DNA Photo-Oxidation. *J. Am. Chem. Soc.* 143, 14766–14779. doi:10.1021/jacs.1c06658
- Basu, U., Otto, S., Heinze, K., and Gasser, G. (2019). Biological Evaluation of the NIR-Emissive Ruby Analogue $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ as a Photodynamic Therapy Photosensitizer. *Eur. J. Inorg. Chem.* 2019, 37–41. doi:10.1002/ejic.201801023
- Becker, P. M., Förster, C., Carrella, L. M., Boden, P., Hunger, D., Slagereen, J., et al. (2020). Spin Crossover and Long-Lived Excited States in a Reduced Molecular Ruby. *Chem. Eur. J.* 26, 7199–7204. doi:10.1002/chem.202001237

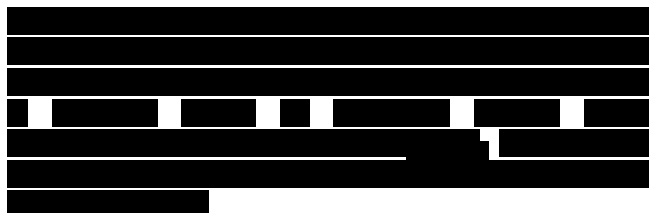
AUTHOR CONTRIBUTIONS

SS conducted the quenching, the catalytic and the UV/Vis/NIR spectroscopic experiments. ■ performed and analyzed all laser flash photolysis and many luminescence experiments. ■ designed the project and wrote the manuscript. All authors discussed the scientific results and wrote parts of the manuscript.

FUNDING

This work has been financially supported by the Deutsche Forschungsgemeinschaft (DFG) under grants HE2778/10-2 and INST 247/1018-1.

ACKNOWLEDGMENTS



SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2022.887439/full#supplementary-material>

- Büldt, L. A., and Wenger, O. S. (2017). Chromium Complexes for Luminescence, Solar Cells, Photoredox Catalysis, Upconversion, and Phototriggered NO Release. *Chem. Sci.* 8, 7359–7367. doi:10.1039/C7SC03372A
- Campagna, S., Puntoriero, F., Nastasi, F., Bergamini, G., and Balzani, V. (2007). “Photochemistry and Photophysics of Coordination Compounds: Ruthenium,” in *Photochemistry and Photophysics of Coordination Compounds I. Topics in Current Chemistry*. Editors V. Balzani and S. Campagna (Berlin, Heidelberg: Springer), 280, 117–214. doi:10.1007/128_2007_133
- Constable, E. C., Housecroft, C. E., Neuburger, M., Schönle, J., and Zampese, J. A. (2014). The Surprising Lability of Bis(2,2′:6′,2′′-Terpyridine)chromium(III) Complexes. *Dalton Trans.* 43, 7227–7235. doi:10.1039/C4DT00200H
- Costa, R. D., Orti, E., Bolink, H. J., Monti, F., Accorsi, G., and Armaroli, N. (2012). Luminescent Ionic Transition-Metal Complexes for Light-Emitting Electrochemical Cells. *Angew. Chem. Int. Ed.* 51, 8178–8211. doi:10.1002/anie.201201471
- Crutchley, R. J., and Lever, A. B. P. (1980). Ruthenium(II) Tris(bipyrazyl) Dication - a New Photocatalyst. *J. Am. Chem. Soc.* 102, 7128–7129. doi:10.1021/ja00543a053
- Farney, E. P., Chapman, S. J., Swords, W. B., Torelli, M. D., Hamers, R. J., and Yoon, T. P. (2019). Discovery and Elucidation of Counteranion Dependence in Photoredox Catalysis. *J. Am. Chem. Soc.* 141, 6385–6391. doi:10.1021/jacs.9b01885
- Förster, C., and Heinze, K. (2020). Photophysics and Photochemistry with Earth-Abundant Metals - Fundamentals and Concepts. *Chem. Soc. Rev.* 49, 1057–1070. doi:10.1039/c9cs00573k

- Fulmer, G. R., Miller, A. J. M., Sherden, N. H., Gottlieb, H. E., Nudelman, A., Stoltz, B. M., et al. (2010). NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* 29, 2176–2179. doi:10.1021/om100106e
- Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L., and Pettersson, H. (2010). Dye-sensitized Solar Cells. *Chem. Rev.* 110, 6595–6663. doi:10.1021/cr900356p
- Heinemann, F., Karges, J., and Gasser, G. (2017). Critical Overview of the Use of Ru(II) Polypyridyl Complexes as Photosensitizers in One-Photon and Two-Photon Photodynamic Therapy. *Acc. Chem. Res.* 50, 2727–2736. doi:10.1021/acs.accounts.7b00180
- Herr, P., Kerzig, C., Larsen, C. B., Häussinger, D., and Wenger, O. S. (2021). Manganese(I) Complexes with Metal-To-Ligand Charge Transfer Luminescence and Photoreactivity. *Nat. Chem.* 13, 956–962. doi:10.1038/s41557-021-00744-9
- Higgins, R. F., Fatur, S. M., Damrauer, N. H., Ferreira, E. M., Rappé, A. K., and Shores, M. P. (2018). Detection of an Energy-Transfer Pathway in Cr-Photoredox Catalysis. *ACS Catal.* 8, 9216–9225. doi:10.1021/acscatal.8b03013
- Higgins, R. F., Fatur, S. M., Shepard, S. G., Stevenson, S. M., Boston, D. J., Ferreira, E. M., et al. (2016). Uncovering the Roles of Oxygen in Cr(III) Photoredox Catalysis. *J. Am. Chem. Soc.* 138, 5451–5464. doi:10.1021/jacs.6b02723
- Hockin, B. M., Li, C., Robertson, N., and Zysman-Colman, E. (2019). Photoredox Catalysts Based on Earth-Abundant Metal Complexes. *Catal. Sci. Technol.* 9, 889–915. doi:10.1039/C8CY02336K
- Horibe, T., Ohmura, S., and Ishihara, K. (2019). Structure and Reactivity of Aromatic Radical Cations Generated by FeCl₃. *J. Am. Chem. Soc.* 141, 1877–1881. doi:10.1021/jacs.8b12827
- Hossain, A., Bhattacharyya, A., and Reiser, O. (2019). Copper's Rapid Ascent in Visible-Light Photoredox Catalysis. *Science* 364, eaav9713. doi:10.1126/science.aav9713
- Huber, N., Li, R., Ferguson, C. T. J., Gehrig, D. W., Ramanan, C., Blom, P. W. M., et al. (2020). A PMMA-Based Heterogeneous Photocatalyst for Visible Light-Promoted [4+2] Cycloaddition. *Catal. Sci. Technol.* 10, 2092–2099. doi:10.1039/d0cy00016g
- Jamieson, M. A., Serpone, N., Henry, M. S., and Hoffman, M. Z. (1979). Temperature Dependence of the Photoaquation of tris(2,2'-bipyridine) Chromium(III) Ion in Alkaline Solution. *Inorg. Chem.* 18, 214–216. doi:10.1021/ic50191a048
- Jiménez, J.-R., Doistau, B., Cruz, C. M., Besnard, C., Cuerva, J. M., Campaña, A. G., et al. (2019). Chiral Molecular Ruby [Cr(dqp)₂]³⁺ with Long-Lived Circularly Polarized Luminescence. *J. Am. Chem. Soc.* 141, 13244–13252. doi:10.1021/jacs.9b06524
- Johnston, L. J., and Schepp, N. P. (1995). Laser Flash Photolysis Studies of the Reactivity of Styrene Radical Cations. *Pure Appl. Chem.* 67, 71–78. doi:10.1351/pac199567010071
- Johnston, L. J., and Schepp, N. P. (1993). Reactivities of Radical Cations: Characterization of Styrene Radical Cations and Measurements of Their Reactivity toward Nucleophiles. *J. Am. Chem. Soc.* 115, 6564–6571. doi:10.1021/ja00068a013
- Kitzmann, W. R., Moll, J., and Heinze, K. (2022). Spin-Flip Luminescence. *Photochem. Photobiol. Sci.* in press. doi:10.1007/s43630-022-00186-3
- Leis, W., Argüello Cordero, M. A., Lochbrunner, S., Schubert, H., and Berkefeld, A. (2022). A Photoreactive Iron(II) Complex Luminophore. *J. Am. Chem. Soc.* 144, 1169–1173. doi:10.1021/jacs.1c13083
- Leppin, J., Schubert, M., Waldvogel, S. R., and Heinze, K. (2015). Initial Radical Cation Pathway in the Mo₂Cl₁₀-Mediated Dehydrogenative Arene Coupling. *Chem. Eur. J.* 21, 4229–4232. doi:10.1002/chem.201406522
- Lewis, F. D., and Kojima, M. (1988). Electron-transfer-induced Photoisomerization, Dimerization, and Oxygenation of Trans- and Cis-Anethole. The Role of Monomer and Dimer Cation Radicals. *J. Am. Chem. Soc.* 110, 8664–8670. doi:10.1021/ja00234a014
- Li, A., Turro, C., and Kodanko, J. J. (2018). Ru(II) Polypyridyl Complexes Derived from Tetradentate Ancillary Ligands for Effective Photocaging. *Acc. Chem. Res.* 51, 1415–1421. doi:10.1021/acs.accounts.8b00066
- Limburg, B., Bouwman, E., and Bonnet, S. (2016). Rate and Stability of Photocatalytic Water Oxidation Using [Ru(bpy)₃]²⁺ as Photosensitizer. *ACS Catal.* 6, 5273–5284. doi:10.1021/acscatal.6b00107
- Lin, S., Ischay, M. A., Fry, C. G., and Yoon, T. P. (2011). Radical Cation Diels-Alder Cycloadditions by Visible Light Photocatalysis. *J. Am. Chem. Soc.* 133, 19350–19353. doi:10.1021/ja2093579
- Lindh, L., Chábera, P., Rosemann, N. W., Uhlig, J., Wärnmark, K., Yartsev, A., et al. (2020). Photophysics and Photochemistry of Iron Carbene Complexes for Solar Energy Conversion and Photocatalysis. *Catalysts* 10, 315. doi:10.3390/catal10030315
- Maestri, M., Bolletta, F., Serpone, N., Moggi, L., and Balzani, V. (1976). Kinetics of Ligand Substitution of tris(2,2'-bipyridine)Chromium(III) in Aqueous Solutions. *Inorg. Chem.* 15, 2048–2051. doi:10.1021/ic50163a007
- Magnuson, A., Anderlund, M., Johansson, O., Lindblad, P., Lomoth, R., Polivka, T., et al. (2009). Biomimetic and Microbial Approaches to Solar Fuel Generation. *Acc. Chem. Res.* 42, 1899–1909. doi:10.1021/ar900127h
- Marcus, R. A. (1993). Electron Transfer Reactions in Chemistry. Theory and experiment. *Rev. Mod. Phys.* 65, 599–610. doi:10.1103/RevModPhys.65.599
- Mari, C., Pierroz, V., Ferrari, S., and Gasser, G. (2015). Combination of Ru(II) Complexes and Light: New Frontiers in Cancer Therapy. *Chem. Sci.* 6, 2660–2686. doi:10.1039/C4SC03759F
- McDaniel, A. M., Tseng, H.-W., Damrauer, N. H., and Shores, M. P. (2010). Synthesis and Solution Phase Characterization of Strongly Photooxidizing Heteroleptic Cr(III) Tris-Dipyridyl Complexes. *Inorg. Chem.* 49, 7981–7991. doi:10.1021/ic1009972
- Montalti, M., Credi, A., Prodi, L., and Gandolfi, M. T. (2006). *Handbook of Photochemistry*. 3rd edition. Boca Raton: CRC Press, Taylor&Francis Group LLC.
- Murphy, R. S., and Bohne, C. (2000). Use of Styrene Radical Cations as Probes for the Complexation Dynamics of Charged Guests with α - and β -Cyclodextrins. *Photochem. Photobiol.* 71, 35. doi:10.1562/0031-8655(2000)071<0035:uoscra>2.0.co;2
- Nakayama, K., Maeta, N., Horiguchi, G., Kamiya, H., and Okada, Y. (2019). Radical Cation Diels-Alder Reactions by TiO₂ Photocatalysis. *Org. Lett.* 21, 2246–2250. doi:10.1021/acs.orglett.9b00526
- Nozaki, H., Otani, I., Noyori, R., and Kawanisi, M. (1968). Photochemical Reactions of Trans-anethole. *Tetrahedron* 24, 2183–2192. doi:10.1016/0040-4020(68)88120-7
- Otto, S., Dorn, M., Förster, C., Bauer, M., Seitz, M., and Heinze, K. (2018a). Understanding and Exploiting Long-Lived Near-Infrared Emission of a Molecular Ruby. *Coord. Chem. Rev.* 359, 102–111. doi:10.1016/j.ccr.2018.01.004
- Otto, S., Förster, C., Wang, C., Resch-Genger, U., and Heinze, K. (2018). A Strongly Luminescent Chromium(III) Complex Acid. *Chem. Eur. J.* 24, 12555–12563. doi:10.1002/chem.201802797
- Otto, S., Grabolle, M., Förster, C., Kreitner, C., Resch-Genger, U., and Heinze, K. (2015). [Cr(dppd)₂]³⁺: A Molecular, Water-Soluble, Highly NIR-Emissive Ruby Analogue. *Angew. Chem. Int. Ed.* 54, 11572–11576. doi:10.1002/anie.201504894
- Otto, S., Nauth, A. M., Ermilov, E., Scholz, N., Friedrich, A., Resch-Genger, U., et al. (2017). Photo-Chromium: Sensitizer for Visible-Light-Induced Oxidative C–H Bond Functionalization-Electron or Energy Transfer? *ChemPhotoChem* 1, 344–349. doi:10.1002/cptc.201700077
- Pal, A. K., Li, C., Hanan, G. S., and Zysman-Colman, E. (2018). Blue-Emissive Cobalt(III) Complexes and Their Use in the Photocatalytic Trifluoromethylation of Polycyclic Aromatic Hydrocarbons. *Angew. Chem. Int. Ed.* 57, 8027–8031. doi:10.1002/anie.201802532
- Reichenauer, F., Wang, C., Förster, C., Boden, P., Ugur, N., Báez-Cruz, R., et al. (2021). Strongly Red-Emissive Molecular Ruby [Cr(bmp)₂]³⁺ Surpasses [Ru(bpy)₃]²⁺. *J. Am. Chem. Soc.* 143, 11843–11855. doi:10.1021/jacs.1c05971
- Scarborough, C. C., Sproules, S., Weyhermüller, T., DeBeer, S., and Wieghardt, K. (2011). Electronic and Molecular Structures of the Members of the Electron Transfer Series [Cr(tbp)₃]ⁿ (N = 3+, 2+, 1+, 0): An X-ray Absorption Spectroscopic and Density Functional Theoretical Study. *Inorg. Chem.* 50, 12446–12462. doi:10.1021/ic201123x
- Scattergood, P. A. (2020). Recent Advances in Chromium Coordination Chemistry: Luminescent Materials and Photocatalysis. *Organomet. Chem.* 43, 1–34. doi:10.1039/9781788017077-00001
- Schubert, M., Franzmann, P., Wünsche von Leupoldt, A., Koszinowski, K., Heinze, K., and Waldvogel, S. R. (2016). Over-Oxidation as the Key Step in the

- Mechanism of the MoCl_5 -Mediated Dehydrogenative Coupling of Arenes. *Angew. Chem. Int. Ed.* 55, 1156–1159. doi:10.1002/anie.201508035
- Schultz, D. M., Sawicki, J. W., and Yoon, T. P. (2015). An Improved Procedure for the Preparation of $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$ via a High-Yielding Synthesis of 2,2'-bipyrazine. *Beilstein J. Org. Chem.* 11, 61–65. doi:10.3762/bjoc.11.9
- Singh, P. S., and Evans, D. H. (2006). Study of the Electrochemical Reduction of Dioxygen in Acetonitrile in the Presence of Weak Acids. *J. Phys. Chem. B* 110, 637–644. doi:10.1021/jp055296f
- Soupart, A., Alary, F., Heully, J.-L., Elliott, P. I. P., and Dixon, I. M. (2020). Theoretical Study of the Full Photosolvolytic Mechanism of $[\text{Ru}(\text{bpy})_3]^{2+}$: Providing a General Mechanistic Roadmap for the Photochemistry of $[\text{Ru}(\text{NN})_3]^{2+}$ -Type Complexes toward Both Cis and Trans Photoproducts. *Inorg. Chem.* 59, 14679–14695. doi:10.1021/acs.inorgchem.0c01843
- Squillacote, M. E., and Liang, F. (2005). Conformational Thermodynamic and Kinetic Parameters of Methyl-Substituted 1,3-Butadienes. *J. Org. Chem.* 70, 6564–6573. doi:10.1021/jo0500277
- Stevenson, S. M., Higgins, R. F., Shores, M. P., and Ferreira, E. M. (2017). Chromium Photocatalysis: Accessing Structural Complements to Diels-Alder Adducts with Electron-Deficient Dienophiles. *Chem. Sci.* 8, 654–660. doi:10.1039/c6sc03303b
- Stevenson, S. M., Shores, M. P., and Ferreira, E. M. (2015). Photooxidizing Chromium Catalysts for Promoting Radical Cation Cycloadditions. *Angew. Chem. Int. Ed.* 54, 6506–6510. doi:10.1002/anie.201501220
- Tanaka, K., Asada, Y., Hoshino, Y., and Honda, K. (2020). Visible-light-induced [4+2] Cycloaddition of Pentafulvenes by Organic Photoredox Catalysis. *Org. Biomol. Chem.* 18, 8074–8078. doi:10.1039/D0OB01151G
- Treiling, S., Wang, C., Förster, C., Reichenauer, F., Kalmbach, J., Boden, P., et al. (2019). Luminescence and Light-Driven Energy and Electron Transfer from an Exceptionally Long-Lived Excited State of a Non-Innocent Chromium(III) Complex. *Angew. Chem. Int. Ed.* 58, 18075–18085. doi:10.1002/anie.201909325
- Twilton, J., Le, C., Zhang, P., Shaw, M. H., Evans, R. W., and MacMillan, D. W. C. (2017). The Merger of Transition Metal and Photocatalysis. *Nat. Rev. Chem.* 1, 0052. doi:10.1038/s41570-017-0052
- Vaidyanathan, V. G., and Nair, B. U. (2004). Nucleobase Oxidation of DNA by (Terpyridyl)chromium(III) Derivatives. *Eur. J. Inorg. Chem.* 2004, 1840–1846. doi:10.1002/ejic.200300718
- Vlcek, A. A., Dodsworth, E. S., Pietro, W. J., and Lever, A. B. P. (1995). Excited State Redox Potentials of Ruthenium Diimine Complexes; Correlations with Ground State Redox Potentials and Ligand Parameters. *Inorg. Chem.* 34, 1906–1913. doi:10.1021/ic00111a043
- Wang, C., Kitzmann, W. R., Weigert, F., Förster, C., Wang, X., Heinze, K., et al. (2022). Matrix Effects on Photoluminescence and Oxygen Sensitivity of a Molecular Ruby. *ChemPhotoChem.* in press. doi:10.1002/cptc.202100296
- Watson, R. T., Desai, N., Wildsmith, J., Wheeler, J. F., and Kane-Maguire, N. A. P. (1999). Interaction of $\text{Cr}(\text{diimine})_3^{3+}$ Complexes with DNA. *Inorg. Chem.* 38, 2683–2687. doi:10.1021/ic980857l
- Wenger, O. S. (2018). Photoactive Complexes with Earth-Abundant Metals. *J. Am. Chem. Soc.* 140, 13522–13533. doi:10.1021/jacs.8b08822
- Wenger, O. S. (2021). Photoactive Nickel Complexes in Cross-Coupling Catalysis. *Chem. Eur. J.* 27, 2270–2278. doi:10.1002/chem.202003974
- Yam, V. W.-W., Chan, A. K.-W., and Hong, E. Y.-H. (2020). Charge-transfer Processes in Metal Complexes Enable Luminescence and Memory Functions. *Nat. Rev. Chem.* 4, 528–541. doi:10.1038/s41570-020-0199-7
- Yang, Y., Liu, Q., Zhang, L., Yu, H., and Dang, Z. (2017). Mechanistic Investigation on Oxygen-Mediated Photoredox Diels-Alder Reactions with Chromium Catalysts. *Organometallics* 36, 687–698. doi:10.1021/acs.organomet.6b00886
- Yoon, T. P., Ischay, M. A., and Du, J. (2010). Visible Light Photocatalysis as a Greener Approach to Photochemical Synthesis. *Nat. Chem* 2, 527–532. doi:10.1038/nchem.687

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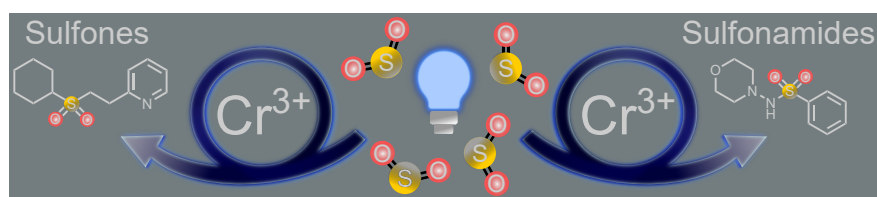
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3.3 Visible-Light Induced Fixation of SO₂ into Organic Molecules with Polypyridine Chromium(III) Complexes

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ChemCatChem **2023**, 15, e202201562. DOI: 10.1002/cctc.202201562.



The *Molecular Rubies* [Cr(ddpd)₂]³⁺ and [Cr(tpe)₂]³⁺ were utilized in the photocatalytically induced incorporation of sulfur dioxide into organic compounds. In addition to photocatalytic experiments, investigations on the reaction mechanism were conducted, using [Cr(tpe)₂]³⁺. These included the determination of cage-escape quantum yields Φ_{CE} for multiple substrates via laser flash photolysis. Obtained values for Φ_{CE} varied between <7% and 73% for similar substrates, which underlined the current unpredictability of cage-escape yields.

Author Contributions

Steven Sittel conducted and analyzed the UV/vis/NIR absorption spectroscopy, cyclic voltammetry, *Stern-Volmer* analyses, NMR analysis of the DABCO/DABSO mixture and performed DFT calculations for the [Ph₂I][R₂N-NH-SO₂] ion pair. [REDACTED] [REDACTED] conducted and analyzed the time-resolved transient absorption spectroscopy, the actinometry and the cage-escape yields. [REDACTED] [REDACTED] conducted and analyzed the photocatalytic experiments. [REDACTED] performed DFT calculations for the 4-aminomorpholine radical cation. [REDACTED] [REDACTED] conceptualized the project. All authors discussed the scientific results and contributed to the creation and editing of the manuscript and the supporting information.

Supporting Information

for this article can be found on pp. 159.

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Visible-Light Induced Fixation of SO₂ into Organic Molecules with Polypyridine Chromium(III) Complexes

Steven Sittel^{+, [a]}

*[a]

Incorporation of sulfur dioxide into organic compounds is achieved by a photocatalytic approach using sensitizers made from earth-abundant chromium(III) ions and visible light leading to sulfones and sulfonamides. We employed three different chromium(III) sensitizers [Cr(ddpd)]³⁺, [Cr(bpmp)]³⁺ and [Cr(tpe)]³⁺ with long excited state lifetimes and different ground and excited state redox potentials as well as varying stability under the reaction conditions (ddpd = *N,N'*-dimethyl-*N,N'*-dipyridin-2-yl-pyridine-2,6-diamine; bpmp = 2,6-bis(2-pyridylmethyl)pyridine; tpe = 1,1,1-tris(pyrid-2-yl)ethane). Key reaction steps

of the catalytic cycles are identified by electrochemical, luminescence quenching, photolysis, laser flash photolysis and catalytic experiments delivering a detailed picture of the challenges in these transformations. The reactivity of the reduced chromium complex was identified as a key property to explain the reaction outcomes. Initial cage escape yield determinations with [Cr(tpe)]³⁺ revealed that desired photo-reactions occur with unusually high quantum efficiencies, whereas side reactions are almost unproductive.

Introduction

Sulfur dioxide (SO₂) is an important chemical feedstock and produced in enormous amounts every year.^[1,2] It is a widely used preservative (E220) in the food industry, e.g. for wine or dried fruits. SO₂ is used as reducing agent to bleach papers or clothes, corn processing, water and waste treatment, oil recovery, ore refining and the sulfonylation of aromatic compounds to give important drugs.^[1–3] SO₂ is also a major air pollutant and has significant impact on public health and the environment.^[4,5] In the last twenty years, there has been increasing interest in the direct incorporation of SO₂ into the

sulfonyl functionality (–SO₂–) in small organic molecules.^[3,6–13] This interest mainly stems from the broad application of sulfonyl containing molecules, such as sulfones or sulfonamides, in particular in drug discovery and development.^[14,15] Compared to traditional methods,^[16] these novel processes enable highly modular and inherently more sustainable synthesis of sulfones or sulfonamides utilizing SO₂ as key building block.^[17] The introduction of easy-to-handle surrogates for the toxic and corrosive SO₂ gas, such as the 1,4-diazabicyclo[2.2.2]octane (DABCO)-sulfur dioxide adduct DABSO, has been a major driving force in this field.^[18–20] Yet, the stoichiometric release of DABCO mitigates atom economy and may pose other concerns such as side reactions.

Among the different approaches, photochemical processes driven by visible-light are particularly attractive for the direct fixation of SO₂.^[21,22] Although there have been some reports on the visible-light driven incorporation of SO₂ in the absence of any external photosensitizer,^[23–25] the use of designated photo-active catalysts provides significant advantages in terms of reaction rates, scope and applicability. The emergence of visible-light photoredox catalysis has opened intriguing possibilities to directly activate otherwise unreactive substrates in single-electron transfer pathways.^[26–28] Photoredox catalysis has led to the development of novel tools for the construction of carbon-sulfur bonds.^[29–31] Visible-light driven fixation of SO₂ so far mainly relies on two types of photocatalysts, transition metal complexes of noble metals and organic chromophores.^[21,22]

Transition metal complexes, such as [Ru(bpy)₃]²⁺ or Ir(ppy)₃ (bpy = 2,2'-bipyridine, ppy = deprotonated 2-phenylpyridine)^[32] possess long excited state lifetimes, which is an important prerequisite for efficient catalysis. Furthermore, their excited state and ground state redox potentials can be adjusted in a straightforward manner employing ligand modifications.^[33,34] These properties make them preferable to organic chromophores in many cases. However, they fall short concerning

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cctc.202201562>



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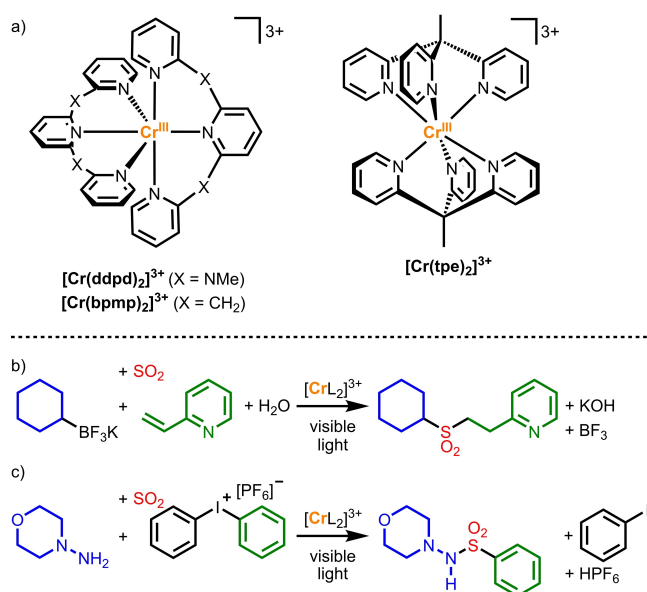


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sustainability, due to the low earth-abundance of precious metals like Ru or Ir.

Consequently, there has been a sustained interest in replacing precious metals in photoactive complexes with earth-abundant metals, such as chromium, manganese, iron or copper.^[35–37] Copper complexes have already been successfully utilized in photocatalytic C–S bond forming reactions.^[38–42] Chromium(III) complexes with polypyridine ligands have been identified as excellent photoluminescent materials with very high excited state lifetimes, even in the presence of oxygen.^[43–47] Yet, their application in organic synthesis has so far been limited to cycloaddition reactions, singlet oxygen generation, triplet-triplet annihilation followed by cycloaddition reactions and a few photoredox catalytic cycles which mostly rely on oxygen as terminal oxidant, which can impart problems due to the formation of reactive oxygen species.^[48–54]

Herein we report the, to the best of our knowledge, first application of chromium(III) photosensitizers in the visible-light mediated fixation of SO₂ into sulfones and sulfonamides complemented by mechanistic studies. In particular, we employ three chromium(III) photosensitizers [Cr(ddpd)]₂³⁺,^[55,56] [Cr(bpmp)]₂³⁺^[57] and [Cr(tpe)]₂³⁺^[58] (Scheme 1a, ddpd = *N,N'*-dimethyl-*N,N'*-dipyridin-2-yl-pyridine-2,6-diamine; bpmp = 2,6-bis(2-pyridylmethyl)pyridine; tpe = 1,1,1-tris(pyrid-2-yl)ethane) possessing extremely long excited state lifetimes of several hundreds of μs and different ground and excited state redox potentials in two three-component SO₂ fixation processes leading to sulfones and sulfonamides, respectively (Scheme 1b,c).^[59,60] Mechanistic studies include electrochemistry of substrates, excited state quenching experiments, steady-state photolysis and quantitative laser flash photolysis (LFP) experiments providing deep insight into photocatalyst and substrate requirements for these visible light induced catalytic reactions.



Scheme 1. a) Chromium(III) photosensitizers employed in this study. b) and c) Visible light induced SO₂ fixation reactions studied.

Results and Discussion

Considering the favorable photooxidative properties of polypyridine chromium(III) complexes, we hypothesized, that Cr^{III} complexes might be suited for reactions proceeding through a reductive quenching cycle. Therefore, we selected the photocatalytic three-component reaction between alkyltrifluoroborates, SO₂ and alkenes from the Wu group (Scheme 1b)^[59] and the visible-light mediated aminosulfonylation of diaryliodonium salts developed by one of our labs (Scheme 1c),^[60] as two representative model transformations. For both processes, an initial single-electron transfer from the starting material (cyclohexyltrifluoroborate CyBF₃K or 4-aminomorpholine 4-AM) to the photoexcited catalyst is the first chemical step of the photocatalytic cycle. From the excited state redox potentials of the photocatalysts^[55,57,58] and ground state potentials of the two substrates (Figure 1) all three photocatalysts [Cr(ddpd)]₂³⁺, [Cr(bpmp)]₂³⁺ and [Cr(tpe)]₂³⁺ are capable of oxidizing 4-AM in their excited states, while only [Cr(bpmp)]₂³⁺ and [Cr(tpe)]₂³⁺ should be able to photooxidize CyBF₃K (Supporting Information, Figures S1–S2).

However, the most oxidizing complex [Cr(bpmp)]₂³⁺ reacts with the two basic substrates already in the ground state by proton transfer, likely proceeding from the slightly acidic methylene bridges of the coordinated bpmp ligand^[53] (Supporting Information, Figures S3–S4). Consequently, [Cr(bpmp)]₂³⁺ is not expected to engage efficiently in photoinduced electron transfer (PET) reactions with these basic substrates. The other two sensitizers [Cr(ddpd)]₂³⁺ and [Cr(tpe)]₂³⁺ are stable in the presence of the substrates.

4-AM quenches the emission of both sensitizers [Cr(ddpd)]₂³⁺ and [Cr(tpe)]₂³⁺ (Supporting Information, Figures S5–S6) as expected from the redox potentials. The emission of [Cr(tpe)]₂³⁺ is also quenched by CyBF₃K (Supporting Information, Figure S7). Although the excited state redox potential of [Cr(ddpd)]₂³⁺ and the oxidation peak potential of CyBF₃K are unfavorable for PET, we observe emission quenching (Supporting Information, Figure S8). This might be explicable by the lower onset potential of CyBF₃K and the irreversible oxidation process (Supporting Information, Figure S2). Upon

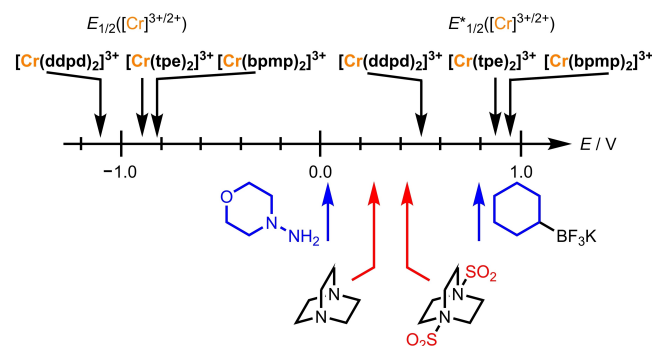


Figure 1. Pertinent ground and excited state redox potentials of the chromium(III) sensitizers^[55,57,58] and peak potentials of the oxidation of substrates and by-products in CH₃CN in V vs. ferrocene/ferrocenium determined by cyclic voltammetry.

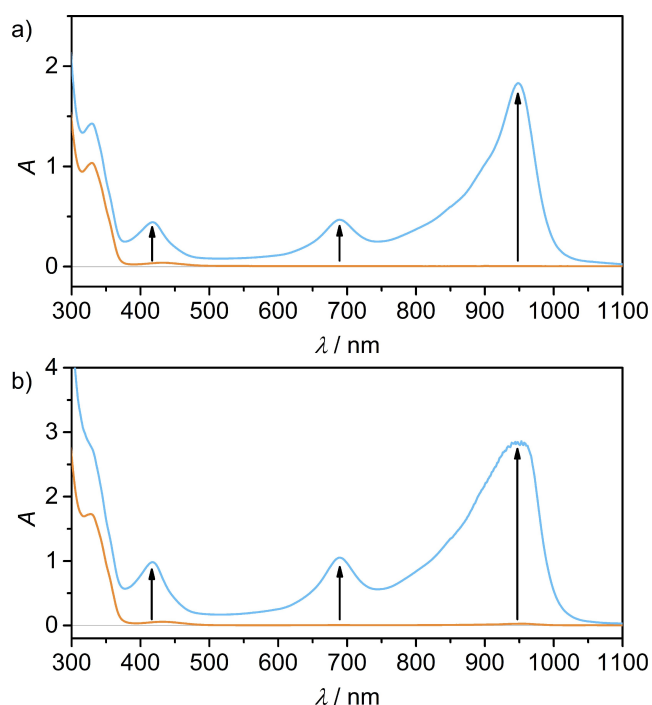


Figure 2. a) UV/vis/NIR absorption spectra of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (1 mM) in a solution of CyBF_3K (2 mM) in CH_3CN prior to irradiation (orange) and after 120 s UHP-LED irradiation ($\lambda_{\text{exc}} = 460$ nm) at 5% and 60 s at 10% output power under argon (blue). b) UV/vis/NIR absorption spectra of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (1 mM) in a solution of 4-AM (100 mM) in CH_3CN prior to irradiation (orange) and after 5 s of UHP-LED irradiation ($\lambda_{\text{exc}} = 460$ nm) at 5% output power under argon (blue).

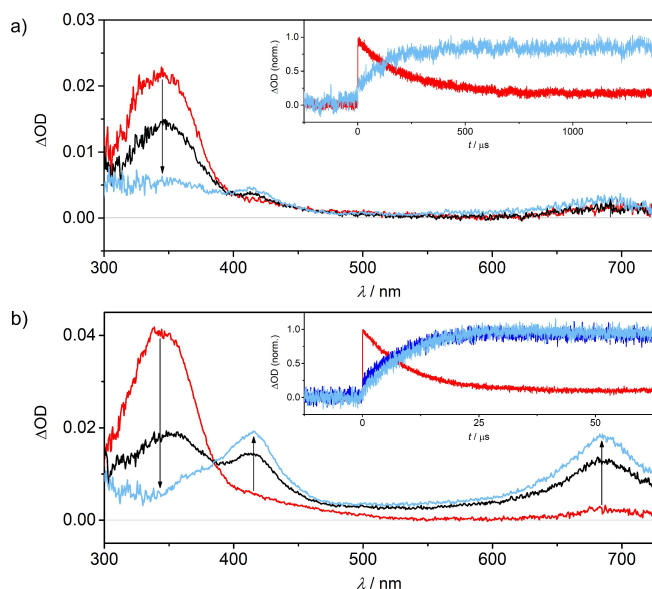


Figure 3. a) Transient absorption spectra of a deaerated CH_3CN solution of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (350 μM) and CyBF_3K (2.0 mM) 10 ns (red), 100 μs (black) and 600 μs (blue) after laser excitation ($\lambda_{\text{exc}} = 355$ nm). Inset: Kinetic traces at 346 nm (decay of $^*[\text{Cr}(\text{tpe})_2]^{3+}$, red) and at 690 nm (formation of $[\text{Cr}(\text{tpe})_2]^{2+}$, blue) indicate the same decay and formation rates. b) Transient absorption spectra of a deaerated CH_3CN solution of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (350 μM) and 4-AM (2.1 mM) 10 ns (red), 10 μs (black) and 30 μs (blue) after laser excitation ($\lambda_{\text{exc}} = 355$ nm). Inset: Kinetic traces at 346 nm (decay of $^*[\text{Cr}(\text{tpe})_2]^{3+}$, red) and at 416 nm as well as 690 nm (formation of $[\text{Cr}(\text{tpe})_2]^{2+}$, dark blue/blue).

continued photolysis ($\lambda_{\text{exc}} = 460$ nm) of the $[\text{Cr}(\text{tpe})_2]^{3+}$ sensitizer in the presence of the substrates CyBF_3K or 4-AM, the characteristic spectral signature ($\lambda_{\text{max}} = 416, 690, 948$ nm) of the reduced complex $[\text{Cr}(\text{tpe})_2]^{2+}$ is observed in both cases (Figure 2; Supporting Information, Figure S9).^[58]

After pulsed laser excitation ($\lambda_{\text{exc}} = 355$ nm) of the $[\text{Cr}(\text{tpe})_2]^{3+}$ sensitizer in the presence of 4-AM, the characteristic bands of $[\text{Cr}(\text{tpe})_2]^{2+}$ are observed as well (Figure 3b). These bands rise with the same rate as the characteristic absorption band of excited $^*[\text{Cr}(\text{tpe})_2]^{3+}$ at 346 nm^[51] disappears (inset of Figure 3b) forming an isosbestic point at 385 nm (Figure 3b). This indicates a clean reaction of $^*[\text{Cr}(\text{tpe})_2]^{3+}$ with the substrate to give $[\text{Cr}(\text{tpe})_2]^{2+}$. Clear signatures of the concomitantly formed 4-AM radical cation were not observed in the transient absorption (TA) spectra, probably due to its much lower molar absorptivity compared to $[\text{Cr}(\text{tpe})_2]^{2+}$. A separation of the end-of-quenching TA spectrum (blue spectrum in Figure 3b) with the independently obtained $[\text{Cr}(\text{tpe})_2]^{2+}$ spectrum gave remaining signals below 500 nm (Figure S10). Time-dependent DFT calculations (Figure S10) predict weak absorption bands for the 4-AM radical cation in that spectral region. Hence, these remaining TA signals likely correspond to the 4-AM radical cation, which seems to be sufficiently stable to undergo desired onward reactions in the multi-component system. The spectroscopic results thus demonstrate the successful PET from the substrates and the stability of the reduced complex $[\text{Cr}(\text{tpe})_2]^{2+}$. The high redox stability of $[\text{Cr}(\text{tpe})_2]^{2+}$ has been noted before and assigned to the ligand-centered reduction, which avoids the formation of labile chromium(II) ions.^[51,58]

Analogous TA experiments were carried out with CyBF_3K as reductive $^*[\text{Cr}(\text{tpe})_2]^{3+}$ quencher, which gave qualitatively identical results as with 4-AM. Interestingly, the formation of $[\text{Cr}(\text{tpe})_2]^{2+}$ is purely dynamic although Coulombic attraction between the oppositely charged photocatalyst and quencher molecules $[\text{Cr}(\text{tpe})_2]^{3+}$ and $[\text{CyBF}_3]^-$ could in principle result in pre-organization and static quenching phenomena. However, the $[\text{Cr}(\text{tpe})_2]^{2+}$ signals are much weaker when CyBF_3K is employed as the quencher (compare relative intensities of the absorption bands in Figure 3a/3b) despite almost quantitative quenching in both systems and the stability of the reduced complex regardless of the quencher. Quantitative quenching via PET does not necessarily correlate with efficient photo-product formation as ultrafast and unproductive recombination in the so-called solvent cage can reduce the yields drastically.^[61] To quantify the cage escape yields of primary photoproducts, i.e. the yields of free PET products that can be detected on a microsecond timescale, quantitative TA experiments are required.^[54,62] The $[\text{Cr}(\text{tpe})_2]^{3+/2+}$ complexes have excellent optical properties for such measurements: The intense absorption band of the excited state $^*[\text{Cr}(\text{tpe})_2]^{3+}$ in the UVA region can serve as internal reference signal and the reduced form $[\text{Cr}(\text{tpe})_2]^{2+}$ can be monitored through its absorption band in the red, where most other species are transparent. For quantitative analysis, the spectra of both key intermediates need to be calibrated prior to the cage escape determinations.

The UV/vis absorption spectrum of $[\text{Cr}(\text{tpe})_2]^{2+}$ was calibrated through the quantitative one-electron reduction of $[\text{Cr}(\text{tpe})_2]^{3+}$ to $[\text{Cr}(\text{tpe})_2]^{2+}$ using cobaltocene as reducing agent (Supporting Information, Figure S9). The spectral calibration of $[\text{Cr}(\text{tpe})_2]^{3+}$ was carried out via laser flash photolysis actinometry with the well-established $[\text{Ru}(\text{bpy})_3]^{2+}$ reference in water. This actinometry system had been successfully employed with excitation wavelengths ranging from 355 nm to 532 nm.^[54,62c,63] The calibration procedure relies on identical excitation conditions (Figure 4a). The resulting TA intensities of both the reference system and the chromium complex are compared (Figure 4b), directly resulting in the difference molar absorption coefficient of the latter at its absorption maximum $\Delta\epsilon_{346}$

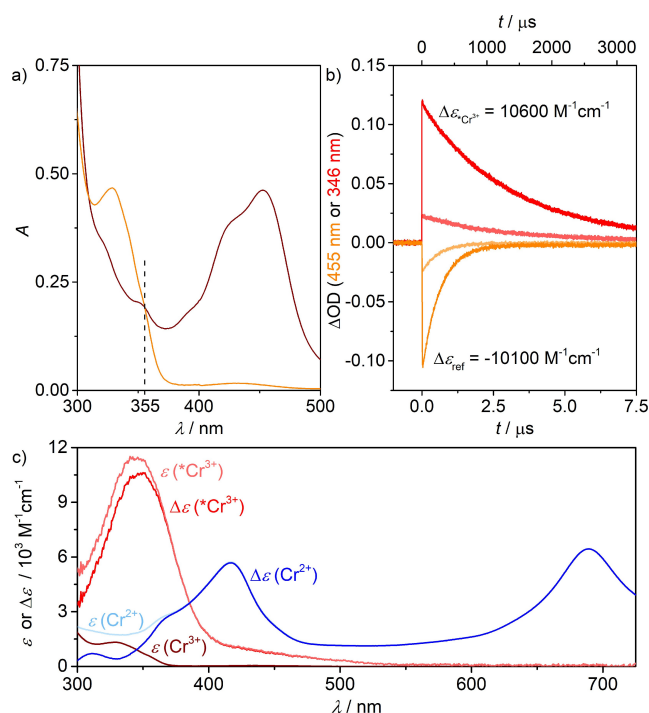


Figure 4. Data sets used for molar absorption coefficient determination of $[\text{Cr}(\text{tpe})_2]^{3+}$ at its absorption maximum (346 nm) using the $[\text{Ru}(\text{bpy})_3]^{2+}$ ground state bleach (455 nm) as actinometry reference. a) UV/vis absorption spectra of the deaerated CH_3CN solution of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (orange) and the deaerated aqueous solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (red) used for relative actinometry. b) Transient absorption traces of $[\text{Cr}(\text{tpe})_2]^{3+}$ at 346 nm (red) and of $[\text{Ru}(\text{bpy})_3]^{2+}$ at 455 nm (orange) upon 355 nm laser excitation with 2.3 mJ and 13.7 mJ laser pulses. c) Calibrated (difference) absorption spectra of the ground state of $[\text{Cr}(\text{tpe})_2]^{3+}$ (dark red) as well as of its excited (red) and reduced species (blue).

($[\text{Cr}(\text{tpe})_2]^{3+}$) = $10600 \text{ M}^{-1} \text{ cm}^{-1}$ (further explanations can be found in the Supporting Information, pages S21–S22). The resulting calibrated spectra are displayed in Figure 4c, both as absolute spectra and as difference spectra with the ground state absorption being subtracted. Whereas the absolute UV/vis spectrum of a given intermediate is an inherent property, its difference spectrum is essential for quantitative TA experiments as the corresponding ground state typically serves as TA baseline.

The results of the preceding paragraph permit quantitative quenching studies and cage escape yield η_{ce} determinations for all potential $[\text{Cr}(\text{tpe})_2]^{3+}$ quenchers (Table 1 and Table S1) by comparing the excited state TA signal at 346 nm and the post-quenching $[\text{Cr}(\text{tpe})_2]^{2+}$ signal at 690 nm, taking the actual quenching efficiency into account. The iodonium salt, which is important for catalyst regeneration (see below) does not quench at all (Supporting Information, Figure S11). Typical η_{ce} values for PET reactions with photoactive Ru^{II} complexes are in the range between 5 and 60%.^[54,61b] Only a few studies are dealing with η_{ce} determinations of photoactive 3d transition metal complexes and they report values below 15%.^[54,64] For the $[\text{Cr}(\text{tpe})_2]^{3+}/4\text{-AM}$ system, η_{ce} is as high as 73%, and the η_{ce} values differ by about one order of magnitude with the different quenchers under study. The direct recombination of spin-correlated radical pairs resulting from reductive quenching of both excited doublet and triplet states is spin-forbidden.^[54] Radical pair intersystem crossing is therefore required prior to unproductive recombination and this is poorly understood for PET reactions with photoexcited doublet precursors. In addition to the spin state changes, the charges of the photoproducts can modify the cage escape yields as well. Coulomb repulsion between the dicationic chromium complex $[\text{Cr}(\text{tpe})_2]^{2+}$ and the 4-AM radical cation might enhance cage escape. Clearly, further studies are required before a reliable comparison can be made. Nevertheless, the relatively high cage escape yields for both substrates of this study are encouraging, highlighting the hidden potential of chromium complexes for photocatalytic applications.

In contrast to the stable green $[\text{Cr}(\text{tpe})_2]^{2+}$ cation, which is essentially described as a chromium(III) ion with a coordinated tpe radical anion, the reduced complex $[\text{Cr}(\text{ddpd})_2]^{2+}$ is a highly sensitive high-spin chromium(II) complex at room temperature.^[65] Photolysis of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in the presence of 4-AM or CyBF_3K also leads to PET, however the resulting reduced photocatalyst decomposes under these conditions and the

Table 1. Key results for the reductive quenching of $[\text{Cr}(\text{tpe})_2]^{3+}$ in CH_3CN .

Quencher	k_q [$10^7 \text{ M}^{-1} \text{ s}^{-1}$]	Kinetic quenching efficiency $\eta_q^{[a]}$ [%]	Cage escape yield $\eta_{\text{ce}}^{[b]}$ [%]	Comment
4-AM	9.6 ^[c]	> 99 (2.1)	73	–
CyBF_3K	0.27 ^[c]	91 (2.0)	27	–
DABCO	250 ^[a]	> 99 (1.45)	< 8	upper limit for η_{ce}
DABSO	12 ^[a]	98.5 (0.27)	< 7	upper limit for η_{ce}
Ph_2IPF_6	–	–	–	no quenching

[a] Obtained from lifetime determinations under the conditions of the cage escape yield measurements. Quencher concentrations in mM are given in brackets, [b] Absolute yield of reduced complex $[\text{Cr}(\text{tpe})_2]^{2+}$ normalized to 100% quenching efficiency determined using quantitative LFP, [c] Obtained through Stern-Volmer analysis. See text for details.

characteristic bands of $[\text{Cr}(\text{ddpd})_2]^{2+}$ cannot be observed on long time scales (Supporting Information, Figures S12–S13).^[65] Yet, the potentially detrimental effect of the $[\text{Cr}(\text{ddpd})_2]^{2+}$ decomposition might be limited by a fast regeneration to $[\text{Cr}(\text{ddpd})_2]^{3+}$ (see below). LFP experiments with $[\text{Cr}(\text{ddpd})_2]^{3+}$ employing 4-AM as reductive quencher show $[\text{Cr}(\text{ddpd})_2]^{2+}$ decaying on a timescale of a few tens of microseconds and very high 4-AM concentrations (200 mM) had to be used to separate

the $[\text{Cr}(\text{ddpd})_2]^{2+}$ formation and decay (Supporting Information, Figure S14).

All three chromium(III) complexes should be competent photocatalysts based on their excited state lifetimes and excited state redox potentials, except $[\text{Cr}(\text{ddpd})_2]^{3+}$ with the CyBF_3K substrate (Figure 1). While $[\text{Cr}(\text{bpmp})_2]^{3+}$ reacts with the substrates already in its ground state in an acid-base reaction, $[\text{Cr}(\text{ddpd})_2]^{3+}$ is stable in the presence of the substrates, in its ground and excited state $^*[\text{Cr}(\text{ddpd})_2]^{3+}$ but not in its reduced state $[\text{Cr}(\text{ddpd})_2]^{2+}$. $[\text{Cr}(\text{tpe})_2]^{3+}$ is stable in the presence of the substrates, in its excited state $^*[\text{Cr}(\text{tpe})_2]^{3+}$ and in its reduced form $[\text{Cr}(\text{tpe})_2]^{2+}$. The catalytic experiments towards visible light-induced fixation of SO_2 (Scheme 1b,c, Tables 2 and 3) were conducted with all photosensitizers.

Without a sensitizer, no product forms (Table 2, entry 1; Scheme 1b) or merely a slow background reaction occurs (Table 3, entry 1; Scheme 1c). The slow light-induced background reaction (Table 3, entry 1) has been noted before.^[60] Hypervalent iodine has been observed to form electron donor-acceptor (EDA) complexes^[66] with nucleophiles or electron-rich arenes,^[67–70] e.g. the EDA complex of diphenyl iodonium hexafluorophosphate and *N*-methylpyrrol.^[70] Hence, we surmise that the diphenyl iodonium cation $[\text{Ph}_2\text{I}]^+$ can form an analogous EDA complex with the SO_2 adduct $[\text{R}_2\text{N}-\text{NH}-\text{SO}_2]^-$ of deprotonated 4-AM. Indeed, DFT / time-dependent DFT calculations (Supporting Information, Figure S15) suggest that the ion pair $[\text{Ph}_2\text{I}][\text{R}_2\text{N}-\text{NH}-\text{SO}_2]$ possesses an absorption band at 373 nm that tails into the visible spectral region. This transition possesses ion pair charge transfer (IPCT) character shifting electron density from the hydrazide to the σ^* orbital of the iodonium C–I bond. Excitation of this IPCT would thus lead to photoreduction of $[\text{Ph}_2\text{I}]^+$ forming $\text{Ph}^\bullet$ and PhI and photo-oxidation of the hydrazide to the radical $[\text{R}_2\text{N}-\text{NH}-\text{SO}_2]^\bullet$. Radical recombination of $\text{Ph}^\bullet$ and $[\text{R}_2\text{N}-\text{NH}-\text{SO}_2]^\bullet$ in the solvent cage would yield the final sulfonamide $\text{R}_2\text{N}-\text{NH}-\text{SO}_2\text{Ph}$.

Expectedly, $[\text{Cr}(\text{bpmp})_2]^{3+}$ does not lead to any product formation or conversion beyond the background reaction (Table 2, entry 2; Table 3, entries 3–6), which is easily accounted for by its ground state reactivity towards the substrates CyBF_3K or 4-AM. The formation of the strongly colored deprotonated $[\text{Cr}(\text{bpmp})(\text{bpmp}-\text{H})]^{2+}$ ion (Supporting Information, Fig. S3) even diminishes the light-induced background reaction due to an inner filter effect (Table 3, entries 1, 3–6).

$[\text{Cr}(\text{ddpd})_2]^{3+}$ does not furnish any sulfone as well (Table 2, entry 3), but gives the sulfonamide in 43–58% yield (Table 3, entries 7–12). Although $^*[\text{Cr}(\text{ddpd})_2]^{3+}$ is quenched by CyBF_3K ($k_q = 0.12 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), the regeneration of $[\text{Cr}(\text{ddpd})_2]^{2+}$ might be too slow in the former reaction. Quenching of 4-AM by $^*[\text{Cr}(\text{ddpd})_2]^{3+}$ is faster ($k_q = 9.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), initially forming $[\text{Cr}(\text{ddpd})_2]^{2+}$. The regeneration of $[\text{Cr}(\text{ddpd})_2]^{3+}$ ($E_{1/2} = -1.11 \text{ V}$; Figure 1) by the diphenyliodonium salt ($E_p = -0.77 \text{ V}$, Supporting Information, Figure S16; Scheme 2b) seems to be sufficiently fast to be competitive with the decomposition of the labile $[\text{Cr}(\text{ddpd})_2]^{2+}$ ion. Comparative LFP studies under conditions of fast $[\text{Cr}(\text{ddpd})_2]^{2+}$ and $[\text{Cr}(\text{tpe})_2]^{2+}$ generation clearly demonstrate that the former efficiently reacts with the iodonium salt, whereas the reaction with the latter is slower by orders of

Table 2. Visible-light mediated fixation of SO_2 into sulfones with Cr^{III} photocatalysts in CH_3CN , 18 h, $\lambda_{\text{max}} = 430 \text{ nm}$.

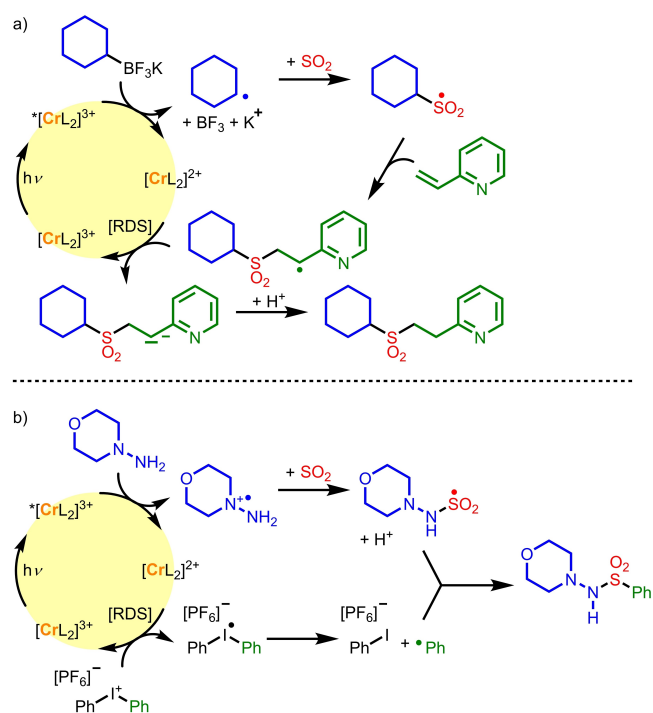
Entry	Photocatalyst $[\text{CrL}_2]^{3+}$	Loading [mol %]	Spectroscopic ^[a] (isolated) yield [%]	variations from standard conditions
1	none	–	–	
2	$[\text{Cr}(\text{bpmp})_2][\text{OTf}]_3$	2	–	
3	$[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$	2	–	
4	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	2	16 (13)	
5	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	5	36 (33)	
6	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	10	25	
7	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	2	traces	no light
8	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	5	33 (31)	not degassed
9	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	5	13	open to air
10	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	2	31 (29)	SO_2 solution
11	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	5	46 (44)	SO_2 solution (4 eq.)
12	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	5	67 (63)	SO_2 solution (2 eq.)

[a] NMR yield using CH_2Br_2 as internal reference.

Table 3. Visible-light mediated fixation of SO_2 into sulfonamides with Cr^{III} photocatalysts in CH_3CN , 18 h, $\lambda_{\text{max}} = 430 \text{ nm}$.

Entry	Photocatalyst $[\text{CrL}_2]^{3+}$	Loading [mol %]	Spectroscopic ^[a] (isolated) yield [%]	variations from standard conditions
1	none	–	15–18	
2	none	–	–	no light, 30 °C
3	$[\text{Cr}(\text{bpmp})_2][\text{OTf}]_3$	2	7	
4	$[\text{Cr}(\text{bpmp})_2][\text{OTf}]_3$	5	5	
5	$[\text{Cr}(\text{bpmp})_2][\text{OTf}]_3$	10	7	
6	$[\text{Cr}(\text{bpmp})_2][\text{OTf}]_3$	10	6	no light
7	$[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$	2	43 (41)	
8	$[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$	2	58 (56)	not degassed
9	$[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$	2	15	open to air
10	$[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$	2	51 (49)	SO_2 solution (2 eq.)
11	$[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$	5	56 (55)	
12	$[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$	10	42 (40)	
13	$[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$	2	traces	no light
14	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	2	33 (31)	
15	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	5	26	
16	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	10	12	
17	$[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$	2	13	no light

[a] NMR yield using CH_2Br_2 as internal reference.



Scheme 2. a) Proposed mechanism of the chromium(III) photocatalyzed SO_2 fixation to sulfone and b) proposed mechanism of the chromium(III) photocatalyzed SO_2 fixation to sulfonamide (RDS = rate determining step).

magnitude (Supporting Information, Figures S17–19). Expectedly, $[\text{Cr}(\text{ddpd})_2]^{3+}$ does not react with the iodonium salt (Supporting Information, Figure S20).

The $[\text{Cr}(\text{tpe})_2]^{3+}$ photosensitizer is moderately active in both SO_2 fixation reactions (Table 2, entries 4–12; Table 3, entries 14–16, Scheme 2). Slow photocatalyst regeneration as the rate determining step (RDS), as already observed in the presence of the diphenyliodonium salt, might be responsible for its moderate activity (Scheme 2). Unexpectedly, increasing the catalyst loading from 5 to 10 mol% does not lead to higher yields, but the yields drop instead. This might be a consequence of the slow $[\text{Cr}(\text{tpe})_2]^{3+}$ regeneration, which results in accumulation of highly colored $[\text{Cr}(\text{tpe})_2]^{2+}$ (Figure 2) with a molar absorption coefficient at 430 nm 147 times higher than that of the photocatalyst $[\text{Cr}(\text{tpe})_2]^{3+}$ (Supporting Information, Figure S9).^[58] The presence of traces of oxygen does not influence the outcome of the CyBF_3K transformation (Table 2, entries 5 and 8). An open reaction vessel (excess of O_2 or loss of SO_2) significantly retards the reaction (Table 2, entry 9). On the other hand, traces of oxygen display a beneficial role in the reaction with 4-AM (Table 3, entry 8). Oxygen might lead to a faster catalyst regeneration in this case, so that the $\text{O}_2/\text{O}_2^{\bullet-}$ pair acts as a redox shuttle. The importance of oxygen as redox mediator has been noted before in chromium(III) photocatalytic reactions.^[48–51] An open reaction vessel (excess of O_2 or loss of SO_2) significantly hampers the reaction (Table 3, entry 9).

The surrogate DABSO was chosen as SO_2 source for both model reactions (Scheme 1b,c). DABSO is only poorly soluble in CH_3CN and the reaction mixtures are suspensions during the

catalytic experiments. Freshly prepared DABSO solutions likely contain a certain amount of free DABCO. Furthermore, DABCO will continuously form from reacted DABSO as the photo-reaction proceeds. ^1H NMR spectra of DABCO/DABSO mixtures show only a single set of resonances suggesting that SO_2 rapidly transfers between the two (Supporting Information, Figure S21). The formed DABCO as well as DABSO itself is also able to react with excited $[\text{Cr}(\text{tpe})_2]^{3+}$ and $[\text{Cr}(\text{ddpd})_2]^{3+}$ species (Figure 1; Supporting Information, Figures S22–S25) and indeed the emission of $[\text{Cr}(\text{tpe})_2]^{3+}$ and $[\text{Cr}(\text{ddpd})_2]^{3+}$ is quenched by DABCO (Supporting Information, Figures S26–S27). The oxidation potentials of DABSO and DABCO are lower than the excited state potentials of the photocatalysts, allowing for reductive quenching (Figure 1, Supporting Information, Figures S28–S29). This potential parallel quenching process might influence the reaction rates or even the yields of the photoreactions employing DABSO as SO_2 source.

To test this hypothesis, we employed SO_2 dissolved in CH_3CN instead of DABSO. Indeed, the yields of the sulfone and sulfonamide increased up to 67% and 51%, respectively (Table 2, entries 10–12; Table 3, entry 10). Detailed cage escape studies with both DABCO and DABSO (Table 1) revealed that quenching with these additives in our reaction mixtures is fast yet extremely unproductive. This explains why they do not inhibit the reaction completely, but merely reduce the achievable yields by about 10–30%. Consequently, (i) it is mandatory to consider all reaction products as potential quenchers for the photocatalysts and (ii) emission quenching studies alone do not provide a clear picture for competing reaction pathways. This finding definitely applies to the chromium(III)-catalyzed reactions studied here as well as to photo(redox) catalytic processes in general.

Conclusion

In this proof-of-concept and mechanistic study of three polypyridine chromium(III) photosensitizers $[\text{Cr}(\text{bpmp})_2]^{3+}$, $[\text{Cr}(\text{ddpd})_2]^{3+}$ and $[\text{Cr}(\text{tpe})_2]^{3+}$, two three-component visible light SO_2 fixation reactions and two different SO_2 sources, $[\text{Cr}(\text{ddpd})_2]^{3+}$ and $[\text{Cr}(\text{tpe})_2]^{3+}$ have been identified as suitable photoredox catalysts to give alkylsulfones or *N*-aminosulfonamides.

Crucial aspects in these multi-component photoreactions are the ground state stability of the photocatalysts $[\text{Cr}(\text{L})_2]^{3+}$ under the reaction conditions (e.g. deprotonation of $[\text{Cr}(\text{bpmp})_2]^{3+}$ by amines), their excited state redox potentials and lifetimes, the quenching efficiency by the various substrates (and by-products, e.g. DABCO) of the multi-component reactions, the cage escape yields after the electron transfer (< 7% to 73%) and the catalyst regeneration rate combined with the stability and absorptivity of the reduced photocatalysts $[\text{Cr}(\text{L})_2]^{2+}$ (e.g. decomposition of $[\text{Cr}(\text{ddpd})_2]^{2+}$ and inner filter effect with accumulated $[\text{Cr}(\text{tpe})_2]^{2+}$).

The two successful examples with $[\text{Cr}(\text{ddpd})_2]^{3+}$ and $[\text{Cr}(\text{tpe})_2]^{3+}$ photocatalysts clearly demonstrate the potential of chromium(III) complexes as earth-abundant metal photosensi-

tizers for a visible-light driven fixation of SO₂. The yields of alkylsulfone and *N*-aminosulfonamide can certainly be improved in the future, for example by optimization of the redox potentials of the chromium(III) photocatalyst by ligand design, avoiding heterogeneous reaction conditions and by adaption of suitable SO₂ sources. Furthermore, the high cage escape yields obtained with [Cr(tpe)₂]³⁺ indicate an enormous potential for the further development of efficient photoredox applications with chromium(III) photocatalysts. This is currently actively pursued in our laboratories.

Experimental Section

Details of the spectroscopic and analytic methods and experiments can be found in the Supporting Information.

General photocatalytic SO₂ fixation to give an alkylsulfone: In a typical reaction 2-vinylpyridine (0.25 mmol, 1.0 eq.), potassium cyclohexyltrifluoroborate CyBF₃K (0.375 mmol, 1.5 eq.), DABSO (0.25 mmol, 1.0 eq.) and the chromium(III) photocatalyst were combined in 2.5 mL of CH₃CN. The resulting suspension of a colorless precipitate in a yellow solution was degassed for 15 minutes in an ultrasonic bath. The reaction mixture was irradiated ($\lambda_{\text{max}} = 430$ nm) for 18 h at room temperature. The suspension was subsequently purified by column chromatography (SiO₂, *n*-hexane:ethylacetate=20:1 → 3:2). The solvent mixture was removed under reduced pressure and the product was isolated as a colorless solid. When a solution of 2 M SO₂ in CH₃CN was used instead of DABSO, it was added to the mixture only after the degassing step. NMR data of the product matched literature values (Supporting Information, Figures S30–S31).^[59]

General photocatalytic SO₂ fixation to give an *N*-aminosulfonamide: In a typical reaction diphenyliodonium hexafluorophosphate Ph₂IPF₆ (0.25 mmol, 1.0 eq.), 4-aminomorpholine 4-AM (0.375 mmol, 1.5 eq.), DABSO (0.25 mmol, 1.0 eq.) and the chromium(III) photocatalyst were combined in 2.5 mL of CH₃CN. The resulting suspension of a colorless precipitate in a yellow solution was degassed for 15 minutes in an ultrasonic bath. The reaction mixture was irradiated ($\lambda_{\text{max}} = 430$ nm) for 18 h at room temperature. The suspension was subsequently purified by column chromatography (SiO₂, *n*-hexane:ethylacetate=20:1 → 3:2). The solvent mixture was removed under reduced pressure and the product was isolated as colorless solid. NMR data of the product matched literature values (Supporting Information, Figures S32–S33).^[60]

Acknowledgements

[Redacted Acknowledgements]

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 supplementary material of this article.

Keywords: Chromium · Photochemistry · Photoredox Catalysis · SO₂ fixation · Sulfonamides

- [1] H. Müller, Sulfur Dioxide, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, Germany, 35th edn, 2000.
- [2] E. Poujol, in *Gases in Agro-Food Processes*, ed. R. Cachon, P. Girardon, A. Voilley, Elsevier, Academic Press, 2019, pp. 75–85.
- [3] P. Vogel, M. Turks, L. Bouchez, D. Marković, A. Varela-Álvarez, J. Á. Sordo, *Acc. Chem. Res.* 2007, 40, 931–942.
- [4] Q. Zhong, H. Shen, X. Yun, Y. Chen, Y. Ren, H. Xu, G. Shen, W. Du, J. Meng, W. Li, J. Ma, S. Tao, *Environ. Sci. Technol.* 2020, 54, 6508–6517.
- [5] P. Grennfelt, A. Englerød, M. Forsius, Ø. Hov, H. Rodhe, E. Cowling, *Ambio* 2020, 49, 849–864.
- [6] A. S. Deeming, E. J. Emmett, C. S. Richards-Taylor, M. C. Willis, *Synthesis* 2014, 2701–2710.
- [7] G. Liu, C. Fan, J. Wu, *Org. Biomol. Chem.* 2015, 13, 1592–1599.
- [8] P. Bissleret, N. Blanchard, *Org. Biomol. Chem.* 2013, 11, 5393–5398.
- [9] K. Hofman, N.-W. Liu, G. Manolikakes, *Chem. Eur. J.* 2018, 24, 11852–11863.
- [10] D. Zeng, M. Wang, W.-P. Deng, X. Jiang, *Org. Chem. Front.* 2020, 7, 3956–3966.
- [11] K. Suta, M. Turks, *Chem. Heterocycl. Compd.* 2018, 54, 584–586.
- [12] M. C. Willis, *Phosphorus Sulfur Relat. Elem.* 2019, 194, 654–657.
- [13] G. Qiu, K. Zhou, L. Gao, J. Wu, *Org. Chem. Front.* 2018, 5, 691–705.
- [14] M. Feng, B. Tang, S. H. Liang, X. Jiang, *Curr. Top. Med. Chem.* 2016, 16, 1200–1216.
- [15] K. A. Scott, J. T. Njardarson, *Top. Curr. Chem.* 2018, 376, 5.
- [16] N.-W. Liu, S. Liang, G. Manolikakes, *Synthesis* 2016, 1939–1973.
- [17] S. Liang, K. Hofman, M. Friedrich, J. Keller, G. Manolikakes, *ChemSusChem* 2021, 14, 4878–4902.
- [18] H. Woolven, C. González-Rodríguez, I. Marco, A. L. Thompson, M. C. Willis, *Org. Lett.* 2011, 13, 4876–4878.
- [19] E. J. Emmett, M. C. Willis, *Asian J. Org. Chem.* 2015, 4, 602–611.
- [20] J. A. Andrews, M. C. Willis, *Synthesis* 2022, 54, 1695–1707.
- [21] S. Ye, X. Li, W. Xie, J. Wu, *Eur. J. Org. Chem.* 2020, 1274–1287.
- [22] S. P. Blum, K. Hofman, G. Manolikakes, S. R. Waldvogel, *Chem. Commun.* 2021, 57, 8236–8249.
- [23] Z. Chen, N.-W. Liu, M. Bolte, H. Ren, G. Manolikakes, *Green Chem.* 2018, 20, 3059–3070.
- [24] A. M. Nair, I. Halder, S. Khan, C. M. R. Volla, *Adv. Synth. Catal.* 2020, 362, 224–229.
- [25] N.-W. Liu, Z. Chen, A. Herbert, H. Ren, G. Manolikakes, *Eur. J. Org. Chem.* 2018, 5725–5734.
- [26] a) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* 2011, 40, 102–113; b) R. C. McAtee, E. J. McClain, C. R. J. Stephenson, *Illuminating Photoredox Catalysis, Trends in Chemistry*, Vol. 1, Issue 1, 2019, Pages 111–125.
- [27] a) M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* 2016, 81, 6898–6926; b) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* 2010, 2, 527–532; c) K. Zeitler, *Angew. Chem. Int. Ed.* 2009, 48, 9785–9789; *Angew. Chem.* 2009, 121, 9969–9974.
- [28] L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* 2018, 57, 10034–10072; *Angew. Chem.* 2018, 130, 10188–10228.
- [29] J. Zhu, W.-C. Yang, X. Wang, L. Wu, *Adv. Synth. Catal.* 2018, 360, 386–400.
- [30] W. Guo, K. Tao, W. Tan, M. Zhao, L. Zheng, X. Fan, *Org. Chem. Front.* 2019, 6, 2048–2066.
- [31] A. Wimmer, B. König, *Beilstein J. Org. Chem.* 2018, 14, 54–83.
- [32] N. A. Romero, D. A. Nicewicz, *Chem. Rev.* 2016, 116, 10075–10166.
- [33] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* 2013, 113, 5322–5363.
- [34] W. R. Kitzmann, K. Heinze, *Angew. Chem. Int. Ed.* 2023, e202213207.
- [35] a) C. B. Larsen, O. S. Wenger, *Chem. Eur. J.* 2018, 24, 2039–2058; b) O. S. Wenger, *J. Am. Chem. Soc.* 2018, 140, 13522–13533.

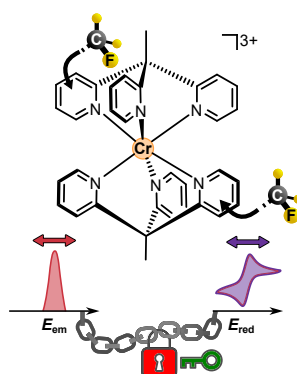
- [36] a) B. M. Hockin, C. Li, N. Robertson, E. Zysman-Colman, *Catal. Sci. Technol.* **2019**, *9*, 889–915; b) C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, *49*, 1057–1070.
- [37] R. Giereth, I. Reim, W. Frey, H. Junge, S. Tschierlei, M. Karnahl, *Sustain. Energy Fuels* **2019**, *3*, 692–700.
- [38] A. Hossain, A. Bhattacharyya, O. Reiser, *Science* **2019**, *364*, 450.
- [39] D. B. Bagal, G. Kachkovskiy, M. Knorn, T. Rawner, B. M. Bhanage, O. Reiser, *Angew. Chem. Int. Ed.* **2015**, *54*, 6999–7002; *Angew. Chem.* **2015**, *127*, 7105–7108.
- [40] T. Rawner, M. Knorn, E. Lutscher, A. Hossain, O. Reiser, *J. Org. Chem.* **2016**, *81*, 7139–7147.
- [41] S. K. Pagire, S. Paria, O. Reiser, *Org. Lett.* **2016**, *18*, 2106–2109.
- [42] X. J. Tang, W. R. Dolbier, *Angew. Chem. Int. Ed.* **2015**, *54*, 4246–4249; *Angew. Chem.* **2015**, *127*, 4320–4323.
- [43] L. A. Büldt, O. S. Wenger, *Chem. Sci.* **2017**, *8*, 7359–7367.
- [44] S. Otto, M. Dorn, C. Förster, M. Bauer, M. Seitz, K. Heinze, *Coord. Chem. Rev.* **2018**, *359*, 102–111.
- [45] W. R. Kitzmann, C. Ramanan, R. Naumann, K. Heinze, *Dalton Trans.* **2022**, *51*, 6519–6525.
- [46] P. A. Scattergood, in *Organometallic Chemistry*, Vol. 43 (Eds.: N. J. Patmore, P. I. P. Elliott), Royal Society of Chemistry, Cambridge, **2020**, pp. 1–34.
- [47] L. Stein, C. Wang, C. Förster, U. Resch-Genger, K. Heinze, *Dalton Trans.* **2022**, *51*, 17664–17670.
- [48] a) S. M. Stevenson, M. P. Shores, E. M. Ferreira, *Angew. Chem. Int. Ed.* **2015**, *54*, 6506–6510; *Angew. Chem.* **2015**, *127*, 6606–6610; b) R. F. Higgins, S. M. Fatur, S. G. Shepard, S. M. Stevenson, D. J. Boston, E. M. Ferreira, N. H. Damrauer, A. K. Rappe, M. P. Shores, *J. Am. Chem. Soc.* **2016**, *138*, 5451–5464.
- [49] a) S. M. Stevenson, R. F. Higgins, M. P. Shores, E. M. Ferreira, *Chem. Sci.* **2017**, *8*, 654–660; b) B. K. Gall, A. K. Smith, E. M. Ferreira, *Angew. Chem. Int. Ed.* **2022**, e202212187.
- [50] C. Förster, K. Heinze, *Chem. Phys. Rev.* **2022**, *3*, 041302.
- [51] S. Sittel, R. Naumann, K. Heinze, *Front. Chem.* **2022**, *10*, 887439.
- [52] S. Otto, A. M. Nauth, E. Emilov, N. Scholz, A. Friedrich, U. Resch-Genger, S. Lochbrunner, T. Opatz, K. Heinze, *ChemPhotoChem* **2017**, *1*, 344–349.
- [53] C. Wang, F. Reichenauer, W. R. Kitzmann, C. Kerzig, K. Heinze, U. Resch-Genger, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202238.
- [54] T. H. Bürgin, F. Glaser, O. S. Wenger, *J. Am. Chem. Soc.* **2022**, *144*, 14181–14194.
- [55] S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572–11576; *Angew. Chem.* **2015**, *127*, 11735–11739.
- [56] C. Wang, S. Otto, M. Dorn, E. Kreidt, J. Lebon, L. Sršan, P. Di Martino-Fumo, M. Gerhards, U. Resch-Genger, M. Seitz, K. Heinze, *Angew. Chem. Int. Ed.* **2018**, *57*, 1112–1116; *Angew. Chem.* **2018**, *130*, 1125–1130.
- [57] F. Reichenauer, C. Wang, C. Förster, P. Boden, N. Ugur, R. Báez-Cruz, J. Kalmbach, L. M. Carrella, E. Rentschler, C. Ramanan, G. Niedner-Schatteburg, M. Gerhards, M. Seitz, U. Resch-Genger, K. Heinze, *J. Am. Chem. Soc.* **2021**, *143*, 11843–11855.
- [58] S. Treiling, C. Wang, C. Förster, F. Reichenauer, J. Kalmbach, P. Boden, J. P. Harris, L. Carrella, E. Rentschler, U. Resch-Genger, C. Reber, M. Seitz, M. Gerhards, K. Heinze, *Angew. Chem. Int. Ed.* **2019**, *58*, 18075–18085; *Angew. Chem.* **2019**, *131*, 18243–18253.
- [59] T. Liu, Y. Li, L. Lai, J. Cheng, J. Sun, J. Wu, *Org. Lett.* **2018**, *20*, 3605–3608.
- [60] N.-W. Liu, S. Liang, G. Manolikakes, *Adv. Synth. Catal.* **2017**, *359*, 1308–1319.
- [61] a) G. J. Kavarnos, N. J. Turro, *Chem. Rev.* **1986**, *86*, 401–449; b) S. Neumann, O. S. Wenger, C. Kerzig, *Chem. Eur. J.* **2021**, *27*, 4115–4123; c) L. Troian-Gautier, W. B. Swords, G. J. Meyer, *Acc. Chem. Res.* **2019**, *52*, 170–179; d) K. Miedlar, P. K. Das, *J. Am. Chem. Soc.* **1982**, *104*, 7462–7469; e) J. Olmsted, T. J. Meyer, *J. Phys. Chem.* **1987**, *91*, 1649–1655.
- [62] a) R. Naumann, M. Goetz, *Chem. Eur. J.* **2018**, *24*, 17557–17567; b) A. Aydogan, R. E. Bangle, A. Cadranet, M. D. Turlington, D. T. Conroy, E. Cauët, M. L. Singleton, G. J. Meyer, R. N. Sampaio, B. Elias, L. Troian-Gautier, *J. Am. Chem. Soc.* **2021**, *143*, 15661–15673; c) C. Kerzig, M. Goetz, *Phys. Chem. Chem. Phys.* **2014**, *16*, 25342–25349.
- [63] a) S. Neumann, C. Kerzig, O. S. Wenger, *Chem. Sci.* **2019**, *10*, 5624–5633; b) P. Müller, K. Brettel, *Photochem. Photobiol. Sci.* **2012**, *11*, 632–636.
- [64] N. Kaul, R. Lomoth, *J. Am. Chem. Soc.* **2021**, *143*, 10816–10821.
- [65] P. M. Becker, C. Förster, L. M. Carrella, P. Boden, D. Hunger, J. van Slageren, M. Gerhards, E. Rentschler, K. Heinze, *Chem. Eur. J.* **2020**, *26*, 7199–7204.
- [66] G. E. M. Crisenza, D. Mazzarella, P. Melchiorre, *J. Am. Chem. Soc.* **2020**, *142*, 5461–5476.
- [67] B. Liu, C.-H. Lim, G. M. Miyake, *J. Am. Chem. Soc.* **2018**, *140*, 12829–12835.
- [68] Y. Kita, H. Tohma, K. Hatanaka, T. Takada, S. Fujita, S. Mitoh, H. Sakurai, S. Oka, *J. Am. Chem. Soc.* **1994**, *116*, 3684–3691.
- [69] T. Dohi, M. Ito, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, *Angew. Chem. Int. Ed.* **2010**, *49*, 3334–3337; *Angew. Chem.* **2010**, *122*, 3406–3409.
- [70] M. Tobisu, T. Furukawa, N. Chatani, *Chem. Lett.* **2013**, *42*, 1203–1205.
- [71] S. Pal, A.-C. Gaumont, S. Lakhdar, I. Gillaizeau, *Org. Lett.* **2019**, *21*, 5621–5625.
- [72] W. Lecroq, P. Bazille, F. Morlet-Savary, M. Breugst, J. Lalevée, A.-C. Gaumont, S. Lakhdar, *Org. Lett.* **2018**, *20*, 4164–4167.

Manuscript received: December 9, 2022
 Revised manuscript received: January 23, 2023
 Accepted manuscript online: January 23, 2023
 Version of record online: March 1, 2023

3.4 Decoupling Redox Potentials and Excited State Energies in Substituted Chromium(III) Chromophores

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Chem. Eur. J. 2025, submitted.



Excited-state energies and reduction potentials are tightly linked in almost all photocatalysts. Thus, it is usually impossible to adjust these properties independently. In contrast, substitution of $[\text{Cr}(\text{tpe})_2]^{3+}$ with one or two trifluoromethyl-groups permitted an anodic shift of the reduction potential by ca. 100 and 200 mV respectively, while leaving the emission energy effectively unaltered. The successful decoupling of these properties is explained by the almost purely metal-centered nature of the excited doublet states and the (mostly) ligand-centered reduction in these $[\text{Cr}(\text{tpe})_2]^{3+}$ -derivatives, which is supported by experimental evidence and quantum chemical calculations.

Author Contributions

Steven Sittel synthesized and characterized the ligand tpe^{CF_3} and the CF_3 -substituted complexes as well as their reduced counterparts, conducted cyclic voltammetry, optical spectroscopy and quantum chemical calculations. [REDACTED] developed the HPLC-methods and purified the complexes. [REDACTED] synthesized and crystallized the precursor $\text{Cr}(\text{OTf})_3(\text{tpe})$. [REDACTED] contributed to the synthesis and purification and characterization of the ligand and the complex $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$. [REDACTED] solved and refined the XRD structure of $\text{Cr}(\text{OTf})_3(\text{tpe})$ (CCDC no. 2479151) and assisted with quantum chemical calculations. [REDACTED] designed the project and helped with the measurement and

interpretation of the experimental data. [REDACTED] designed the project, helped with the interpretation of the data and wrote the manuscript. All authors discussed the scientific results and contributed to the final version of the manuscript.

Supporting Information

for this article can be found on pp. 254.

Decoupling Redox Potentials and Excited State Energies in Substituted Chromium(III) Chromophores

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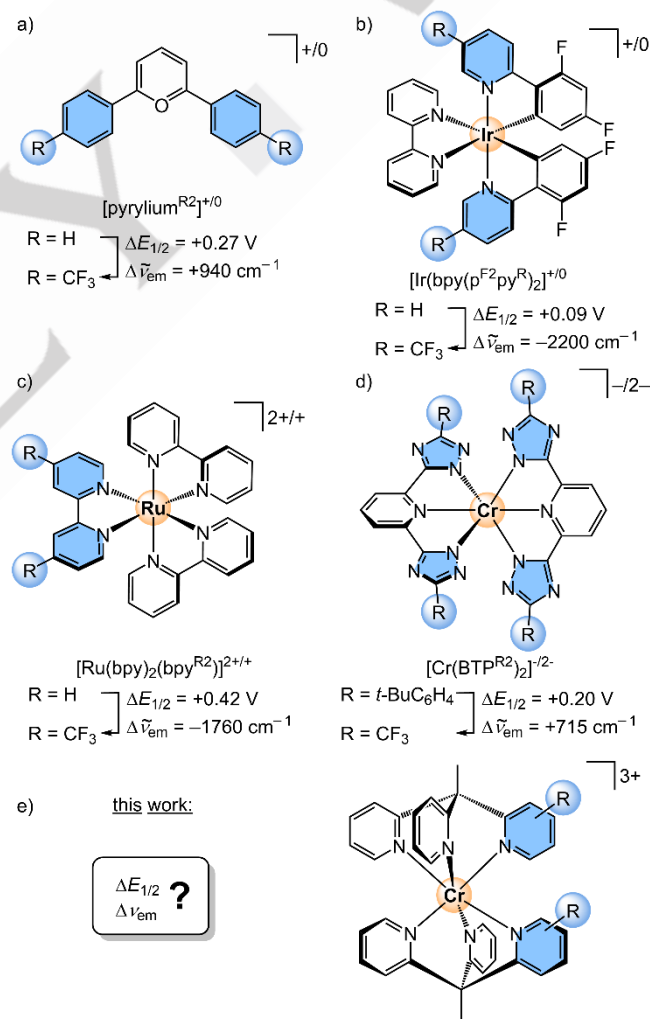
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Abstract: Redox and excited state properties of classical organic and precious metal charge-transfer photocatalysts can be tuned by substituent effects – however, not independently as redox and chromophore units are strongly entangled. In contrast, substituent effects should selectively address electrochemical properties of photoactive complexes based on metal-centred spin-flip excited states lacking charge-transfer character without compromising excited state properties. Yet, detailed structure-activity relationships for spin-flip chromophores are lacking. We demonstrate that the redox potentials of polypyridine chromium(III) complexes, that feature purely metal-centred spin-flip states, can be selectively tuned by incremental substituent effects, while the excited state energies and lifetimes remain unaffected. This delivers a unique series of chromophores with identical optical properties, but redox potentials tuned by increments. We believe, that such precisely designed chromophore series provide a unique tool for the systematic investigation of photoredox reactions and recombination processes relevant to photoredox catalytic cycles.

Introduction

Long excited state lifetimes, tunable redox potentials and high photo- and redox stabilities mark desirable properties of photoactive materials. An electron-withdrawing or donating substituent^[1] located close to the redox-active moiety of a molecule, for example when a coordinated ligand is reduced or oxidized, will affect the redox potentials. Similarly, electron-withdrawing or -donating substituents affect the wavefunction of the chromophoric moiety, so that excited state properties will be modified by substituent effects as well. Due to the entanglement of redox and chromophoric units of typical organic and metal complex charge-transfer (CT) chromophores, substituents influence both properties concomitantly.^[2-6] This concept is often simply described by the respective HOMOs and LUMOs and their energies. This seemingly general finding has been amply demonstrated with organic emitters and CT metal complex emitters,^[2-5] such as cyanoarenes,^[7] 9-mesityl acridinium ions,^[8,9] pyrylium ions^[10] or ruthenium(II), iridium(III) or copper(I)

derivatives (see Scheme 1 for selected examples of CF₃ substitution).^[11-17]



Scheme 1. a) – d) Effects of CF₃ substitution on redox potential $E_{1/2}$ and emission energy ν_{em} in typical organic and inorganic chromophores^[10-13,14,17] and e) chromium(III) complexes studied in this work.

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The group electronegativity of CF_3 groups ($\text{EN}_{\text{CF}_3} = 3.0$) is similar to the electronegativity of chlorine ($\text{EN}_{\text{Cl}} = 3.0$) on the Pauling scale.^[18] Hence, trifluoromethyl substituents are expected to substantially affect redox and excited state properties in organic and CT chromophores. For example, substituting pyrylium cations $[\text{pyrylium}]^+$ with two CF_3 groups increases the $[\text{pyrylium}]^{+/0}$ potential by $\Delta E_{1/2} = +0.27$ V and shifts the fluorescence band by $\Delta \tilde{\nu}_{\text{em}} = +940$ cm^{-1} to higher energies (Scheme 1a).^[10] Installation of CF_3 substituents at the pyridine donors in 5-position in $[\text{Ir}(\text{bpy})(\text{ppy}^{\text{F2,R}})_2]^+$ complexes increases the $[\text{Ir}(\text{bpy})(\text{ppy}^{\text{F2,R}})_2]^{+/0}$ potential by +0.09 V and lowers the emission energy by -2200 cm^{-1} (Scheme 1b, bpy = 2,2'-bipyridine; Hppy = 2-phenylpyridine).^[14] Strong effects on both redox potentials and excited state energies (absorption or emission) were observed by $\text{CH}_3 \rightarrow \text{CF}_3$ substitution on β -diketiminato ancillary ligands in copper(I) and cyclometalated iridium(III) complexes.^[15,16] Two CF_3 substituents in a 4,4'-substituted bipyridine ligand shift the potential of the $[\text{Ru}(\text{bpy})_3]^{2+/+}$ couple by +0.42 V to higher values and the emission band maximum by -1760 cm^{-1} (Scheme 1c).^[13]

Tripodal pyridine ligands can impart favorable photophysical properties to metal ions, in particular earth-abundant metal ions,^[19–22] including vanadium(II),^[23] chromium(III),^[24–27] iron(II),^[28,29] nickel(II)^[30] and molybdenum(0).^[31,32] This includes long excited state photoluminescence (PL) lifetimes thanks to increased ligand field strengths^[23–30] and/or high local symmetry^[23–27] as well as high (photo)chemical stability due to the *trans* effect.^[31,32] In particular, the extremely long PL lifetime of the spin-flip (SF)^[33–36] excited state of the chromium(III) complex $[\text{Cr}(\text{tpe})_2]^{3+}$ (tpe = 1,1,1-tris(pyrid-2-yl)ethane) with several milliseconds at 293 K,^[24] a useful excited redox potential and exceptional photo and redox stability enables challenging photoredox catalytic reactions, including up-hill processes, re-using and even recycling of the photocatalyst with over 90 % yield.^[24–26] Yet, the distinct influence of substituents on the redox and excited state properties of such SF chromophores is unknown.^[35]

Substituent effects^[1] on the PL energy and lifetime of purely metal-centered SF states without significant ligand contributions, as found in many chromium(III) complexes, are expected to be much smaller than in CT complexes,^[6] while ligand-based redox potentials should be significantly affected. However, installation of two CF_3 units per tridentate ligand in anionic chromium(III) complexes $[\text{Cr}(\text{BTP}^{\text{R2}})_2]^-$ both shifts the redox potential (by +0.20 V) and the emission energy (by +715 cm^{-1}), likely because of ligand admixture to the SF excited states (Scheme 1d).^[17] Hence, the predicted decoupling of redox and excited state properties in pure SF emitters has not been experimentally confirmed.^[6,33] Yet, such a series could be very useful for systematically studying photoinduced electron transfer and competing charge recombination processes^[37] (cage escape)^[38] with tuned ground and excited state redox potentials, but identical excited state energies.

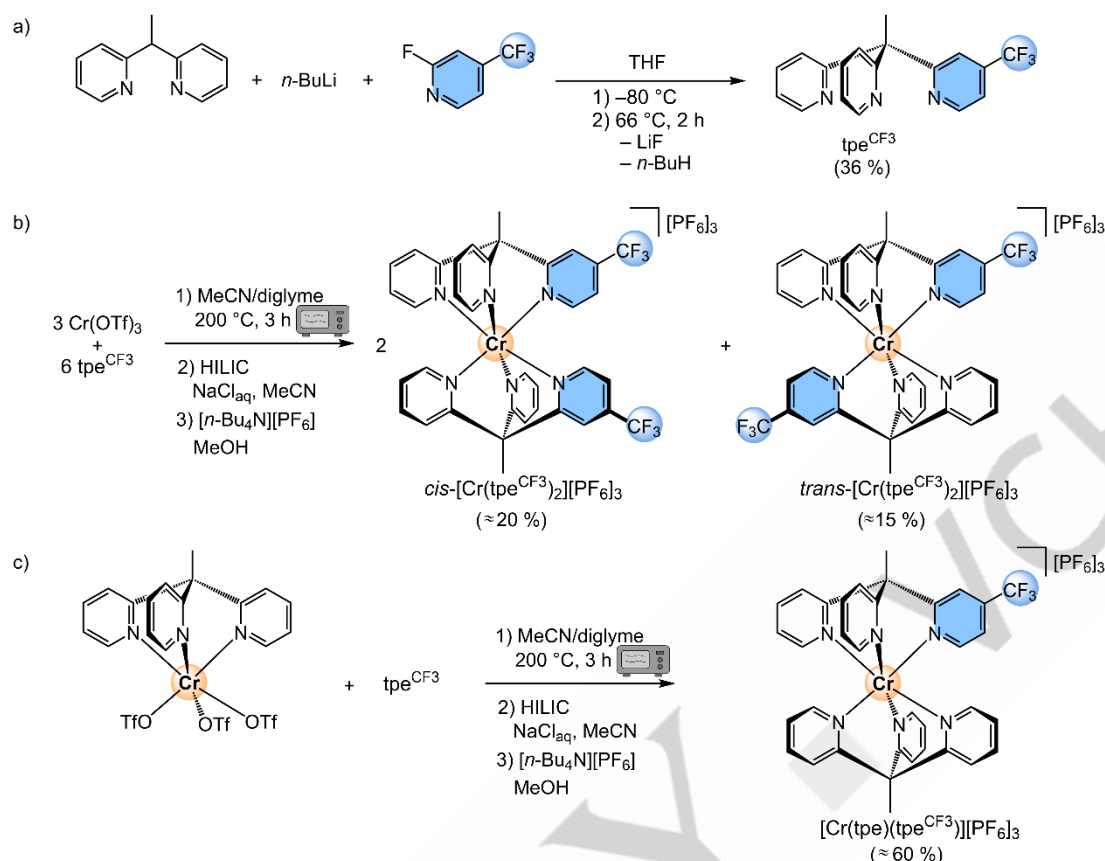
In the present study, we leverage the redox potential of tripodal polypyridine chromium(III) chromophores with very pure metal-centered SF states by installing electron-withdrawing trifluoromethyl substituents^[1,18] at the ligand without

compromising the favorable photophysical properties (Scheme 1e). First, we describe the synthesis of a CF_3 -substituted tripodal pyridine ligand tpe^{CF_3} and delineate a synthetic pathway to coordinate such a very electron-deficient pyridine ligand to already electron-poor chromium(III) ions to give the CF_3 -substituted complexes with one or two trifluoromethyl substituents. Then we discuss the PL and redox properties as well as stabilities of the reduced CF_3 -substituted chromium(III) complexes. Finally, quantum chemical calculations (density functional theory, DFT; complete-active-space self-consistent field-N-electron valence perturbation theory to second order, CASSCF-NEVPT2) underpin the experimental findings, which will allow future *in silico* design of redox-active SF chromophores.

Results and Discussion

Synthesis and Purification. The novel trifluoromethylated tripodal ligand tpe^{CF_3} was obtained in a two-step procedure from commercially available starting materials. 1,1-Bis(2-pyridyl)ethane, prepared from 2-ethylpyridine and 2-fluoropyridine according to a literature procedure,^[39,40] was treated with *n*-butyl lithium and subsequently with 2-fluoro-4-(trifluoromethyl)pyridine to give crystalline tpe^{CF_3} in 38 % isolated yield (Scheme 2a). This new ligand was fully characterized by heteronuclear NMR and IR spectroscopy and mass spectrometry (Figures S1–S8). The bands for the symmetric and asymmetric C–F stretching vibrations of the CF_3 substituent are found at 1329 and 1131 cm^{-1} , respectively.^[41]

Due to the electron-poor nature of the CF_3 -substituted ligand, classical syntheses using substitutionally labile chromium(II) salts^[25,42] or via *in situ* reduction of chromium(III) to chromium(II) with zinc^[43] that worked well for the unsubstituted ligand tpe ,^[25] are not feasible, as chromium(II) ions reduce the tpe^{CF_3} ligand to its radical anion thus preventing complex formation. To coordinate the very electron-poor CF_3 -substituted ligand directly to electron-deficient chromium(III) ions, $\text{Cr}(\text{OTf})_3$ ^[44] with labile triflate ligands^[45,46] was treated with two equivalents of tpe^{CF_3} in a microwave-assisted reaction at 200 °C to give the homoleptic complexes *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (Scheme 2b). HPLC analysis confirmed the presence of a statistical 2:1 mixture of the two isomers (Figure S9). Hydrophilic interaction liquid chromatography (HILIC, Figure S10) succeeded in separating the isomers. Salt metathesis with $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ finally delivered the *cis*- and *trans*-isomers with two CF_3 substituents as yellow, crystalline PF_6 salts (Scheme 2b). Assignment of the *cis/trans* configuration to the two isomeric complexes is first based on the initial statistical *cis:trans* ratio of 2:1 obtained in the synthesis. As further confirmation, an HPLC experiment using a chiral column and detection via circular dichroism spectroscopy was conducted. While the achiral *trans*-isomer is unaffected by the chiral column, the chiral racemic *cis*-isomers split into the enantiomers in a 1:1 ratio on the chiral column (Figure S11) allowing a definitive assignment of the configuration.



Scheme 2. Synthesis of a) the ligand tpe^{CF_3} , b) the homoleptic *cis*- and *trans*-complex isomers $\text{cis-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_3$ and $\text{trans-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_3$ and c) the heteroleptic monosubstituted complex $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_3$.

The heteroleptic complex $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ required a sequential synthetic approach^[47–49] via the intermediate *tpe* triflate complex $\text{Cr}(\text{OTf})_3(\text{tpe})$ (Scheme 2c). $\text{Cr}(\text{OTf})_3(\text{tpe})$ was obtained from $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and tpe ^[25] followed by halide abstraction with trimethylsilyl trifluoromethanesulfonate as purple crystalline material, suitable for single crystal X-ray analysis (Figure S12, Table S1, CCDC 2479151). All triflates are coordinated to the chromium(III) center with Cr–O distances below 2 Å (Table S1), similar to other polypyridine triflate chromium(III) complexes, such as *mer*- $\text{Cr}(\text{OTf})_3(\text{tpy})$ and *mer*- $\text{Cr}(\text{ddpd})(\text{OTf})_3$ ($\text{tpy} = 2,2':6',2''$ -terpyridine, $\text{ddpd} = N,N'$ -dimethyl- N,N' -dipyridine-2-yl-pyridine-2,6-diamine),^[47–49] yet in a facial fashion due to the tripodal *tpe* ligand. Again, coordination of tpe^{CF_3} to chromium(III) in $\text{Cr}(\text{OTf})_3(\text{tpe})$ substituting the triflate ligands required microwave activation at 200°C . These harsh conditions, however, lead to partial ligand scrambling, so that the resulting material consists of the desired heteroleptic $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ complex (major product, 67 %) in addition to the homoleptic complexes $[\text{Cr}(\text{tpe})_2]^{3+}$ and (likely) $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (minor products) according to HPLC analysis (Figure S13). To separate the heteroleptic complex from the homoleptic ones, the mixture was subjected to HILIC (Figure S14). Yellow, crystalline $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_3$ was finally obtained after salt metathesis with $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ and recrystallization (Scheme 2c).

In all complex syntheses, the yields of the raw products before HILIC are much higher than for the purified ones. The purity of all

CF_3 -substituted complexes was confirmed by analytical HPLC analysis (Figures S10, S14). All CF_3 -substituted complexes were furthermore characterized by ESI⁺ mass spectrometry in MeCN (Figures S15–S17) showing peaks for the respective trication and corresponding ion clusters with one and two counter ions, respectively. No peaks for dissociated tpe^{CF_3} were observed suggesting appreciable complex stability in spite of the electron deficiency of the tpe^{CF_3} ligand. IR bands for the symmetric and asymmetric C–F stretching vibrations of the CF_3 groups^[41] of the complexes $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_3$, $\text{cis-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_3$ and $\text{trans-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_3$ are found at $1335/1159 \text{ cm}^{-1}$, $1334/1144 \text{ cm}^{-1}$ and $1337/1149 \text{ cm}^{-1}$, respectively, in addition to the intense characteristic P–F vibrational bands of the counter ions (Figures S18–S20).

Photophysical Properties. The UV/vis/near-infrared (NIR) absorption spectra of all CF_3 -substituted complexes very much resemble that of the unsubstituted complex $[\text{Cr}(\text{tpe})_2]^{3+}$ ^[24] with the low-energy spin-allowed ligand field transitions ($^4\text{A}_2 \rightarrow ^4\text{T}_2$) appearing at $\lambda_{\text{abs}} = 431, 433, 432$ and 432 nm ($\tilde{\nu}_{\text{abs}} = 23200, 23100, 23150, 23150 \text{ cm}^{-1}$) for $[\text{Cr}(\text{tpe})_2]^{3+}$,^[24] $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$, $\text{cis-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ and $\text{trans-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$, respectively (Figures S21–S23). The molar absorption coefficients of all complexes are with $\epsilon = 35 \text{ M}^{-1} \text{ cm}^{-1}$ identical as well. This finding suggests that the local center of symmetry of the $\text{Cr}(\text{py})_6$ coordination is not disturbed in the monosubstituted complex $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ and in the *cis*-complex $\text{cis-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$, so that Laporte's rule^[50]

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applies strongly for all complexes. Consequently, the metal-centered quartet states are unaffected by the CF₃ substituents in the Franck-Condon geometry with respect to energy and symmetry-breaking.

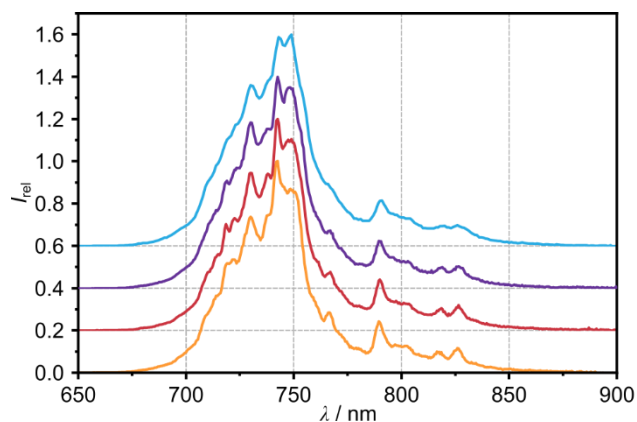


Figure 1. Stacked normalized PL spectra of [Cr(tpe)₂][PF₆]₃ (orange),^[24,25,27] [Cr(tpe)(tpe^{CF3})] [PF₆]₃ (red, offset by 0.2), *cis*-[Cr(tpe^{CF3})₂][PF₆]₃ (purple, offset by 0.4) and *trans*-[Cr(tpe^{CF3})₂][PF₆]₃ (blue, offset by 0.6) in MeCN at 293 K.

All complexes emit in the NIR spectral region in solution at 293 K from their lowest-energy doublet states (²E/²T₁) with the highest peak maxima at λ_{em} = 748, 743, 743 and 748 nm ($\tilde{\nu}_{em}$ = 13370, 13460, 13460 and 13370 cm⁻¹) for [Cr(tpe)₂]³⁺,^[24,25,27] [Cr(tpe)(tpe^{CF3})]³⁺, *cis*-[Cr(tpe^{CF3})₂]³⁺ and *trans*-[Cr(tpe^{CF3})₂]³⁺, respectively (Figure 1, Figures S21–S23). The excitation spectra closely follow the absorption spectra confirming that the PL arises from the complexes (Figures S21–S23). The largest energy difference of the PL maxima amounts to Δ $\tilde{\nu}_{em}$ = 90 cm⁻¹ close to the spectral resolution. This confirms our expectation that the energy of the emissive doublet states in these polypyridine chromium(III) complexes is essentially independent from the number (one/two) and relative position (*cis/trans*) of the trifluoromethyl substituents at the tripodal ligands. Furthermore, the characteristic emission band pattern of the centrosymmetric complex [Cr(tpe)₂]³⁺ (representing progressions of ungerade Cr–N enabling modes)^[24] is fully mirrored by the CF₃-substituted complexes substantiating that symmetry-breaking is absent in these complexes (Figure 1). This electronic symmetry-conservation of the electronic states in spite of the symmetry-breaking imposed by the nuclei had been already inferred from the quartet absorption bands (Figures S21–S23).

The PL quantum yields (Φ = 8.2 (different solvent), 4.9, 6.0 and 6.2 %) and PL lifetimes (τ = 3.5, 2.6, 3.0 and 3.3 ms) are very high and very similar^[51,52] as well for the complexes [Cr(tpe)₂]³⁺,^[24,25,27] [Cr(tpe)(tpe^{CF3})]³⁺, *cis*-[Cr(tpe^{CF3})₂]³⁺ and *trans*-[Cr(tpe^{CF3})₂]³⁺, respectively (Figures S21–S23). The small differences in Φ and τ are very likely due to the presence of traces of quenching molecules.^[51,52] The resulting radiative and non-radiative rate constants are very small and similar as well (k_r = 19 – 23 s⁻¹ and k_{nr} = 260 – 370 s⁻¹).

In air-saturated MeCN solution, the excited state lifetimes are reduced from the millisecond range (2.6 – 3.5 ms) to τ_{O_2} = 320,^[24]

333, 360 and 360 μs (Figures S21–S23) suggesting quenching of the emission by triplet oxygen as often observed for chromium(III) complexes with long-lived excited doublet states.^[17,24,25,36,44,53–55]

The quenching efficiency is very similar for all complexes as well. In contrast to bulky mesityl or 2,4,6-triisopropylphenyl substituents attached to molecular rubies that protect the chromium(III) center from oxygen quenching,^[36] the CF₃ substituents in 4-positions of the pyridines in the present complexes exert no shielding effect.

In summary, the excited state properties ($\tilde{\nu}_{abs}$, ϵ , $\tilde{\nu}_{em}$, τ , Φ , k_r , k_{nr} , τ_{O_2}) of the metal-centered excited quartet and doublet states of the chromium(III) chromophores are essentially unaffected by the presence, number and position of CF₃ substituents. This confirms our expectation that purely metal-centered excited states are only weakly affected by substituent effects.

Redox properties. All tricationic complexes are reduced in two reversible one-electron reduction steps [CrL₂]^{3+/2+} and [CrL₂]^{2+/+} (Figure 2, Figures S24–S26). The [CrL₂]^{3+/2+} and [CrL₂]^{2+/+} reduction potentials amount to $E_{1/2}([CrL_2]^{3+/2+})$ = –0.50, –0.39, –0.30, –0.28 V and $E_{1/2}([CrL_2]^{2+/+})$ = –1.16, –1.04, –0.89, –1.00 V for [Cr(tpe)₂]³⁺,^[24,25,27] [Cr(tpe)(tpe^{CF3})]³⁺, *cis*-[Cr(tpe^{CF3})₂]³⁺ and *trans*-[Cr(tpe^{CF3})₂]³⁺, respectively.

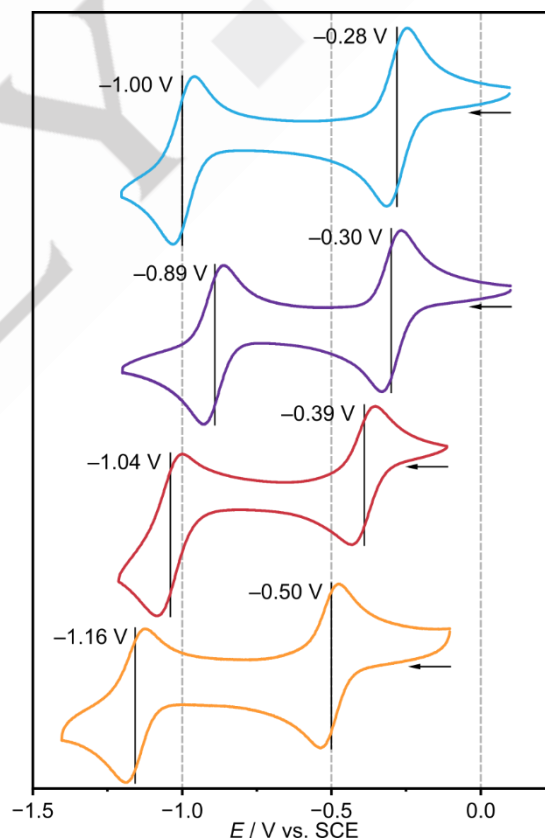


Figure 2. Cyclic voltammograms of [Cr(tpe)₂][PF₆]₃ (orange), [Cr(tpe)(tpe^{CF3})] [PF₆]₃ (red), *cis*-[Cr(tpe^{CF3})₂][PF₆]₃ (purple) and *trans*-[Cr(tpe^{CF3})₂][PF₆]₃ (blue) 1 mM in a 100 mM solution of [n-Bu₄N][PF₆] in MeCN.

Clearly, the number of CF₃ substituents significantly affects the [CrL₂]^{3+/2+} and [CrL₂]^{2+/+} processes. The reduction potentials are

indeed incrementally shifted to higher values by ca. +0.1 V per CF_3 substituent with the exception of the *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+/+}$ couple. This confirms the expectation that substituent effects are additive,^[56,57] even for processes that are mixed metal/ligand-centered due to the redox non-innocence of pyridine ligands^[24,58-61] (see section Quantum Chemical Assessment). Only the *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+/+}$ couple deviates from the incremental correlation, likely because the *trans*-coordinated CF_3 -substituted pyridines are strongly conjugated (see section Quantum Chemical Assessment).

The $[\text{CrL}_2]^{3+/2+}$ redox processes were additionally probed by chemical reduction of the tricationic complexes in MeCN using cobaltocene CcH as reductant. CcH selectively addresses the first reduction process of the complexes avoiding over-reduction ($E_{1/2}(\text{CcH}^{+/0}) = -0.93 \text{ V}$ ^[62,63]). Upon addition of CcH, the pale-yellow MeCN solutions of the tricationic complexes immediately turn deep green.

The characteristic color arises from intense bands spanning the entire visible spectral region up to 1100 nm in the NIR (Figure 3, Figures S27–S30). The most prominent NIR bands of the dicationic complexes peak at $\lambda_{\text{abs}} = 944, 983, 994$ and 1048 nm ($\tilde{\nu}_{\text{abs}} = 10590, 10170, 10060, 9540 \text{ cm}^{-1}$, Figures S27–S30). Clearly, the number and position of CF_3 substituents affect the energies of these absorption bands. This finding suggests that CF_3 -substituted pyridines significantly contribute to the involved wavefunctions of the NIR transitions of the dicationic complexes. This contrasts the purely metal-centered excited states of the tricationic complexes (see above) and will be further elaborated in the quantum chemistry section.

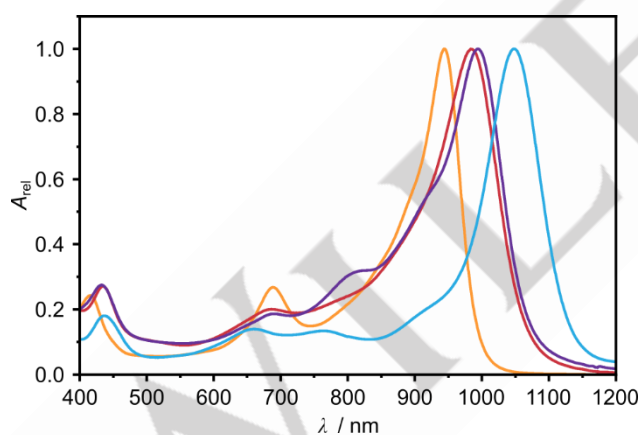


Figure 3. Normalized vis/NIR absorption spectra of $[\text{Cr}(\text{tpe})_2]^{2+}$ (orange), $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{2+}$ (red), *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+}$ (purple) and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+}$ (blue) in MeCN obtained by quantitative reduction of the respective tricationic complexes with cobaltocene. The resulting cobaltocenium cation does not absorb significantly in this spectral region,^[64] so that the spectra correspond to the dicationic chromium complexes.

Treatment of the dark-coloured solutions of the dications $[\text{CrL}_2]^{2+}$ with ferrocenium hexafluorophosphate $[\text{FcH}][\text{PF}_6]$ immediately leads to discoloration, quantitatively regenerating the tricationic complexes $[\text{CrL}_2]^{3+}$ (Figures S31–S34). Consequently, the $[\text{CrL}_2]^{3+/2+}$ redox process is fully reversible not only on the

electrochemical, but even on the much longer chemical time scale. This stability confirms that the redox process is not entirely metal-centred as chromium(II) would be very labile, but that the additional electron with respect to $[\text{CrL}_2]^{3+}$ is also delocalized on the pyridine ligands – likely preferring the electron-deficient CF_3 -substituent ones. Oxidation of the dications with oxygen from air is also possible, but the redox process is very slow due to the unfavourable driving force (Figures S35–S38). In particular, the CF_3 -substituted complexes $[\text{CrL}_2]^{2+}$ are almost inert towards air (Figures S37–S38).

Quantum Chemical Assessment. All complex trications (quartet ground state; lowest doublet state) and dications (triplet ground state; quintet state) were optimized by DFT methods on the B3LYP/TZVPP level of theory (Figures S39–S42, Tables S2–S5). Cr–N(py CF_3) bond lengths are only slightly elongated with respect to Cr–N(py) bond lengths, by ca. 0.01, 0.01 and 0.005 Å in the $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$, *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ complexes, respectively (Tables S2–S5).

As ligand field states, in particular SF states of chromium(III) complexes, are often poorly described by DFT methods, we resorted to multireference CASSCF-NEVPT2 calculations calculated at the DFT-optimized ground state geometry for these properties. The active space comprised the dominant bonding/antibonding orbitals formed between chromium and the ligand, namely the five 3d orbitals, two occupied Cr–N σ bonding orbitals and five 4d orbitals giving an active space of (7,12) (Tables S6–S9).^[35,44,49] The energies of the thus calculated metal-centered quartet and doublet states are displayed in Figure 4 (Tables S10–S11).

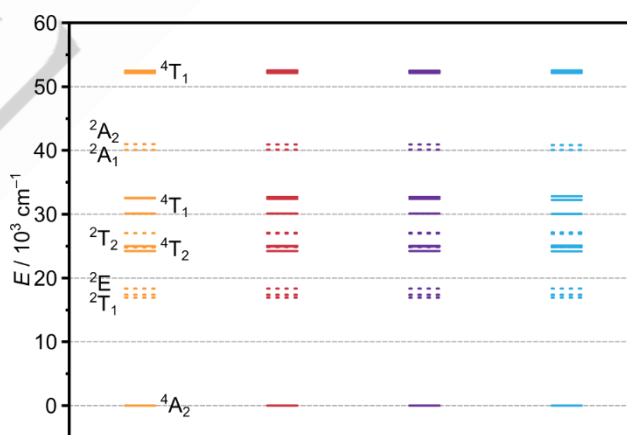


Figure 4. CASSCF(7,12)-SC/NEVPT2 calculated quartet (solid lines) and doublet (dashed lines) energies (doublet states scaled by 0.89^[44,49]) of $[\text{Cr}(\text{tpe})_2]^{3+}$ (orange), $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ (red), *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (purple) and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (blue). Term symbols are given for $[\text{Cr}(\text{tpe})_2]^{3+}$ (O point group notation).

The calculated energies of the quartet and doublet excited states of all complexes are essentially identical (Figure 4, Tables S10–S11), confirming the experimentally determined constant ${}^4\text{A}_2 - {}^4\text{T}_2$ and ${}^4\text{A}_2 - {}^2\text{E}/{}^2\text{T}_1$ energy differences throughout the series. The high complex symmetry for all complexes is reflected in the weak

splitting of the 4T_1 and 4T_2 states (Figure 4, Tables S10–S11). The ligand field splitting in the ground state geometry is very large, separating the emissive doublet states ($^2E/{}^2T_1$) from the lowest-energy quartet state $^4T_2(1)$. The calculated energies of the lowest-energy doublet states match the experimental ones reasonably well. The agreement increases further, when a scaling factor of 0.89, that has been determined for a series of pyridine chromium(III) complexes on this level of theory, is applied ($15225\text{ cm}^{-1} \rightarrow 13550\text{ cm}^{-1}$; $656\text{ nm} \rightarrow 738\text{ nm}$).^[44,49] This good agreement confirms that CT states (which are not considered in the active space) do not significantly mix with the doublet states.^[17,23,65–69] Hence, the calculations underpin our assumption that the metal-centered states, including the SF states, in these chromium(III) complexes are unaffected by substituent effects and symmetry-breaking.

The reduced complexes $[\text{Cr}(\text{tpe})_2]^{2+}$,^[24] $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{2+}$, *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+}$ and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+}$ were optimized by DFT methods as well. The optimized triplet states were found to be more stable than the quintet states on this level of theory (Tables S6–S9). Hence, we will discuss the dications in their respective triplet states. The Mulliken spin densities at the chromium center are reduced from 3.2 in the trications to only 2.5 in $[\text{Cr}(\text{tpe})_2]^{2+}$ and 2.6 in the CF_3 -substituted dications (Tables S6–S9). This suggests an appreciable redox non-innocence of the pyridine ligands,^[24,58–61] which is more pronounced in the complexes with electron-poor tpe^{CF_3} ligand. The triplet states can thus largely be described as chromium(III) with a ligand radical is antiferromagnetically coupled to the chromium center. The β spin density distribution in $[\text{Cr}(\text{tpe})_2]^{2+}$ is delocalized over two *trans*-coordinated coplanar pyridines of different *tpe* ligands (Figure 5).^[24] The Cr–N bonds to these reduced pyridines are shortened by 0.03 Å relative to those of the trication (Tables S6–S9). In the heteroleptic complex $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{2+}$, the β spin density is localized on the CF_3 -substituted pyridine (Figure 5), fully agreeing with the expectation. The Cr–N bond to this pyridine radical anion reduces by 0.08 Å relative to that of the trication (Tables S6–S9). In the doubly substituted complexes *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+}$ and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+}$, the β spin density is distributed over both CF_3 -substituted pyridines (Figure 5) and the Cr–N bond lengths to these are compressed by 0.04 Å (Tables S6–S9).

The strongly colored dicationic complexes $[\text{CrL}_2]^{2+}$ possess numerous strong absorption bands in the vis-NIR spectral region (Figures S27–S30). These are qualitatively well reproduced by time-dependent DFT (TD-DFT) calculations. The intense transitions correspond to metal-to-ligand transitions according to the electron density difference maps (Figures S27–S30).

Gratifyingly, the DFT-calculated $[\text{CrL}_2]^{3+/2+}$ redox potentials of the CF_3 -substituted complexes relative to that of $[\text{Cr}(\text{tpe})_2]^{3+/2+}$ (set to zero) correctly reproduce the observed experimental trend and are with $\Delta E_{1/2}(\text{DFT}) = +0.12$, $+0.21$ and $+0.25\text{ V}$ even very close to the experimentally determined ones with $\Delta E_{1/2}(\text{exp}) = +0.11$, $+0.20$ and $+0.22\text{ V}$ (see above, Tables S6–S9, Figure 5). Consequently, our DFT calculations on the $[\text{CrL}_2]^{3+/2+}$ complexes are very reasonable.

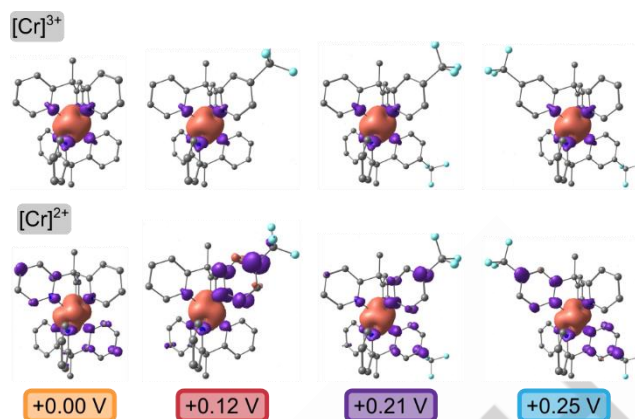


Figure 5. DFT-optimized geometries and spin-densities of the $[\text{Cr}(\text{tpe})_2]^{3+/2+}$, $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+/2+}$, *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+/2+}$ and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+/2+}$ complexes and DFT-calculated redox potentials given relative to the $[\text{Cr}(\text{tpe})_2]^{3+/2+}$ couple set to $E_{1/2} = 0.00\text{ V}$. Orange: α spin density, purple: β spin density; isosurface value 0.003 a.u.; hydrogen atoms omitted for clarity.

In summary, the DFT and CASSCF-NEVPT2 calculations reproduce the experimental data (redox potentials and excited state energies) in this series of CF_3 -substituent complexes very well. This finding gives confidence that future quantum chemical calculations on substituted chromium(III) complexes will predict redox potentials and excited state energies of chromium(III) complexes sufficiently well. This will allow systematic computational screenings of chromium(III) chromophores.

Conclusion

The redox-active polypyridine chromium(III) complex $[\text{Cr}(\text{tpe})_2]^{3+}$ possesses favorable properties for photocatalysis, such as reversible one-electron reduction, millisecond excited state lifetime and high stability.

Substituting $[\text{Cr}(\text{tpe})_2]^{3+}$ with one or two CF_3 groups in $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$, *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ incrementally shifts the $[\text{Cr}(\text{tpe}^{\text{R}})_2]^{3+/2+}$ redox potential to more positive values. The energy and high lifetime of the emissive spin-flip excited states remain, however, unchanged. This unusual decoupling of redox potential and excited state energy was achieved by localizing the redox process largely onto the CF_3 -substituted pyridine ligands and confining the electronic excited state to the chromium center. Computational modeling of redox potentials and excited state energies confirmed the experimentally determined properties. The structure-activity relationships identified here for chromium(III) complexes with tripodal ligands lay the foundation for computational property prediction and experimental realization of chromium(III)-based photoredox catalysts.

Supporting Information

The Supporting Information contains the employed methods, the synthesis procedures, processed spectroscopic, analytical and computational data (pdf) and the Cartesian coordinates of DFT optimized geometries (xyz). All the raw data from this manuscript have been uploaded to Zenodo and are freely available via the DOI <https://doi.org/xx>. The authors have cited additional references within the Supporting Information.^[71-99]

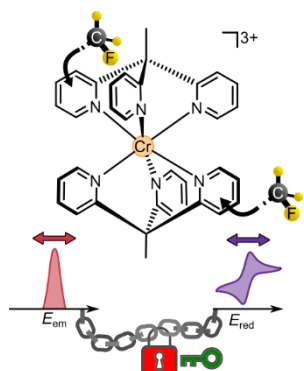
Acknowledgements

Keywords: chromium • photophysics • redox chemistry • structure-property relationships • trifluoromethylation

- [1] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, 91, 165–195.
- [2] D. Kim, V. Q. Dang, T. Teets, *Chem. Sci.* **2024**, 15, 77–94.
- [3] D. Kim, T. Teets, *Chem. Phys. Rev.* **2022**, 3, 021302.
- [4] J.-H. Shon, T. S. Teets, *ACS Energy Lett.* **2019**, 4, 558–566.
- [5] Y. Wu, D. Kim, T. S. Teets, *Synlett* **2022**, 33, 1154–1179.
- [6] W. R. Kitzmann, K. Heinze, *Angew. Chem. Int. Ed.* **2023**, 62, e202213207.
- [7] E. Speckmeier, T. G. Fischer, K. Zeitler, *J. Am. Chem. Soc.* **2018**, 140, 15353–15365.
- [8] S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko, H. Lemmetyinen, *J. Am. Chem. Soc.* **2004**, 126, 1600–1601.
- [9] A. Joshi-Pangu, F. Lévesque, H. G. Roth, S. F. Oliver, L.-C. Campeau, D. Nicewicz, D. A. DiRocco, *J. Org. Chem.* **2016**, 81, 7244–7249.
- [10] J. Konzal, M. Murley, A. Wolter, L. Camou, A. Oberbroeckling, M. Dekker, G. Wagner, K. Jennejohn, M. Peters, N. Hayes, C. Franklin, S. Tobin, E. Collier, I. MacKenzie, *Chem. Eur. J.* **2025**, 31, e202403543.
- [11] F. Glaser, S. De Kreijger, K. Achilleos, L. Narayan Satheesh, A. Ripak, N. Chantry, C. Bourgois, S. Quiquempoix, J. Scriven, J. Rubens, M. Vander Wee-Léonard, M. Daenen, M. Gillard, B. Elias, L. Troian-Gautier, *ChemPhotoChem* **2024**, 8, e202400134.
- [12] D. L. Ashford, C. R. K. Glasson, M. R. Norris, J. J. Concepcion, S. Keinan, M. K. Brennaman, J. L. Templeton, T. J. Meyer, *Inorg. Chem.* **2014**, 53, 5637–5646.
- [13] M. Furue, K. Maruyama, T. Oguni, M. Naiki, M. Kamachi, *Inorg. Chem.* **1992**, 31, 3792–3795.
- [14] A. Singh, K. Teegardin, M. Kelly, K. S. Prasad, S. Krishnan, J. D. Weaver, *J. Organomet. Chem.* **2015**, 776, 51–59.
- [15] R. A. Maya, A. Maity, T. S. Teets, *Organometallics* **2016**, 35, 2890–2899.
- [16] D. Kim, T. G. Gray, T. S. Teets, *Chem. Commun.* **2022**, 58, 11446–11449.
- [17] G. Morselli, T. H. Eggenweiler, M. Villa, A. Prescimone, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, asap. DOI: 10.1021/jacs.5c08541.
- [18] P. R. Wells, *Prog. Phys. Org. Chem.* **1968**, 6, 111–145.
- [19] G. Morselli, C. Reber, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, 147, 11608–11624.
- [20] M. Dorn, N. R. East, C. Förster, W. R. Kitzmann, J. Moll, F. Reichenauer, T. Reuter, L. Stein, K. Heinze, d-d and Charge Transfer Photochemistry of 3d Metal Complexes in *Comprehensive Inorganic Chemistry III* (Section Ed. V. W.-W. Yam), **2023**, 707–788.
- [21] C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, 49, 1057–1070.
- [22] B. M. Hockin, C. Li, N. Robertson, E. Zysman-Colman, *Catal. Sci. Technol.* **2019**, 9, 889–915.
- [23] A. König, R. Naumann, C. Förster, J. Klett, K. Heinze, *J. Am. Chem. Soc.* **2025**, 147, 20833–20842.
- [24] S. Treiling, C. Wang, C. Förster, F. Reichenauer, J. Kalmbach, P. Boden, J. P. Harris, L. Carrella, E. Rentschler, U. Resch-Genger, C. Reber, M. Seitz, M. Gerhards, K. Heinze, *Angew. Chem. Int. Ed.* **2019**, 58, 18075–18085.
- [25] S. Sittel, J. Neuner, J. M. Grenz, C. Förster, R. Naumann, K. Heinze, *Adv. Synth. Catal.* **2025**, 367, e202500075.
- [26] S. Sittel, A. C. Sell, K. Hofman, C. Wiedemann, J. P. Nau, C. Kerzig, G. Manolikakes, K. Heinze, *Chem. Cat. Chem.* **2023**, 15, e202201562.
- [27] S. Sittel, R. Naumann, K. Heinze, *Front. Chem.* **2022**, 10, 887439.
- [28] T. Reuter, A. Kruse, R. Schoch, M. Bauer, S. Lochbrunner, K. Heinze, *Chem. Commun.* **2021**, 57, 7541–7544.
- [29] T. Reuter, D. Zorn, R. Naumann, J. Klett, C. Förster, K. Heinze, *Angew. Chem. Int. Ed.* **2024**, 136, e202406438.
- [30] N. R. East, C. Dab, C. Förster, K. Heinze, C. Reber, *Inorg. Chem.* **2023**, 62, 9025–9034.
- [31] W. R. Kitzmann, M.-S. Bertrams, P. Boden, A. C. 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, 16597–16609.
- [32] A. C. Fischer, C. Förster, W. R. Kitzmann, K. Heinze, *Inorg. Chem.* **2025**, 64, 6100–6114.
- [33] W. R. Kitzmann, J. Moll, K. Heinze, *Photochem. Photobiol. Sci.* **2022**, 21, 1309–1331.
- [34] W. R. Kitzmann, C. Ramanam, R. Naumann, K. Heinze, *Dalton Trans.* **2022**, 51, 6519–6525.
- [35] C. Förster, K. Heinze, *Adv. Inorg. Chem.* **2024**, 83, 111–159.
- [36] L. Stein, C. Wang, C. Förster, U. Resch-Genger, K. Heinze, *Dalton Trans.* **2022**, 51, 17664–17670.
- [37] F. Draper, S. DiLuzio, H. J. Sayre, L. N. Pham, M. L. Coote, E. H. Doeven, P. S. Francis, T. U. Connell, *J. Am. Chem. Soc.* **2024**, 146, 26830–26843.
- [38] M. J. Goodwin, J. C. Dickenson, A. Ripak, A. M. Deetz, J. S. McCarthy, G. J. Meyer, L. Troian-Gautier, *Chem. Rev.* **2024**, 124, 7379–7464.
- [39] J. Cong, D. Kinschel, Q. Daniel, M. Safdari, E. Gabrielsson, H. Chen, P. H. Svensson, L. Sun, L. Kloo, *J. Mater. Chem. A* **2016**, 4, 14550–14554.
- [40] N. S. W. Jonasson, L. J. Daumann, *Chem. Eur. J.* **2019**, 25, 12091–12097.
- [41] E. E. Ferguson, L. Mikkelsen, J. R. Nielsen, D. C. Smith, *J. Chem. Phys.* **1953**, 21, 1731–1735.
- [42] N. Serpone, M. A. Jamieson, M. S. Henry, Z. Hoffman, F. Bolletta, M. Maestri, *J. Am. Chem. Soc.* **1979**, 101, 2907–2916.
- [43] R. D. Gillard, P. R. Mitchell, *J. Chem. Soc. A* **1968**, 2129.
- [44] F. Reichenauer, R. Naumann, C. Förster, W. R. Kitzmann, A.-P. M. Reponen, S. Feldmann, K. Heinze, *Chem. Sci.* **2024**, 15, 20251–20262.
- [45] G. A. Lawrance, *Adv. Inorg. Chem.* **1986**, 34, 145–194.

- [46] G. A. Lawrance, *Chem. Rev.* **1986**, *86*, 17–33.
- [47] J.-R. Jiménez, B. Doistau, C. Besnard, C. Piguet, *Chem. Commun.* **2018**, *54*, 13228–13231.
- [48] E. C. Constable, C. E. Housecroft, M. Neuburger, J. Schönle, J. A. Zampese, *Dalton Trans.* **2014**, *43*, 7227–7235.
- [49] F. Reichenauer, D. Zorn, R. Naumann, C. Förster, K. Heinze, *Inorg. Chem.* **2024**, *63*, 23487–23496.
- [50] O. Laporte, W. F. Meggers, *J. Opt. Soc. Am.* **1925**, *11*, 459–463.
- [51] The small differences of these very long PL lifetimes are likely due to minor trace impurities that can reductively quench the strongly oxidizing excited state.^[24–27] For example, decreasing $\tau_0 = 3.5$ ms to $\tau_q = 2.6$ ms requires only 10^{-6} M of quencher Q assuming a quenching rate constant $k_q = 10^8 \text{ M}^{-1} \text{ s}^{-1}$ according to the Stern-Volmer equation $k_q = \frac{1}{[Q]} \left(\frac{1}{\tau_q} - \frac{1}{\tau_0} \right)$.^[52]
- [52] O. Stern, M. Volmer, *Phys. Z.* **1919**, *20*, 183–188.
- [53] S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572–11576.
- [54] S. Otto, A. M. Nauth, E. Ermilov, N. Scholz, A. Friedrich, U. Resch-Genger, S. Lochbrunner, T. Opatz, K. Heinze, *ChemPhotoChem* **2017**, *1*, 344–349.
- [55] F. Reichenauer, C. Wang, C. Förster, P. Boden, N. Ugur, R. Báez-Cruz, J. Kalmbach, L. M. Carrella, E. Rentschler, C. Ramanan, G. Niedner-Schatteburg, M. Gerhards, M. Seitz, U. Resch-Genger*, K. Heinze, *J. Am. Chem. Soc.* **2021**, *143*, 11843–11855.
- [56] A. B. P. Lever, *Inorg. Chem.* **1990**, *29*, 1271–1285.
- [57] S. Lu, V. V. Strelets, M. F. Ryan, W. J. Pietro, A. B. P. Lever, *Inorg. Chem.* **1996**, *35*, 1013–1023.
- [58] C. C. Scarborough, S. Sproules, T. Weyhermüller, S. DeBeer, K. Wieghardt, *Inorg. Chem.* **2011**, *50*, 12446–12462.
- [59] C. C. Scarborough, K. M. Lancaster, S. DeBeer, T. Weyhermüller, S. Sproules, K. Wieghardt, *Inorg. Chem.* **2012**, *51*, 3718–3732.
- [60] A. Gowda, J. L. Petersen, C. Milsman, *Inorg. Chem.* **2018**, *57*, 1919–1934.
- [61] K. Krämer, M. Schmitz, H. Kelm, C. van Wüllen, H.-J. Krüger, *Chem. Eur. J.* **2024**, *30*, e202301099.
- [62] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877–910.
- [63] V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta* **2000**, *298*, 97–102.
- [64] N. N. Rukhlyada, E. V. Leonova, N. S. Kochetkova, N. V. Bychkov, *Russ. Chem. Bull.* **1983**, *32*, 1196–1200.
- [65] N. Sinha, J.-R. Jiménez, B. Pfund, A. Prescimone, C. Piguet, O. S. Wenger, *Angew. Chem. Int. Ed.* **2021**, *60*, 23722–23728.
- [66] Y. Cheng, J. He, W. Zou, X. Chang, Q. Yang, W. Lu, *Chem. Commun.* **2023**, *59*, 1781–1784.
- [67] S. Sittel, R. Naumann, C. Förster, M. E. Huber, J. Meyer, K. Heinze, submitted.
- [68] J. Sander, F. Gauder, S. J. Schickanz, T. Maulbetsch, J. Kalmbach, D. Zorn, R. Naumann, C. Förster, D. Kunz, K. Heinze, submitted.
- [69] N. R. East, R. Naumann, C. Förster, C. Ramanan, G. Diezemann, K. Heinze, *Nat. Chem.* **2024**, *16*, 827–834.
- [70] J. P. Harris, C. Reber, H. E. Colmer, *Can. J. Chem.* **2017**, *95*, 547–552.
- [71] STOE & Cie, X-Area, STOE & Cie GmbH: Darmstadt, Germany.
- [72] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33–38.
- [73] A. L. Spek, *Acta Crystallogr. Sect. D* **2009**, *65*, 148–155.
- [74] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.
- [75] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
- [76] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- [77] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
- [78] P. J. Larkin, *Infrared and Raman Spectroscopy*, Elsevier Inc., 2018, 2nd ed..
- [79] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
- [80] F. Neese, F. Wennmohs, U. Becker, C. Riplinger, *J. Chem. Phys.* **2020**, *152*, 224108.
- [81] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2022**, *12*, e1606.
- [82] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [83] B. Miehlisch, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200–206.
- [84] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2009**, *356*, 98–109.
- [85] R. Izsák, F. Neese, *J. Chem. Phys.* **2011**, *135*, 144105.
- [86] D. A. Pantazis, X.-Y. Chen, C. R. Landis, F. Neese, *J. Chem. Theory Comput.* **2008**, *4*, 908–919.
- [87] S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117–129.
- [88] V. Barone, M. Cossi, *J. Phys. Chem.* **1998**, *102*, 1995–2001.
- [89] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.
- [90] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.
- [91] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [92] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [93] B. O. Roos, P. R. Taylor, P. E. Sigbahn, *Chem. Phys.* **1980**, *48*, 157–173.
- [94] P. E. M. Siegbahn, J. Almlöf, A. Heiberg, B. O. Roos, *J. Chem. Phys.* **1981**, *74*, 2384–2396.
- [95] F. Weigend, M. Kattannek, R. Ahlrichs, *J. Chem. Phys.* **2009**, *130*, 164106.
- [96] S. Kossmann, F. Neese, *Chem. Phys. Lett.* **2009**, *481*, 240–243.
- [97] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, J.-P. Malrieu, *J. Chem. Phys.* **2001**, *114*, 10252–10264.
- [98] C. Angeli, R. Cimiraglia, J.-P. Malrieu, *J. Chem. Phys.* **2002**, *117*, 9138–9153.
- [99] K. Pierloot, *Int. J. Quantum Chem.* **2011**, *111*, 3291–3301.

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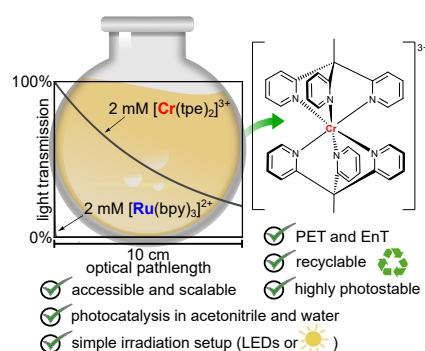


Redox and excited state properties of organic and precious metal charge-transfer photocatalysts are strongly entangled. In contrast, redox potentials of polypyridine chromium(III) complexes, that feature purely metal-centred spin-flip states, are selectively tuned by incremental substituent effects of the CF₃ group, while excited state energies and lifetimes remain unaffected. Such precisely designed chromophores provide a unique tool for the systematic investigation of elementary reaction steps relevant to photoredox catalytic cycles

3.5 Gram-Scale Photocatalysis with a Stable and Recyclable Chromium(III) Photocatalyst in Acetonitrile and in Water

Authors: Steven Sittel, [REDACTED]

Adv. Synth. Catal. **2025**, 367, e202500075. DOI: 10.1002/adsc.202500075.



[Cr(tpe)₂]³⁺ was used to tackle some of the prevailing bottlenecks in photocatalysis research, which include catalysts accessibility and reaction scalability. To this end, cheap and easy gram-scale syntheses of both the ligand and complex from commercially available starting materials were developed. The chromium(III) compound was employed in a total of five photocatalytic transformations, in acetonitrile and in water. A simple, laboratory-scale reaction setup was described, using highly powered LEDs and common glassware. Additionally, the high photostability of [Cr(tpe)₂]³⁺ was further demonstrated in photolysis experiments and via recycling (up to >90% recovery) of the catalyst after photoreactions.

Author Contributions

Steven Sittel optimized the syntheses of tpe and [Cr(tpe)₂]³⁺, conducted most of the photocatalytic experiments including the determinations of quantum yields, the cyclic voltammetry, some of the photolysis experiments and wrote the original draft of the manuscript. [REDACTED] conducted some of the photocatalytic experiments and some of the photolysis experiments. [REDACTED] conducted some of the photocatalytic experiments. [REDACTED] solved and refined the XRD structure of [Cr(tpe)₂][NO₃]₃ (CCDC no. 2387074). [REDACTED] designed the project and helped with the interpretation of the experimental data. [REDACTED] revised and finalized the manuscript. All authors discussed the scientific results and contributed to the final version of the manuscript.

Supporting Information

for this article can be found on pp. 188.

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Gram-Scale Photocatalysis with a Stable and Recyclable Chromium(III) Photocatalyst in Acetonitrile and in Water

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^a

Manuscript received: January 21, 2025; Revised manuscript received: March 12, 2025;
Version of record online: April 10, 2025



Supporting information for this article is available on the WWW under <https://doi.org/10.1002/adsc.202500075>

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Abstract: The use of stable photosensitizers made on a multigram-scale from cheap and available starting materials offers an extraordinary opportunity to translate small-scale proof-of-concept photoreactions to widespread applications in non-specialized laboratories, thereby promoting the implementation of light-driven syntheses. Herein, we report an easy, multigram-scale preparation of the exceptionally photo- and redoxstable chromium(III) complex $[\text{Cr}(\text{tpe})_2]^{3+}$ (tpe = 1,1,1-tris(pyrid-2-yl)ethane) at room temperature. This photocatalyst was successfully employed in acetonitrile and in the “green” solvent water as demonstrated in visible-light induced Schenck-Ene reactions, Newman-Kwart rearrangements, radical cation Diels-Alder cycloadditions, oxidative decarboxylation and trifluoromethylation reactions with excellent substrate conversions and high turnover numbers. Gram-scale photocatalytic reactions were conducted using a simple round-bottom flask as reaction vessel and irradiation with energy-efficient blue LEDs or even with sunlight. The stable photocatalyst was successfully recycled in up to 90–92% yields after the photoreactions.

Keywords: Chromium; Photocatalysis; Photoredox Catalysis; Recycling; Upscaling

Introduction

Homogeneous photocatalysis and in particular photoredox catalysis has augmented the chemist's toolbox by generating organic triplet molecules or organic radicals using visible light and a suitable photocatalyst (PC). These mild conditions open up unique mechanistic pathways that are not accessible thermally and hold the potential for more sustainable synthetic chemistry (Figure 1a/1b).^[1–9] Efforts of many research groups all over world have provided a panoply of PCs with different key properties.^[10] The applicability of a PC in a given photocatalytic reaction is determined by its chemical, optical and electrochemical properties (Figure 1c) such as solubility in a given solvent, stability under the applied conditions, maximum

absorption wavelength (λ_{max}), molar absorption coefficient at the excitation wavelength (ϵ_{max}), excited state energy (E_{0-0}) and excited state lifetime (τ) as well as ground and excited state reduction or oxidation potentials $E_{1/2}$ and $*E_{1/2}$.^[10,11] For example, the excited state redox potential $*E_{1/2}$ determines the scope of substrates that can be oxidized or reduced by the excited PC. Meanwhile, rationally designed new PCs (Figure 1d) span a large range of excited state redox potentials, which cover large substrate and reaction scopes.^[2,10,12] While the wide range of excited state potentials and the resulting large substrate scopes highlight the potential and opportunities that photoredox catalysis holds, widespread application outside dedicated photochemistry research groups has not been achieved. Industrial use of photocatalysis is subject of

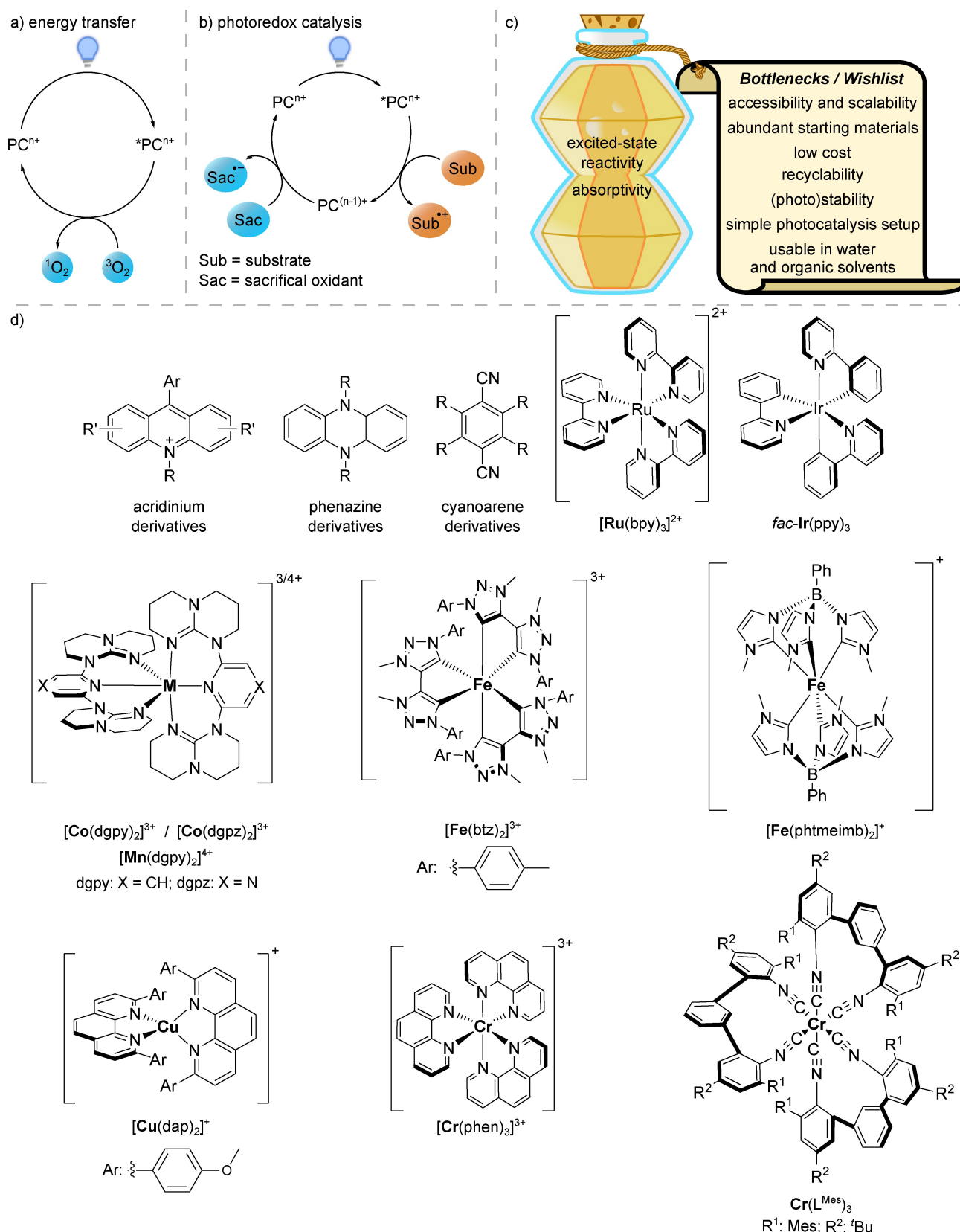


Figure 1. Schemes of a) energy transfer (to $^3\text{O}_2$) and b) photoredox catalysis with reductive quenching by a substrate Sub using a PC. c) Absorptivity and excited state reactivity are key aspects of PCs, yet the bottlenecks for widespread applications of photocatalysis beyond the cuvette or milligram-scale are often overlooked. d) Commonly employed organic and noble metal complex PCs and examples of earth-abundant metal complex PCs.

current research with respect to reactor design and scalability, in particular in the pharmaceutical and agrochemical sector.^[13–16] Still, industrial and, perhaps even more strikingly, laboratory scale application of photoredox catalysis is very limited.^[17–21] Given the impressive variety of PCs and photochemical transformations available, lack of reactivity or insufficient substrate scopes are not the main factors that prevent the use of photocatalysis in synthetic laboratories. Arguably, the most prevailing bottlenecks for photoredox catalytic transformations in synthetic laboratories are accessibility, cost, stability and recyclability of the PC, along with challenges in reactor design and the oftentimes low reaction quantum yield (Figure 1c). In the majority of the reported photocatalytic applications, complexes of noble transition metals, e.g. derivatives of $[\text{Ru}(\text{bpy})_3]^{2+}$ or *fac*- $\text{Ir}(\text{ppy})_3$ (Figure 1d, bpy = 2,2'-bipyridine; Hppy = 2-phenylpyridine), have been studied and employed as PCs, thanks to their strong visible light absorption, reversible redox chemistry, tunable ground and excited redox potentials and long lifetimes of the excited triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) states.^[2,10,11,22,23] However, the low abundance and hence high price of their central ions render these PCs inherently unsustainable and expensive.^[24] Aiming to circumvent these drawbacks and to explore new reactivities, metal-free PCs have been developed more recently. These include strongly reducing phenazine derivatives and strongly oxidizing acridinium salts and cyanoarenes (Figure 1d).^[10,23] However, these organic PCs often suffer from drawbacks, such as poor photostability or redox stability and limited solubility in the “green” solvent water.^[12,25–28]

In addition to organic PCs, PCs containing earth-abundant metals have gained a lot of attention, comprising both strongly reducing and oxidizing complexes (Figure 1d).^[10,29–31] Among the strongest photoreductants are arylisocyanide or carbonyl complexes of group VI metals. These possess long-lived $^3\text{MLCT}$ excited states and reach excited state potentials of up to $^*E_{\text{red}} = -2.3$ V vs. SCE for $\text{Cr}(\text{LMes})_3$ (Figure 1d).^[32–34] Complexes of the $3d^{10}$ ion copper(I) have been employed in numerous photocatalytic transformations, exploiting their reducing $^3\text{MLCT}$ excited states (e.g. $[\text{Cu}(\text{dap})_2]^+$; $^*E_{\text{red}} = -1.43$ V vs. SCE; dap = 2,9-bis(p-anisyl)-1,10-phenanthroline).^[29–31,35–37] Complexes with electron-poor metal centers possess oxidizing LMCT excited states which can achieve nanosecond excited state lifetimes.^[29,38] The carbene iron(III) complexes $[\text{Fe}(\text{btz})_3]^{3+}$ and $[\text{Fe}(\text{phtmeimb})_2]^+$ ($^*E_{\text{red}} = +1.9$ V and $+1.4$ V vs. SCE; btz = 3,3'-dimethyl-1,1'-bis(p-tolyl)-4,4'-bis(1,2,3-triazol-5-ylidene); phtmeimb[−] = tris(3-methylimidazolin-2-ylidene)(phenyl)borate, Figure 1d) absorb green light and engage in bimolecular reactions from their $^2\text{LMCT}$ states.^[38–41] Photooxidants with cobalt(III) and

manganese(IV) have been described (up to $^*E_{\text{red}} = +2.75$ V and $+1.80$ V vs. SCE, Figure 1d), however their application in photocatalysis has remained very limited.^[42–44] The LMCT excited state of the uranyl cation $[\text{U}^{\text{VI}}\text{O}_2]^{2+}$ ($^*E_{\text{red}} = +2.35$ V) is capable of oxidizing alkanes via hydrogen atom transfer under aerated conditions.^[45–47] Chromium(III) complexes feature very long-lived doublet metal-centered excited states, so called spin-flip (SF) states.^[48–50] These SF states can efficiently form singlet oxygen $^1\text{O}_2$ from $^3\text{O}_2$ regenerating the quartet ground state of the complex. This capability has been exploited for the photocatalyzed α -functionalization of aliphatic amines.^[51,52] Although these SF states lack charge transfer character, they can be reductively quenched in bimolecular reactions,^[31] which has been already exploited in various proof-of-concept photoredox catalytic reactions.^[51,53–60] Some of these polypyridine chromium(III) complexes are even highly redox and photostable.^[51,52] Despite these highly attractive chemical, photophysical and electrochemical properties,^[31,48,50,61,62] chromium(III) complexes have thus far been underexplored in photo(redox) catalysis. In particular, large-scale reactions including PC recycling have not yet been reported.^[51,53–59] Typically, the limited chemical and/or photostability of most homogeneous PCs causing them to degrade over the course of photochemical reactions, prohibits recycling of the PCs and effectively increases cost and decreases sustainability, due to the need for fresh material. Additionally, this instability of the PC potentially leads to contamination of the reaction product, necessitating more tedious purification steps and increasing waste production (e.g. solvents).

To make photocatalysis more attractive for the laboratory and industrial scale, an ideal PC should be easily accessible on a larger scale using only earth-abundant materials (accessibility and scalability). This PC should be chemically robust and photostable to allow simple and efficient product purification and PC recycling. Its optical absorption properties should be compatible with a simple reactor setup and its solubility should allow photocatalysis in organic solvents and in water.

In order to achieve these goals towards a sustainable and straightforward application of photocatalysis in non-specialized laboratories, we report the multi-gram-scale synthesis of a chromium(III)-based PC, probe its chemical robustness and photostability and apply this PC in exemplary energy transfer catalysis^[63,64] providing $^1\text{O}_2$ ^[65–68] and redox-neutral and oxidative photoredox catalysis^[2,69] both in organic solvents and in water. We disclose upscaling of the photocatalysis with this PC to the multigram-scale using only common laboratory glassware, we demonstrate the use of sunlight instead of blue LEDs and we report the recycling of the PC.

Results and Discussion

Features of $[\text{Cr}(\text{tpe})_2]^{3+}$

We selected the tricationic chromium(III) complex $[\text{Cr}(\text{tpe})_2]^{3+}$ (tpe = 1,1,1-tris(pyrid-2-yl)ethane) as a strongly photooxidizing, redox- and photostable PC.^[51,56,70] The complex is highly soluble in acetonitrile or in water depending on the counter ion (see below). This PC features SF states at an energy $E_{0,0} = 1.75$ eV with an extremely long excited state lifetime of 3.5 ms in MeCN and 2.5 ms in H₂O recommending these SF states for efficient bimolecular quenching (Figure 2a; Figures S5 and S6). The complex is reduced at $E_{\text{red}}([\text{Cr}]^{3+}/[\text{Cr}]^{2+}) = -0.50$ V vs. SCE in MeCN (Figure S12) resulting in an excited state reduction potential of $E_{\text{red}}^*([\text{Cr}]^{3+}/[\text{Cr}]^{2+}) = +1.25$ V vs. SCE in MeCN.^[70] These values shift cathodically by about 0.2 V in water (Figure S13), yet the oxidative power of

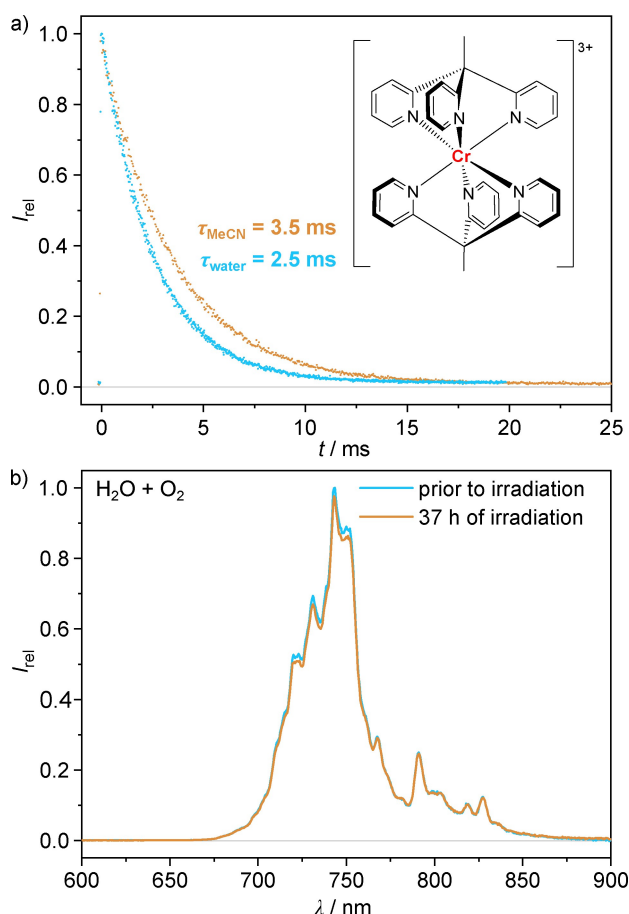


Figure 2. a) Emission decay traces of $[\text{Cr}(\text{tpe})_2]^{3+}$ in deaerated MeCN and in deaerated H₂O, recorded at 742 nm after excitation at 451 nm; structure of the complex cation $[\text{Cr}(\text{tpe})_2]^{3+}$. b) Emission spectra of solutions of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in water under aerated conditions before and after irradiation at 460 nm using a 6.5 W UHP-LED for 37 h. Spectra are normalized to the emission maximum prior to irradiation.

the SF states remain high so that many organic substrates are amenable to oxidation both in organic solvents and in water.

The Cr complex absorbs blue light ($\lambda_{\text{abs}} = 431$ nm in MeCN; $\epsilon_{431} = 35 \text{ M}^{-1} \text{ cm}^{-1}$), allowing to use efficient blue LEDs for excitation (Figures S1 and S2).^[71] The small molar absorption coefficient of $[\text{Cr}(\text{tpe})_2]^{3+}$ might seem counterintuitive for its application as PC,^[10,22,72] in particular when considering that many traditional PCs possess strongly allowed transitions in the visible spectral region, such as $[\text{Ru}(\text{bpy})_3]^{2+}$ with $\epsilon_{452} = 13000 \text{ M}^{-1} \text{ cm}^{-1}$.^[11] However, very high molar absorption coefficients pose severe challenges for the design of efficient photoreactors. For example, if $[\text{Ru}(\text{bpy})_3]^{2+}$ is used at a typical concentration of 2 mM, 99% of the incident light will be absorbed within the first 0.8 mm of the reaction solution according to the Beer-Lambert law (Figure S3).^[73,74] Since the light cannot penetrate the solution any further, all $[\text{Ru}(\text{bpy})_3]^{2+}$ molecules beyond this thin layer are catalytically inactive at any given moment, which is not a desirable scenario considering the high cost of precious metal PCs. The strong light absorption within the first few millimeters leads to local temperature spikes due to the high amount of energy absorbed per unit volume and to a high local concentration of organic radicals in a photoredox catalytic reaction. This can give rise to inhomogeneous kinetics within the photoreactor and to side reactions of the radicals. To circumvent these issues, flow reactors with very short optical path lengths have been receiving a lot of attention.^[15,73,75–78] While the sophisticated design of these reactors is truly remarkable, these photoreactors are often expensive and poorly accessible for most laboratories, especially outside dedicated photochemistry research groups. In contrast, the most popular reaction vessels among chemists worldwide, like round-bottom flasks, are cheap and ubiquitous. Depending on their size, round-bottom flasks have optical path lengths of 5 to 15 cm or more. Assuming an optical path length of 10 cm, a 2 mM solution of $[\text{Cr}(\text{tpe})_2]^{3+}$ ($\epsilon_{431} = 35 \text{ M}^{-1} \text{ cm}^{-1}$) absorbs ca. 80% of the incident light over the entire length of the reactor (Figure S3). Despite the exponential nature of light attenuation, this leads to a comparably uniform distribution of photons throughout the reaction vessel, enlarging the photocatalytically active volume. Temperature spikes and side reactions are thus diminished. These properties recommend $[\text{Cr}(\text{tpe})_2]^{3+}$ as PC, especially in laboratory-scale reactions using standard glassware. Near quantitative absorption of the incident photons can be achieved by employing even longer path lengths or higher concentrations of $[\text{Cr}(\text{tpe})_2]^{3+}$. While increasing the concentration of expensive noble-metal PCs, less stable PCs or PCs, which require tedious multistep syntheses,^[32,33] is unsustainable, $[\text{Cr}(\text{tpe})_2]^{3+}$ can be employed in larger amounts due to its

simple, cheap and high-yielding preparation and its recyclability (see below). The photostability of $[\text{Cr}(\text{tpe})_2]^{3+}$ was probed by irradiating $[\text{Cr}(\text{tpe})_2]^{3+}$ in acetonitrile and water solutions with a UHP-LED ($\lambda_{\text{exc}} = 460 \text{ nm}$, 6.5 W) under aerated and deaerated conditions. Negligible decomposition occurred after continuous irradiation over 25 to 42 h at this high photon intensity, according to the essentially unchanged photoluminescence spectra in all cases (Figure 2b; Figures S7–S9). Even under air, essentially no photodecomposition is noticeable despite the generation of $^1\text{O}_2$.^[52] The O_2 and H_2O tolerance of $[\text{Cr}(\text{tpe})_2]^{3+}$ and $^*\text{[Cr(tpe)}_2]^{3+}$ (Figure 2b) is highly beneficial allowing a very simple experimental setup of the photocatalytic reaction under non-inert conditions. Hence, this chromium(III)-based PC is photostable in acetonitrile and in water, retains a millisecond excited state lifetime and a high excited state potential in both solvents and can be employed in standard laboratory glassware. Its optimized multigram-scale

two-step preparation from commercially available starting materials will be discussed next.

Multigram-scale Preparation of the Photocatalyst $[\text{Cr}(\text{tpe})_2]^{3+}$

The tridentate ligand tpe had been prepared by deprotonation of 2-ethylpyridine with *n*-butyllithium (*n*-BuLi) as a base in THF, followed by quenching with 2-fluoropyridine.^[79–81] As the high reactivity and low selectivity of *n*-BuLi lead to side reactions at room temperature, cooling the reaction mixture with dry ice and dropwise addition of the *n*-BuLi solution are required. Both cooling and dropwise addition are energy-intensive and time-consuming for multigram-scale reactions involving large quantities of *n*-BuLi solutions. We hence replaced *n*-BuLi by lithium bis(trimethylsilyl)amide (LiHMDS) in refluxing THF in a one-pot synthesis (Figure 3a). On a 2 g-scale tpe was obtained in 85% yield. On a larger scale, spectroscopically pure tpe was obtained in 72%

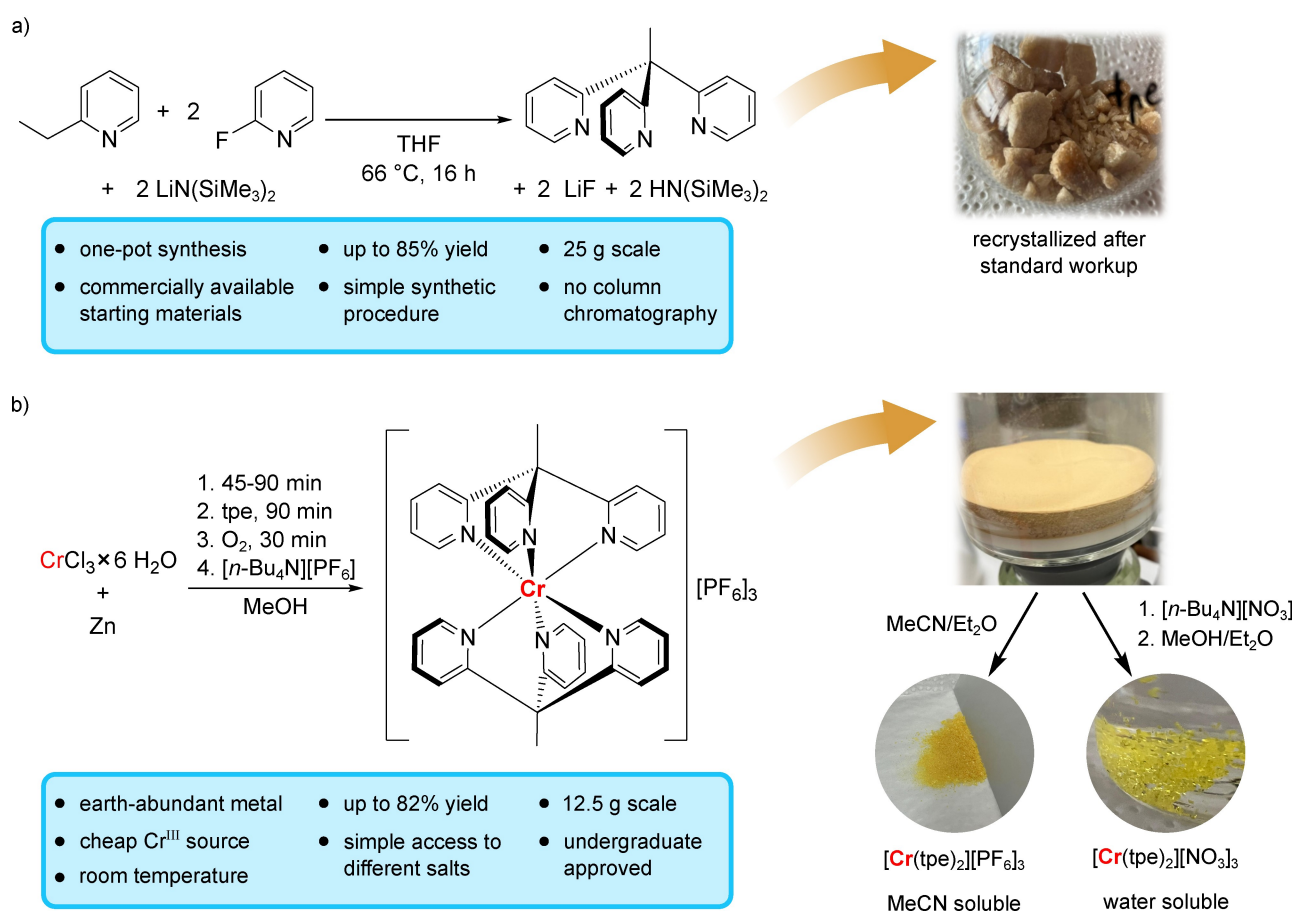


Figure 3. a) Synthesis of the tridentate ligand tpe. The photograph on the right-hand side shows 25.3 g of the ligand after standard workup and recrystallization from acetone. b) Synthesis of the PC $[\text{Cr}(\text{tpe})_2]^{3+}$ and access to its $[\text{PF}_6]^-$ and $[\text{NO}_3]^-$ salts. The photographs on the right-hand side show 12.5 g of the crude product after precipitation as $[\text{PF}_6]^-$ salt as well as the respective $[\text{PF}_6]^-$ and $[\text{NO}_3]^-$ salts after crystallization.

isolated yield (27.5 g; Figure S33, more details are given in the Supporting Information). Recrystallization from acetone gives highly pure tpe in 66% yield (25.3 g; Figure S34) without requiring further purification by column chromatography and thus reducing the amount of required solvent and produced waste.

Chromium(III) complexes are typically prepared from labile chromium(II) precursors.^[82–85] $[\text{Cr}(\text{tpe})_2]^{3+}$ itself had been successfully prepared from anhydrous CrCl_2 as chromium source and the ligand tpe followed by air oxidation on a 0.5 g scale.^[70] However, CrCl_2 is rather expensive and requires an inert atmosphere for long-term storage. Hence, we replaced CrCl_2 with the much cheaper and more accessible $\text{CrCl}_3 \times 6 \text{ H}_2\text{O}$ salt and used zinc as a cheap reductant to generate chromium(II) ions *in situ* (Figure 3b).^[86] Addition of the thus prepared chromium(II) solution to a solution of tpe and subsequent air oxidation yields the target complex. This facile room-temperature synthesis route is high-yielding (up to 82%), scalable (confirmed up to 12.5 g) and lowers the material cost per mole (ca. 600 g) of $[\text{Cr}(\text{tpe})_2]^{3+}$ from ca. 4600 to ca. 2800 \$ accounting for both the ligand and complex syntheses (for details of this estimation see the Supporting Information). On smaller scales (below 0.5 g $\text{CrCl}_3 \times 6 \text{ H}_2\text{O}$) the procedure can be further simplified to a one-pot reaction, by quickly adding the ligand solution to the chromium(II)/zinc mixture only slightly diminishing the yield to ca. 65%. Due to its simplicity and reliability, this procedure has even been integrated into an undergraduate laboratory course at our chemistry department paving the way for a broad application.

Depending on the choice of solvent in the photocatalytic reaction with the chromium(III)-based PC, $[\text{Cr}(\text{tpe})_2]^{3+}$ is isolated as the hexafluorophosphate salt $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ or the nitrate salt $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$, which are soluble in MeCN (ca. 10 g L^{-1}) and excellently soluble in water ($> 100 \text{ g L}^{-1}$), respectively. The successful counterion exchange was confirmed by an XRD structure analysis of the $[\text{NO}_3]^-$ salt (Figure S14) and by infrared spectroscopy of both salts (Figures S15 and S16). Detailed procedures for the ligand and complex salt preparations are provided in the supporting information.

$[\text{Cr}(\text{tpe})_2]^{3+}$ as Photosensitizer in Energy Transfer Catalysis and Photoredox Catalysis

A sustainable energy transfer catalysis requires a high stability of the PC in its ground and excited states under the reaction conditions and towards the generated excited substrates. For photoredox catalysis, a high stability of the reduced (or oxidized) intermediates is necessary in addition. Exemplary, we demonstrate the suitability of the chromium(III)-based PC in established reactions for both scenarios, namely for a light-sensitized energy transfer catalysis (Schenck-Ene

reaction, Scheme 1a) and four redox-neutral and oxidative photoredox catalytic cycles, namely the Newman-Kwart rearrangement, the Diels-Alder cycloaddition, the photooxidative decarboxylation and the trifluoromethylation (Scheme 1b–e).

The ability to generate $^1\text{O}_2$ from the SF states of chromium(III) complexes is well-established.^[51,52] Here we exemplarily employ $[\text{Cr}(\text{tpe})_2]^{3+}$ as a photosensitizer in the type II oxygenation of an unactivated alkene (Schenck-Ene reaction).^[67,68,87] The thus generated allylic hydroperoxides are useful precursors for the preparation of e.g. allylic alcohols, epoxy alcohols or unsaturated carbonyls.^[68,88–91] Oleic acid as test substrate, $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ as photosensitizer in MeCN and blue light successfully leads to quantitative and clean conversion of the olefin to the corresponding hydroperoxides *trans*-9-hydroperoxyoctadec-10-enoic acid and *trans*-10-hydroperoxyoctadec-8-enoic acid in a 1:1 ratio (Scheme 1a)^[92] as determined by ^1H NMR spectroscopy (Figure S36). The initial reaction quantum yield Φ_R was estimated at 0.1 (Figure S20). No conversion of the substrate occurred in the absence of $[\text{Cr}(\text{tpe})_2]^{3+}$, O_2 or light (Figure S38).

As $[\text{Cr}(\text{tpe})_2]^{3+}$ is strongly oxidizing in its long-lived SF excited state both in MeCN and in H_2O , we exemplarily discuss four photoredox catalytic applications using $[\text{Cr}(\text{tpe})_2]^{3+}$ in both solvents.

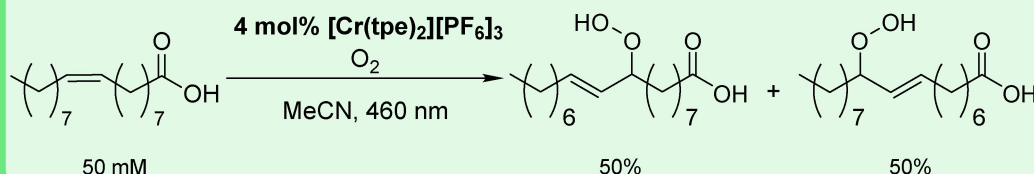
The Newman-Kwart rearrangement is a key step in the most important synthetic access to thiophenols from the corresponding phenols.^[93–95] However, the originally described approach requires high reaction temperatures (200–300 °C) and electron-deficient arenes, limiting substrate scope and compromising selectivity and product purity. Alternative approaches to the Newman-Kwart rearrangement at less energy-demanding ambient temperature rely on the oxidative induction of the rearrangement by chemical oxidation,^[96,97] electrochemical oxidation,^[98] heterogeneous photoredox catalysis,^[99] homogenous photoredox catalysis with an organic pyrrylium PC and blue light,^[100] and with 9,10-dicyanoanthracene using an osmium(II) complex sensitizer with red laser light via triplet-triplet annihilation upconversion.^[101]

$^*\text{[Cr}(\text{tpe})_2]^{3+}$ should be thermodynamically competent to oxidize the phenol derivative *O*-(4-methoxyphenyl) dimethylcarbamothioate ($E_{\text{red}} = +1.1 \text{ V}$ vs. SCE; Scheme 1b) to initiate the rearrangement.^[100] Indeed, a Stern-Volmer analysis confirmed the quenching of $^*\text{[Cr}(\text{tpe})_2]^{3+}$ by the substrate ($k_q = 1.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$; Figure S17).

Photocatalytic experiments confirmed that $[\text{Cr}(\text{tpe})_2]^{3+}$ is a suitable PC for this transformation in MeCN, resulting in $> 99\%$ conversion to the rearranged product *S*-(4-methoxyphenyl) dimethylcarbamothioate (Figures S40 and S45). During the first 10 minutes of irradiation, an induction period is observed, which we attribute to photochemical oxida-

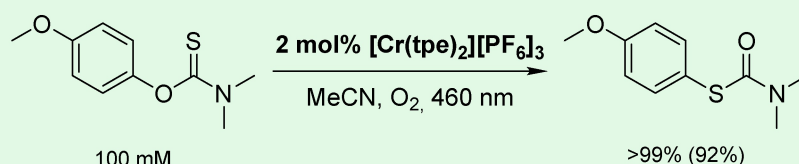
Energy Transfer Catalysis

a) Schenck-Ene Reaction

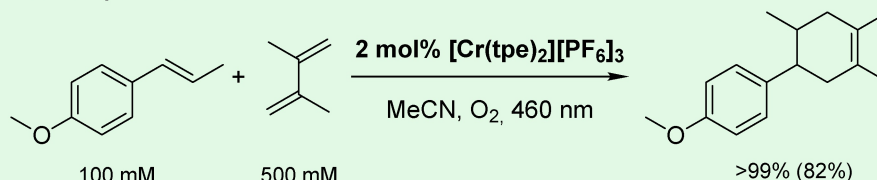


Photoinduced Electron Transfer Catalysis

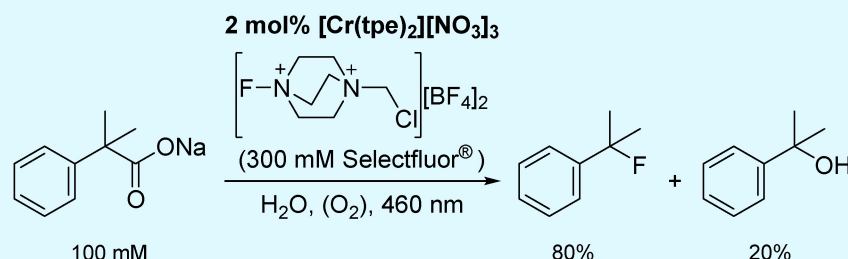
b) Newman-Kwart Rearrangement



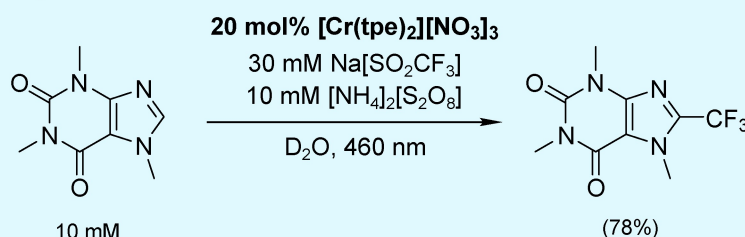
c) Diels-Alder Cycloaddition



d) Photooxidative Decarboxylation



e) Trifluoromethylation



Scheme 1. Photocatalytic reactions catalyzed by $[\text{Cr}(\text{tpe})_2]^{3+}$ in MeCN (green) and water (blue). Conversion of the starting material was determined via ^1H NMR spectroscopy. Isolated yields are given in parenthesis.

tion of trace impurities in the reaction mixture. After this induction period, the reaction proceeds with a high reaction quantum yield of $\Phi_{\text{R}} = 0.6$ (Figure S21). No conversion occurs in the absence of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ or light (Figure S44). Although the rearrangement is net redox-neutral, conducting the reaction in the

presence of air accelerates the conversion (Figure S44). Likely, O_2 serves as redox mediator in this reaction, promoting the re-oxidation of the reduced PC and thus preventing detrimental charge recombination.^[51] Hence, this photo-induced rearrangement is preferably performed simply under air, which obviates additional

sacrificial oxidants. This procedure was used to determine the achievable turnover number (TON) of the PC in this photocatalytic reaction. To this end, a MeCN solution of the PC (0.1 mM) and the substrate *O*-(4-methoxyphenyl) dimethylcarbamothioate (100 mM) was irradiated for 16 h. During this time, the substrate was fully converted to the product, corresponding to a TON of 1000 (Figure S41).

The visible light induced radical cation Diels-Alder cycloaddition^[102] between *trans*-anethole and 2,3-dimethyl-1,3-butadiene using $[\text{Cr}(\text{tpe})_2]^{3+}$ as PC in MeCN on a small scale had been previously reported (Scheme 1c).^[51] To estimate the TON for this reaction, a 0.1 mM MeCN solution of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$, containing 100 mM of *trans*-anethole and 500 mM of 2,3-dimethyl-1,3-butadiene was irradiated for 4.5 h achieving full conversion of *trans*-anethole to the cycloaddition product (Figure S48). As a chain-mechanism is involved in the cycloaddition mechanism,^[103] the thus estimated TON=1000 does not correspond to 1000 catalytic cycles of the PC. The unity quantum yield ($\Phi_R=1$; Figure S22), which was estimated for the laboratory-scale experiments (discussed later in the manuscript), indicates that a chain mechanism indeed contributes to this transformation. These high numbers for both the light induced Newman-Kwart rearrangement and the radical cation Diels-Alder cycloaddition underline the high stability of $[\text{Cr}(\text{tpe})_2]^{3+}$ and the intermediates $^*[\text{Cr}(\text{tpe})_2]^{3+}$ and $[\text{Cr}(\text{tpe})_2]^{2+}$ under the photocatalytic conditions. In real-world applications, a PC concentration as low as 0.1 mM would be suboptimal, as a lot of excitation light would be wasted. Hence, higher PC concentrations are preferred to accelerate the reactions, which is feasible due to the good availability of the PC (see above) and its recyclability (see below).

While acetonitrile is a popular solvent for many photocatalytic reactions and $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ is soluble and stable in MeCN, conducting photocatalysis in the “green” solvent water is especially desirable.^[27] Yet, many PCs are insoluble in water or possess only short excited state lifetimes in water.^[27,104,105] The easily accessible, water-soluble ($>100 \text{ g L}^{-1}$) nitrate salt $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ solves these issues. Absorption and emission energies of the complex remain almost unchanged and the excited state lifetime is shortened by merely 30% to 2.5 ms (Figure S6). This is still an extremely long lifetime and bimolecular reactions in the excited state should be efficient even in water. The reduction potential of the $[\text{Cr}(\text{tpe})_2]^{3+/2+}$ half-reaction is shifted cathodically by merely 0.2 V (Figure S13), still allowing for oxidation of challenging substrates in the long-lived excited state.

Photocatalytic decarboxylative coupling reactions (e.g. Scheme 1d) have gained popularity, as they provide access to structurally diverse organic building blocks for the formation of challenging C–C and C–F

bonds in Giese- and Hunsdiecker-type reactions, respectively.^[106–108] While the classical approaches to these reactions typically suffer from the need for toxic additives and/or harsh reaction conditions, photocatalytic approaches have the potential to circumvent these issues.^[109] Typical oxidation potentials of carboxylates lie around 1.3–1.7 V vs. SCE,^[110] suggesting that their irreversible oxidation by $^*[\text{Cr}(\text{tpe})_2]^{3+}$ in water is slightly uphill. In agreement with this thermodynamic estimation, the rate constant obtained from a Stern-Volmer quenching analysis of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ with sodium 2-phenylisobutyrate in water is with $k_q=5.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ rather small (Figure S18). We irradiated a solution of sodium 2-phenylisobutyrate with $[\text{Cr}(\text{tpe})_2]^{3+}$ as PC and Selectfluor[®], which provides electrophilic fluorine as the coupling partner after the decarboxylation of the oxidized carboxylate.^[111–113] Under aerated conditions, complete consumption of 2-phenylisobutyrate occurred (Figures S52 and S60). 2-Fluoro-2-phenylpropane and 2-phenyl-2-propanol were obtained in a 4:1 ratio according to ¹H NMR spectroscopy (Figures S55 and S56). Conducting the experiment under deaerated conditions yielded similar results, hence, working under air-free conditions is unnecessary. The alcohol by-product likely forms via oxidation of the generated cumyl radical to its carbocation and subsequent nucleophilic attack of water, similar to the reported interception of a benzyl cation by water yielding benzylalcohol.^[114] Oxidation of the cumyl radical ($E_{\text{red}}=+0.16 \text{ V vs. SCE}$)^[115] under the reaction conditions either by Selectfluor[®] ($E_{\text{red}}=+0.33 \text{ V vs. SCE}$)^[116] or its oxidizing defluorinated derivatives TEDA⁺ ($E_{\text{red}}=+0.79 \text{ V vs. SCE}$)^[117] or TEDA²⁺ (no potential reported)^[111,118] is thermodynamically feasible (TEDA = *N*-(chloromethyl)triethylenediamine; Figure S4). As oxygen is unnecessary to sustain photocatalysis, Selectfluor[®] or its derivatives can act as oxidants for the reduced photocatalyst $[\text{Cr}(\text{tpe})_2]^{2+}$.^[119] Furthermore, TEDA²⁺ has been reported as a chain carrier in various reactions.^[111,118] Hence, it is conceivable that TEDA²⁺ contributes to a chain mechanism in the present reaction as well. However, $[\text{Cr}(\text{tpe})_2]^{3+}$ as PC and light were necessary to induce the reaction (Figure S54). This demonstrates that $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ is a suitable PC in water, displaying sufficient oxidative power to oxidize an activated carboxylate. The reaction quantum yield was not determined for this transformation, as the oily products separate from the aqueous solution and the fluorinated product is volatile.

Similar to the photo-initiated oxidation of a carboxylate providing the carbon-centered radical after extrusion of CO₂, $^*[\text{Cr}(\text{tpe})_2]^{3+}$ should be able to oxidize sulfonates, such as the bench-stable Langlois reagent sodium trifluoromethanesulfonate Na[SO₂CF₃] delivering $^*\text{CF}_3$ radicals after loss of SO₂.^[120] Indeed,

$\text{Na}[\text{SO}_2\text{CF}_3]$ ($E_{\text{red}} = +1.02 \text{ V}$ vs. SCE)^[121] quenches the emission of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in water with a quenching rate constant $k_q = 3.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (Figure S19). Trifluoromethylated compounds are high-value products in the pharmaceutical and agrochemical sectors, as fluorine atoms strongly influence the biological activity of molecules. Mild and selective trifluoromethylation is therefore a hot topic and several synthetic pathways, including photoredox catalysis have been developed.^[17,121–125] To test the applicability of $[\text{Cr}(\text{tpe})_2]^{3+}$ in light-activated trifluoromethylation and to demonstrate its tolerance towards highly reactive $\cdot\text{CF}_3$ radicals, we employed $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ as PC in the trifluoromethylation of caffeine in water (Scheme 1e). D_2O was employed to facilitate reaction control by ^1H NMR spectroscopy. Irradiation of the reaction mixture under air resulted in a mixture of unidentified products. This likely results from the reaction of photogenerated $\cdot\text{CF}_3$ radicals with oxygen, yielding highly reactive species, including fluorophosgene.^[126] It was therefore necessary to exclude oxygen from the reaction mixture. As re-oxidation of $[\text{Cr}(\text{tpe})_2]^{2+}$ is very slow in the absence of an oxidant,^[51] ammonium peroxodisulfate was added to the reaction mixture. Under these conditions, 78% of the caffeine substrate was transformed to the trifluoromethylated product 1,3,7-trimethyl-8-(trifluoromethyl)-7H-purine-2,6-dione after 4 h of irradiation (Figures S62 and S66). The reaction quantum yield was estimated at $\Phi_R = 0.004$ (Figure S23). In the absence of the PC, the product was detected in only 13% yield, while without ammonium peroxodisulfate or without light, no product forms (Figure S65). The successful photoredox catalyzed trifluoromethylation in water demonstrates the capability of $[\text{Cr}(\text{tpe})_2]^{3+}$ to operate in the presence of $\cdot\text{CF}_3$ radicals, the strong ammonium peroxodisulfate oxidant and its highly reactive intermediates.^[119,127,128] Furthermore, we have identified ammonium peroxodisulfate as cheap, water-soluble sacrificial oxidant, which serves as an alternative to molecular oxygen for the re-oxidation of $[\text{Cr}(\text{tpe})_2]^{2+}$, when O_2 interferes with the organic reaction intermediates such as $\cdot\text{CF}_3$ radicals.

Upscaling the Photocatalysis with $[\text{Cr}(\text{tpe})_2]^{3+}$ and Recycling of the Photocatalyst

The Schenck-Ene reaction, the Newman-Kwart rearrangement and the radical cation Diels-Alder cycloaddition reactions were conducted on a gram-scale. Thanks to the low molar absorption coefficient of $[\text{Cr}(\text{tpe})_2]^{3+}$ making a longer path length beneficial, a round-bottom flask is in principle a suitable vessel for the irradiation of $[\text{Cr}(\text{tpe})_2]^{3+}$ as discussed above. Hence, 100 mL round-bottom flasks were used as reaction vessels. A blue UHP-LED as light source was placed next to the flask (Figure 4a). The non-purified



Figure 4. a) Photograph of the laboratory scale irradiation setup using a 100 mL round-bottom flask and a 460 nm UHP-LED. Intensity lowered to 5% to reduce overexposure on the photograph. b) Photograph of the irradiation setup using a 100 mL round-bottom flask and sunlight.

PC $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ was employed at a concentration of 2 mM in MeCN. This setup is very simple, cheap, quickly assembled and accessible in many chemical laboratories.

In the Schenck-Ene reaction 1.2 g oleic acid (50 mM substrate concentration) and the PC were irradiated in an open flask under vigorous stirring. This substrate was quantitatively and cleanly converted to the hydroperoxides within 4 h of irradiation with the UHP-LED according to NMR spectroscopy, while the hydroperoxides themselves were not isolated for safety reasons (Scheme 1a).

A quantitative Newman-Kwart rearrangement of the phenol derivative *O*-(4-methoxyphenyl) dimethylcarbamothioate was achieved using 1.7 g substrate (100 mM) within 60 min irradiation in the setup shown in Figure 4a (Scheme 1b). The pure thiophenol derivative was obtained after solvent evaporation and extraction of the residue with diethyl ether in 92% yield (1.55 g; Figure S40). Encouraged by the fast and quantitative photoreaction under these conditions, the Newman-Kwart rearrangement of *O*-(4-methoxyphenyl) dimethylcarbamothioate was also performed employing sunlight instead of the UHP-LED (Figure 4b). Full conversion of the substrate (20 mM) to the product was achieved after 8 h.

With the setup shown in Figure 4a, 1.2 g *trans*-anethole (100 mM, Figure S47) were quantitatively converted to the Diels-Alder cycloaddition product within 25 min of LED irradiation (Scheme 1c). The product was isolated after extraction with diethyl ether in 82% yield (1.52 g; Figure S49). Previously, this Diels-Alder cycloaddition had been performed with identical substrate concentrations, 1 mM of $[\text{Cr}(\text{tpe})_2]^{3+}$, a shorter optical path length of ca. 1 cm and

a weaker excitation source (Aldrich® Micro Photochemical Reactor) requiring 6 h for completion.^[51] This comparison underscores the importance of selecting a suitable light source and intensity, choosing optimal PC concentrations and optimizing the reactor setup and path length, when designing photochemical reactions to maximize the effective use of light as a reactant.

For all three photocatalytic gram-scale reactions, the PC was recovered after use. UV/vis spectroscopic analysis prior to and after the irradiation of the Newman-Kwart and Diels-Alder reaction mixtures indicated a high PC stability (Figures S28 and S29). After extraction of the respective organic products from the reaction mixtures, the remaining solid was dissolved in hot acetonitrile delivering spectroscopically clean and crystalline $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ after cooling and ether diffusion in 90–92% isolated yield (Figures S10 and S11). During the Schenck-Ene reaction, no significant catalyst decomposition was observed spectroscopically as well (Figure S27). To avoid isolating the hydroperoxide products, the PC was recovered from the reaction mixture in this case by adding $[n\text{-Bu}_4\text{N}][\text{NO}_3]$, precipitating $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$, which is less soluble in MeCN than the hexafluorophosphate salt. By this alternative procedure, 51% of the starting material was isolated. The only partial recovery results from incomplete precipitation of the nitrate salt in the presence of $[\text{PF}_6]^-$. The successful recycling of $[\text{Cr}(\text{tpe})_2]^{3+}$ as either $[\text{NO}_3]^-$ or $[\text{PF}_6]^-$ salt demonstrates the outstanding stability of the complex in photocatalytic applications and effectively lowers its cost and the amount of waste produced by reusing the same material and by avoiding laborious workup procedures.

Conclusion

This study demonstrates that the chromium(III) complex $[\text{Cr}(\text{tpe})_2]^{3+}$ with its exceptionally long excited state lifetime in the millisecond range can be successfully employed in photo(redox) catalytic applications in acetonitrile and in water. Its outstanding intrinsic photo- and redoxstability enables high turnover numbers and even the simple recovery of the intact photocatalyst after the photoreactions in high yields. This chromium(III)-based photocatalyst furnishes highly efficient Schenck-Ene reactions, photoinduced Newman-Kwart rearrangements and Diels-Alder cycloadditions in acetonitrile. The high photooxidative power of $[\text{Cr}(\text{tpe})_2]^{3+}$ even in water is exploited in the oxidation of an activated sodium carboxylate giving the decarboxylated fluorinated product with Select-fluor® as fluorine source. Analogously, photooxidation of sodium trifluoromethanesulfinate delivers $\cdot\text{CF}_3$ radicals which add to caffeine as model substrate. Ammonium peroxodisulfate was identified as a suitable, cheap sacrificial oxidant for this oxygen sensitive

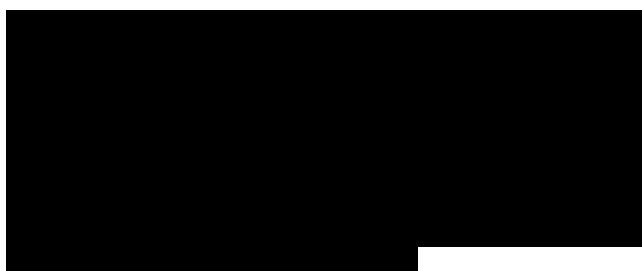
reaction. Beyond small scale experiments, gram-scale photoreactions were demonstrated with this photocatalyst using simple, widely available round-bottom flasks and energy-efficient blue LEDs or even sunlight. The photocatalyst itself was prepared at room-temperature in quantities up to 12.5 g from cheap, commercially available starting materials in few reaction steps.

This study highlights a photo(redox) catalyst made from earth-abundant elements with highly desirable properties for widespread applications in synthetic laboratories, namely good accessibility, high stability in different oxidation states, recyclability, water solubility, applicability in various photoreaction types and utilization of a very simple experimental setup. This photocatalyst thus contributes to a more widespread translation of light-driven chemistry to synthetic laboratories and beyond.

Supporting Information

The Supporting Information contains experimental details, syntheses, optical and electrochemical characterization of the title complex, Stern-Volmer data, XRD data, IR spectra, ^1H and ^{19}F NMR spectra (PDF). A separate file (.zip) containing the original NMR data is provided in addition.

Acknowledgements



References

- [1] J. W. Tucker, C. R. J. Stephenson, *J. Org. Chem.* **2012**, 77, 1617.
- [2] M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, 81, 6898.
- [3] F. Meyer, P. S. Halasyamani, G. Masson, *ACS Org. Inorg. Au* **2022**, 3, 1.
- [4] R. C. McAtee, E. J. McClain, C. R. J. Stephenson, *Trends Chem.* **2019**, 1, 111.
- [5] B. König, *Eur. J. Org. Chem.* **2017**, 2017, 1979.
- [6] A. Y. Chan, I. B. Perry, N. B. Bissonnette, B. F. Buksh, G. A. Edwards, L. I. Frye, O. L. Garry, M. N. Lavagnino, B. X. Li, Y. Liang, E. Mao, A. Millet, J. V. Oakley, N. L. Reed, H. A. Sakai, C. P. Seath, D. W. C. MacMillan, *Chem. Rev.* **2022**, 122, 1485.

- [7] L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* **2018**, *57*, 10034.
- [8] I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. König, *Acc. Chem. Res.* **2016**, *49*, 1566.
- [9] S. B. Cahoon, T. P. Yoon in *Free Radicals: Fundamentals and Applications in Organic Synthesis 1* (Hrsg.: L. Fensterbank, C. Ollivier), Georg Thieme Verlag KG, Stuttgart, **2021**.
- [10] D. Kim, T. S. Teets, *Chem. Phys. Rev.* **2022**, *3*, 021302.
- [11] D. M. Arias-Rotondo, J. K. McCusker, *Chem. Soc. Rev.* **2016**, *45*, 5803.
- [12] N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075.
- [13] E. E. Callard-Langdon, A. Steven, R. J. Kahan, *ChemCatChem* **2023**, *15*, e202300537.
- [14] E. Kayahan, M. Jacobs, L. Braeken, L. C. Thomassen, S. Kuhn, T. van Gerven, M. E. Leblebici, *Beilstein J. Org. Chem.* **2020**, *16*, 2484.
- [15] L. Buglioni, F. Raymenants, A. Slattery, S. D. A. Zondag, T. Noël, *Chem. Rev.* **2022**, *122*, 2752.
- [16] N. C. Neyt, D. L. Riley, *React. Chem. Eng.* **2021**, *6*, 1295.
- [17] J. W. Beatty, J. J. Douglas, K. P. Cole, C. R. J. Stephenson, *Nat. Commun.* **2015**, *6*, 7919.
- [18] J. C. G. Kürschner, L. Brüss, L. Naesborg, *Chem. Eur. J.* **2023**, *29*, e202300627.
- [19] P. Püllmann, D. Homann, T. A. Karl, B. König, M. J. Weissenborn, *Angew. Chem. Int. Ed.* **2023**, *62*, e202307897.
- [20] Y.-M. Tian, W. Silva, R. M. Gschwind, B. König, *Science* **2024**, *383*, 750.
- [21] K. P. Cole, J. J. Douglas, T. Hammerstad, C. R. J. Stephenson, *Org. Process Res. Dev.* **2023**, *27*, 399.
- [22] D. Kim, V. Q. Dang, T. S. Teets, *Chem. Sci.* **2024**, *15*, 77.
- [23] J. D. Bell, J. A. Murphy, *Chem. Soc. Rev.* **2021**, *50*, 9540.
- [24] W. M. Haynes, D. R. Lide, T. J. Bruno, *CRC Handbook of Chemistry and Physics*, 97. Ed., CRC Press, **2016**.
- [25] E. M. S. Stennett, M. A. Ciuba, M. Levitus, *Chem. Soc. Rev.* **2014**, *43*, 1057.
- [26] A. P. Demchenko, *Methods Appl. Fluoresc.* **2020**, *8*, 22001.
- [27] C. Russo, F. Brunelli, G. C. Tron, M. Giustiniano, *J. Org. Chem.* **2023**, *88*, 6284.
- [28] S. Fukuzumi, K. Ohkubo, *Org. Biomol. Chem.* **2014**, *12*, 6059.
- [29] C. B. Larsen, O. S. Wenger, *Chem. Eur. J.* **2018**, *24*, 2039.
- [30] B. M. Hockin, C. Li, N. Robertson, E. Zysman-Colman, *Catal. Sci. Technol.* **2019**, *9*, 889.
- [31] C. Förster, K. Heinze, *Chem. Phys. Rev.* **2022**, *3*, 41302.
- [32] N. Sinha, C. Wegeberg, D. Häussinger, A. Prescimone, O. S. Wenger, *Nat. Chem.* **2023**, *15*, 1730.
- [33] T. Jin, D. Wagner, O. S. Wenger, *Angew. Chem. Int. Ed.* **2024**, *63*, e202314475.
- [34] W. R. Kitzmann, M.-S. Bertrams, P. Boden, A. C. 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*, 16597.
- [35] Y. Zhang, Q. Wang, Z. Yan, D. Ma, Y. Zheng, *Beilstein J. Org. Chem.* **2021**, *17*, 2520.
- [36] C. Sandoval-Pauker, G. Molina-Aguirre, B. Pinter, *Polyhedron* **2021**, *199*, 115105.
- [37] M. Pirtsch, S. Paria, T. Matsuno, H. Isobe, O. Reiser, *Chem. Eur. J.* **2012**, *18*, 7336.
- [38] L. H. M. de Groot, A. Ilic, J. Schwarz, K. Wärnmark, *J. Am. Chem. Soc.* **2023**, *146*, 9369.
- [39] A. Ilic, J. Schwarz, C. Johnson, L. H. M. de Groot, S. Kaufhold, R. Lomoth, K. Wärnmark, *Chem. Sci.* **2022**, *13*, 9165.
- [40] Y. J. Jang, H. An, S. Choi, J. Hong, S. H. Lee, K.-H. Ahn, Y. You, E. J. Kang, *Org. Lett.* **2022**, *24*, 4479.
- [41] A. Aydogan, R. E. Bangle, A. Cadranell, M. D. Turlington, D. T. Conroy, E. Cauët, M. L. Singleton, G. J. Meyer, R. N. Sampaio, B. Elias, L. Troian-Gautier, *J. Am. Chem. Soc.* **2021**, *143*, 15661.
- [42] A. K. Pal, C. Li, G. S. Hanan, E. Zysman-Colman, *Angew. Chem. Int. Ed.* **2018**, *57*, 8027.
- [43] N. R. East, R. Naumann, C. Förster, C. Ramanan, G. Diezemann, K. Heinze, *Nat. Chem.* **2024**, *16*, 827.
- [44] A. Y. Chan, A. Ghosh, J. T. Yarranton, J. Twilton, J. Jin, D. M. Arias-Rotondo, H. A. Sakai, J. K. McCusker, D. W. C. MacMillan, *Science* **2023**, *382*, 191.
- [45] H. D. Burrows, T. J. Kemp, *Chem. Soc. Rev.* **1974**, *3*, 139.
- [46] W.-D. Wang, A. Bakac, J. H. Espenson, *Inorg. Chem.* **1995**, *34*, 6034.
- [47] L. Capaldo, D. Merli, M. Fagnoni, D. Ravelli, *ACS Catal.* **2019**, *9*, 3054.
- [48] W. R. Kitzmann, J. Moll, K. Heinze, *Photochem. Photobiol. Sci.* **2022**, *21*, 1309.
- [49] C. Förster, K. Heinze, *Adv. Inorg. Chem.* **2024**, p. 111–159.
- [50] W. R. Kitzmann, K. Heinze, *Angew. Chem. Int. Ed.* **2023**, *62*, e202213207.
- [51] S. Sittel, R. Naumann, K. Heinze, *Front. Chem.* **2022**, *10*, 887439.
- [52] S. Otto, A. M. Nauth, E. Ermilov, N. Scholz, A. Friedrich, U. Resch-Genger, S. Lochbrunner, T. Opatz, K. Heinze, *ChemPhotoChem* **2017**, *1*, 344.
- [53] S. M. Stevenson, M. P. Shores, E. M. Ferreira, *Angew. Chem. Int. Ed.* **2015**, *54*, 6506.
- [54] F. J. Sarabia, E. M. Ferreira, *Org. Lett.* **2017**, *19*, 2865.
- [55] T. H. Bürgin, F. Glaser, O. S. Wenger, *J. Am. Chem. Soc.* **2022**, *144*, 14181.
- [56] S. Sittel, A. C. Sell, K. Hofmann, C. Wiedemann, J. P. Nau, C. Kerzig, G. Manolikakes, K. Heinze, *ChemCatChem* **2023**, *15*, e202201562.
- [57] C. Wang, H. Li, T. H. Bürgin, O. S. Wenger, *Nat. Chem.* **2024**, *16*, 1151.
- [58] R. F. Higgins, S. M. Fatur, S. G. Shepard, S. M. Stevenson, D. J. Boston, E. M. Ferreira, N. H. Damrauer, A. K. Rappé, M. P. Shores, *J. Am. Chem. Soc.* **2016**, *138*, 5451.

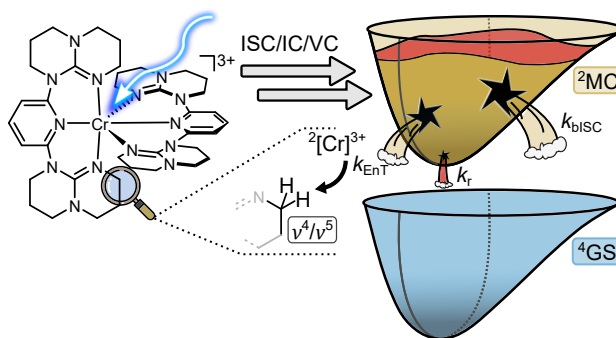
- [59] F. J. Sarabia, Q. Li, E. M. Ferreira, *Angew. Chem. Int. Ed.* **2018**, *57*, 11015.
- [60] Z. Shen, J.-L. Tu, *Eur. J. Org. Chem.* **2024**, e202401016.
- [61] C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, *49*, 1057.
- [62] M. Dorn, N. R. East, C. Förster, W. R. Kitzmann, J. Moll, F. Reichenauer, T. Reuter, L. Stein, K. Heinze in *Comprehensive Inorganic Chemistry III*, Elsevier, **2023**, p. 707–788.
- [63] F. Strieth-Kalthoff, M. J. James, M. Teders, L. Pitzer, F. Glorius, *Chem. Soc. Rev.* **2018**, *47*, 7190.
- [64] S. Dutta, J. E. Erchinger, F. Strieth-Kalthoff, R. Kleinmans, F. Glorius, *Chem. Soc. Rev.* **2024**, *53*, 1068.
- [65] M. DeRosa, *Coord. Chem. Rev.* **2002**, *233–234*, 351.
- [66] P. Bayer, R. Pérez-Ruiz, A. Jacobi von Wangelin, *ChemPhotoChem* **2018**, *2*, 559.
- [67] P. Bayer, J. Schachtner, M. Májek, A. Jacobi von Wangelin, *Org. Chem. Front.* **2019**, *6*, 2877.
- [68] M. Prein, W. Adam, *Angew. Chem. Int. Ed.* **1996**, *35*, 477.
- [69] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322.
- [70] S. Treiling, C. Wang, C. Förster, F. Reichenauer, J. Kalmbach, P. Boden, J. P. Harris, L. M. Carrella, E. Rentschler, U. Resch-Genger, C. Reber, M. Seitz, M. Gerhards, K. Heinze, *Angew. Chem. Int. Ed.* **2019**, *58*, 18075.
- [71] P. Kusuma, P. M. Pattison, B. Bugbee, *Hortic. Res.* **2020**, *7*, 56.
- [72] R. Bevernaegie, S. A. M. Wehlin, E. J. Piechota, M. Abraham, C. Philouze, G. J. Meyer, B. Elias, L. Troian-Gautier, *J. Am. Chem. Soc.* **2020**, *142*, 2732.
- [73] S. D. A. Zondag, D. Mazzarella, T. Noël, *Annu. Rev. Chem. Biomol. Eng.* **2023**, *14*, 283.
- [74] T. Noël, E. Zysman-Colman, *Chem. Catalysis* **2022**, *2*, 468.
- [75] J. W. Tucker, Y. Zhang, T. F. Jamison, C. R. J. Stephenson, *Angew. Chem. Int. Ed.* **2012**, *51*, 4144.
- [76] L. D. Elliott, J. P. Knowles, P. J. Koovits, K. G. Maskill, M. J. Ralph, G. Lejeune, L. J. Edwards, R. I. Robinson, I. R. Clemens, B. Cox, D. D. Pascoe, G. Koch, M. Eberle, M. B. Berry, K. I. Booker-Milburn, *Chem. Eur. J.* **2014**, *20*, 15226.
- [77] T. H. Rehm, *Chem. Eur. J.* **2020**, *26*, 16952.
- [78] M. Zhang, P. Roth, *Curr. Opin. Chem. Eng.* **2023**, *39*, 100897.
- [79] A. Santoro, C. Sambaglio, P. C. McGowan, M. A. Halcrow, *Dalton Trans.* **2015**, *44*, 1060.
- [80] E. A. Ünal, D. Wiedemann, J. Seiffert, J. P. Boyd, A. Grohmann, *Tetrahedron Lett.* **2012**, *53*, 54.
- [81] K. Anandababu, R. Ramasubramanian, H. Wadepohl, P. Comba, N. Johnee Britto, M. Jaccob, R. Mayilmurugan, *Chem. Eur. J.* **2019**, *25*, 9540.
- [82] A. M. McDaniel, H.-W. Tseng, N. H. Damrauer, M. P. Shores, *Inorg. Chem.* **2010**, *49*, 7981.
- [83] S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572.
- [84] N. Sinha, J.-R. Jiménez, B. Pfund, A. Prescimone, C. Piguet, O. S. Wenger, *Angew. Chem. Int. Ed.* **2021**, *60*, 23722.
- [85] J.-R. Jiménez, B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *J. Am. Chem. Soc.* **2019**, *141*, 13244.
- [86] R. D. Gillard, P. R. Mitchell, *J. Chem. Soc. A* **1968**, 2129.
- [87] M. S. Baptista, J. Cadet, P. Di Mascio, A. A. Ghogare, A. Greer, M. R. Hamblin, C. Lorente, S. C. Nunez, M. S. Ribeiro, A. H. Thomas, M. Vignoni, T. M. Yoshimura, *Photochem. Photobiol.* **2017**, *93*, 912.
- [88] H. H. Wasserman, J. L. Ives, *Tetrahedron* **1981**, *37*, 1825.
- [89] W. Adam, A. Richter, J. Markus, *Acc. Chem. Res.* **1994**, *27*, 57.
- [90] W. Adam, M. Braun, A. Griesbeck, V. Lucchini, E. Staab, B. Will, *J. Am. Chem. Soc.* **1989**, *111*, 203.
- [91] E. D. Mihelich, D. J. Eickhoff, *J. Org. Chem.* **1983**, *48*, 4135.
- [92] N. A. Porter, J. S. Wujek, *J. Org. Chem.* **1987**, *52*, 5085.
- [93] M. S. Newman, H. A. Karnes, *J. Org. Chem.* **1966**, *31*, 3980.
- [94] H. Kwart, E. R. Evans, *J. Org. Chem.* **1966**, *31*, 410.
- [95] G. Lloyd-Jones, J. Moseley, J. Renny, *Synthesis* **2008**, *2008*, 661.
- [96] T. Gendron, R. Pereira, H. Y. Abdi, T. H. Witney, E. Årstad, *Org. Lett.* **2020**, *22*, 274.
- [97] S. K. Pedersen, A. Ulfkjær, M. N. Newman, S. Yogarasa, A. U. Petersen, T. I. Sølling, M. Pittelkow, *J. Org. Chem.* **2018**, *83*, 12000.
- [98] A. F. Roesel, M. Ugandi, N. T. T. Huyen, M. Májek, T. Broese, M. Roemelt, R. Francke, *J. Org. Chem.* **2020**, *85*, 8029.
- [99] P. Enders, K. Prane, E. Schöнке, T. Taeufer, D. Michalik, J. Rabeah, R. Francke, *ChemCatChem* **2023**, *15*, e202300744.
- [100] A. J. Perkowski, C. L. Cruz, D. A. Nicewicz, *J. Am. Chem. Soc.* **2015**, *137*, 15684.
- [101] F. Glaser, O. S. Wenger, *Chem. Sci.* **2022**, *14*, 149.
- [102] S. Lin, M. A. Ischay, C. G. Fry, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, *133*, 19350.
- [103] M. A. Cismesia, T. P. Yoon, *Chem. Sci.* **2015**, *6*, 5426.
- [104] A. C. Sell, J. C. Wetzel, M. Schmitz, A. W. Maijenburg, G. Woltersdorf, R. Naumann, C. Kerzig, *Dalton Trans.* **2022**, *51*, 10799.
- [105] D. Jespersen, B. Keen, J. I. Day, A. Singh, J. Briles, D. Mullins, J. D. Weaver, *Org. Process Res. Dev.* **2019**, *23*, 1087.
- [106] B. Giese, J. A. González-Gómez, T. Witzel, *Angew. Chem. Int. Ed.* **1984**, *23*, 69.
- [107] A. Borodine, *Justus Liebigs Ann. Chem.* **1861**, *119*, 121.
- [108] L. McMurray, T. M. McGuire, R. L. Howells, *Synth.* **2020**, *52*, 1719.
- [109] J. Schwarz, B. König, *Green Chem.* **2018**, *20*, 323.
- [110] H. Roth, N. Romero, D. Nicewicz, *Synlett* **2016**, *27*, 714.

- [111] B. Lantaño, A. Postigo, *Org. Biomol. Chem.* **2017**, *15*, 9954.
- [112] G. Tarantino, C. Hammond, *ACS Catal.* **2018**, *8*, 10321.
- [113] S. Ventre, F. R. Petronijevic, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2015**, *137*, 5654.
- [114] J. Xu, N. Liu, L. Zou, F. Cheng, X. Shen, T. Liu, H. Lv, R. Khan, B. Fan, *Asian J. Org. Chem.* **2019**, *8*, 261.
- [115] D. D. M. Wayner, D. J. McPhee, D. Griller, *J. Am. Chem. Soc.* **1988**, *110*, 132.
- [116] G. P. Girina, A. A. Fainzil'berg, L. G. Feoktistov, *Russ. J. Electrochem.* **2000**, *36*, 162.
- [117] D.-M. Yan, Q.-Q. Zhao, L. Rao, J.-R. Chen, W.-J. Xiao, *Chem. Eur. J.* **2018**, *24*, 16895.
- [118] F. J. Aguilar Troyano, K. Merken, A. Gómez-Suárez, *Asian J. Org. Chem.* **2020**, *9*, 992.
- [119] N. L. Reed, T. P. Yoon, *Chem. Soc. Rev.* **2021**, *50*, 2954.
- [120] H. Guyon, H. Chachignon, D. Cahard, *Beilstein J. Org. Chem.* **2017**, *13*, 2764.
- [121] Y. Qiu, A. Scheremetjew, L. H. Finger, L. Ackermann, *Chem. Eur. J.* **2020**, *26*, 3241.
- [122] T. Koike, M. Akita, *Top. Catal.* **2014**, *57*, 967.
- [123] D. A. Nagib, D. W. C. MacMillan, *Nature* **2011**, *480*, 224.
- [124] I. Abdaj, C. Bottecchia, J. Alcazar, T. Noël, *Synthesis* **2017**, *49*, 4978.
- [125] S. Barata-Vallejo, B. Lantaño, A. Postigo, *Chem. Eur. J.* **2014**, *20*, 16806.
- [126] K. R. Ryan, I. C. Plumb, *J. Phys. Chem.* **1982**, *86*, 4678.
- [127] D. A. House, *Chem. Rev.* **1962**, *62*, 185.
- [128] S. A. Shafiee, J. Aarons, H. H. Hamzah, *J. Electrochem. Soc.* **2018**, *165*, H785–H798.

3.6 Thermally Activated and Non-activated Excited State Decay of $[\text{Cr}(\text{dgpy})_2]^{3+}$

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Inorg. Chem. 2025, submitted.



The complex $[\text{Cr}(\text{dgpy})_2]^{3+}$ contains a total of four guanidine donor-units between its two ligands. This contrasts the more typical polypyridyl ligands utilized in highly emissive *Molecular Rubies*. The photophysical characterization of this complex revealed a bathochromic shift of the emission energy compared to e.g. $[\text{Cr}(\text{ddpd})_2]^{3+}$ (775 nm $\rightarrow$ 835 nm), indicating a stronger *nephelauxetic effect* induced by the guanidine moieties. In addition, a strikingly low quantum yield ($\Phi_{\text{PL},0} = 0.5\%$) and short excited-state lifetime ($\tau_0 = 63 \mu\text{s}$) were observed. Experimental and quantum chemical investigations revealed intramolecular energy-transfer to the methylene groups of the saturated guanidine units, as well as thermally activated bISC as the dominant non-radiative decay pathways.

Author Contributions

Steven Sittel synthesized and characterized the complex $[\text{Cr}(\text{dgpy})_2]^{3+}$ and performed the quantum chemical calculations. Steven Sittel and [REDACTED] measured and interpreted the emission data. [REDACTED] solved and refined the XRD structure (CCDC no. 2448606) and assisted with the quantum chemical calculations. [REDACTED] performed and interpreted mass spectrometric gas phase studies (electron transfer dissociation, ETD and collision-induced dissociation, CID). [REDACTED] designed the project, helped with the interpretation of the data and wrote the manuscript. All authors discussed the scientific results and contributed to the final version of the manuscript.

Supporting Information

for this article can be found on pp. 298.

Thermally Activated and Non-activated Excited State Decay of $[\text{Cr}(\text{dgp})_2]^{3+}$

Steven Sittel,^a

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Keywords: chromium, ligand field theory, multiphonon relaxation, photophysics, spin-flip luminescence

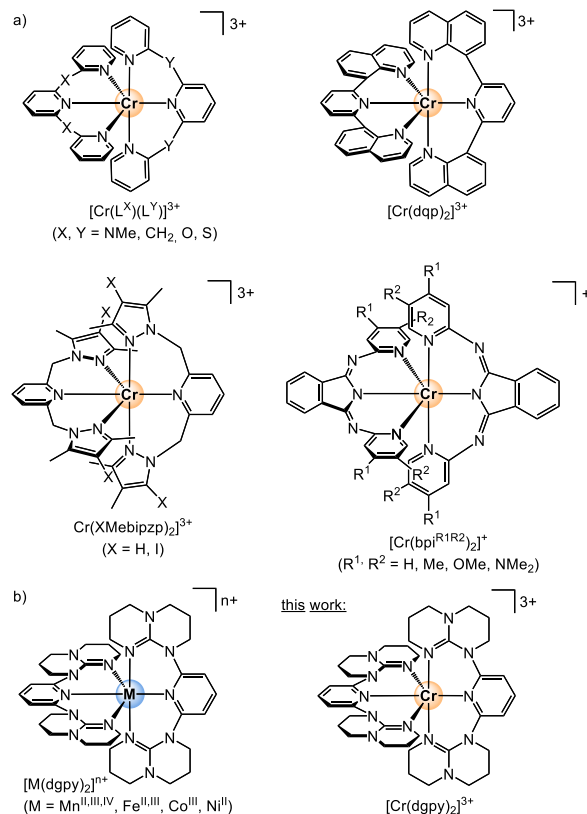
ABSTRACT: Photoactive and luminescent chromium(III) complexes are typically coordinated by aromatic N-heterocyclic chelate ligands such as polypyridines. Photoluminescence quantum yields and lifetimes can achieve up to 30 % and several milliseconds, respectively. The effect of aliphatic N-donor ligands (guanidines) on the non-radiative decay of emissive doublet states remained, however, underexplored. Here we describe the preparation, structure, redox chemistry, gas phase stability and photophysical properties of the complex $[\text{Cr}(\text{dgp})_2][\text{PF}_6]_3$ with pyridine and guanidine donors (dgp = 2,6-diguanidylpyridine). Variable-temperature luminescence spectroscopy, near-infrared overtone spectroscopy as well as quantum chemical calculations identified the major thermally activated and non-activated decay pathways and inform on future design criteria for photoactive chromium(III) complexes.

INTRODUCTION

Pseudo-octahedral polypyridine chromium(III) complexes are notable among photoactive first-row transition metal complexes for their outstanding photophysical and photochemical properties.¹⁻⁸ In a strong ligand field – imposed by chelate ligands forming six-membered rings – chromium(III) ions have long-lived doublet excited states (^2MC : ^2E and $^2\text{T}_1$ in octahedral symmetry) that emit red to near-infrared (NIR) spin-flip (SF) photoluminescence (PL).^{2,5,9} Advances in highly emissive chromium(III) “molecular ruby” complexes have renewed interest in this area (e.g. $[\text{Cr}(\text{L}^{\text{X}})(\text{L}^{\text{Y}})]^{3+}$ or $[\text{Cr}(\text{dqp})]^{3+}$,¹⁸⁻²¹ Chart 1), enabling applications in sensing,²²⁻²⁴ upconversion,^{25,26} circularly polarized luminescence,^{20,21,27-30} and photocatalysis.^{18,19,31-34} The nephelauxetic effect^{10,11,35-37} has been recognized as key to shifting the SF states to lower energy, for example using cyanide,³⁸ carbanionic,^{39,40} amide^{28,41-44} or carbene ligands^{45,46} or other metal centers with d^3 or d^2 electron configuration such as molybdenum(III),⁴⁷ vanadium(III),^{48,49} vanadium(II)⁵⁰ or manganese(IV).^{51,52}

The radiative rate constant k_r for the spin- and Laporte-forbidden SF phosphorescence in pseudo-octahedral chromium(III) complexes is typically below $k_r < 200 \text{ s}^{-1}$ (e.g. Chart 1, Chart S1).⁷ Hence, the achievable PL quantum yield Φ is dominated by the non-radiative rate constant k_{nr} , which can span several orders of magnitude ($10^2 - 10^5 \text{ s}^{-1}$, Figure 1a).⁷

Chart 1. a) Selected pseudo-octahedral chromium(III) complexes with strong-field ligands, but highly variable PL quantum yields (more examples are shown in Chart S1).^{10-21,41-43,53} b) Homoleptic metal complexes of the ligand dgp.^{51,54-57}



Heavy atoms as substituents can increase both k_r and k_{nr} via the heavy atom effect, i.e. increased spin-orbit coupling. Yet this increased spin-orbit coupling can affect k_r and k_{nr} to a similar extent so that Φ remains constant ($X = H \rightarrow X = I$ substitution in $[\text{Cr}(\text{XMe}bipzp)_2]^{3+}$; Chart 1, Figure 1a).⁵³ The heavy atom effect can even favor k_{nr} over k_r ($X = O \rightarrow X = S$ substitution in $[\text{Cr}(\text{L}^X)_2]^{3+}$; Chart 1), so that Φ even decreases.¹⁰

Two major non-radiative SF state decay pathways have been proposed. The first process is thermally activated back-inter-system crossing (bISC) from the doublet SF states to distorted quartet metal-centered excited states (^4MC), which rapidly evolve to the $^4\text{A}_2$ ground state.^{2,7} This decay path depends on the ligand field splitting in the Franck-Condon (FC) geometry and on the flexibility of the ligand sphere to accommodate the distorted ^4MC state with elongated metal-ligand bonds. Both factors determine the energy of the relaxed lowest-energy ^4MC state and thus the activation barrier E_a for the thermally activated bISC $^2\text{MC} \rightarrow ^4\text{MC}$.

The second relaxation path of SF excited states of chromium(III) complexes (weak coupling limit) has been described by the energy gap law (eq. 1),⁵⁸ which had been successful for charge transfer excited states (strong coupling limit).^{59–62} While the series of complexes with bpi^{R1R2-} ligands (Chart 1) follows the energy gap relation (eq. 1) well,⁴¹ other Cr complexes do not seem to follow this relation (Figure 1a, see Chart S1 for structures of all complexes). $\ln(k_{nr}) \propto -\tilde{\nu}$ (eq. 1)

Clearly, a strict dependence of Φ or k_{nr} on the SF energy $\tilde{\nu}$ is not obvious. This applies even to the rather homogeneous class of chromium(III) emitters with meridional tridentate ligands forming six-membered chelate rings (Chart 1, Chart S1, Figure 1a). For example, the SF energy $\tilde{\nu}$ of chromium(III) complexes with L^X ($X = \text{CH}_2, \text{O}, \text{NMe}$), Me- $bipzp$ and dqp ligands cover approximately 1200 cm^{-1} , but k_{nr} does not change significantly (Figure 1a). Introduction of iodine approximately keeps $\tilde{\nu}$, but significantly increases k_{nr} (Figure 1a, $[\text{Cr}(\text{XMe}bipzp)_2]^{3+}$).⁵³ Substitution of $X = \text{O}$ by $X = \text{S}$ barely changes $\tilde{\nu}$ as well, but increases k_{nr} by orders of magnitude (Figure 1a, $[\text{Cr}(\text{L}^X)_2]^{3+}$).

A more specific interpretation of the energy gap law in the weak coupling limit is known as resonant vibrational energy transfer to high-frequency X–H overtones ν_{XH}^n of the ligand or the solvent, typically C–H, N–H or O–H overtones.^{63,64} Indeed, deuteration of the coordinating ligands has been shown to increase Φ by decreasing k_{nr} , while keeping k_r and $\tilde{\nu}$ constant.^{14,15,65} The rate constant for this multiphonon relaxation via resonant energy transfer to high-energy oscillators k_{nr} depends on the energy-donor-acceptor distance with d^{-6} , an orientation factor κ and the Förster-type spectral overlap integral SOI (eq. 2 and 3).^{63,64} Due to the strong dependence on the distance with d^{-6} , only X–H oscillators close to the metal center, i.e. in the first coordination sphere, are efficient energy acceptors. The SOI integrates over the product of the area-normalized emission intensity $I_{norm}(\tilde{\nu})$ and the extinction coefficient of the respective overtone vibration $\varepsilon_{vib}(\tilde{\nu})$ scaled by $\tilde{\nu}^{-4}$ (eq. 3).

$$k_{nr} \propto \kappa^2 d^{-6} \text{SOI} \quad (\text{eq. 2})$$

$$\text{SOI} = \int I_{norm}(\tilde{\nu}) \varepsilon_{vib}(\tilde{\nu}) \tilde{\nu}^{-4} d\tilde{\nu} \quad (\text{eq. 3})$$

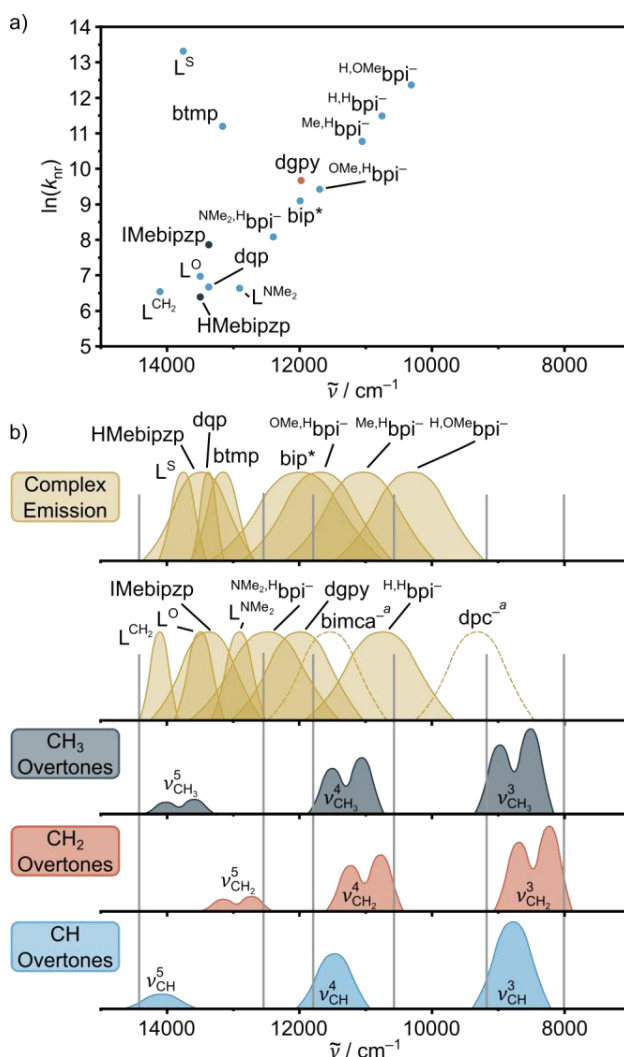


Figure 1. a) Plot of $\ln(k_{nr})$ (at room temperature) versus SF emission energy $\tilde{\nu}$ according to eq. 1 for various chromium(III) complexes with the indicated ligands (Chart 1, Chart S1). b) Schematic plot of normalized emission bands of homoleptic chromium(III) complexes with the indicated ligands and C–H overtone absorption bands for CH_3 ,^{46,66} CH_2 ⁶⁷ and CH^{15} units. Note that the intensities of the higher C–H overtones decrease much stronger than schematically indicated here, that CH_n overtone regions additionally can contain combination bands,⁶⁷ that CH_2 in rings splits into axial and equatorial C–H modes and that CH_3 overtones can split when attached to rings,⁶⁶ which is qualitatively indicated. ^a Non-emissive complex at room temperature; data from absorption or 77 K spectrum.

If the SF emission band extends over several X–H overtones, summation of the individual SOIs is required. Due to the scaling with $\tilde{\nu}^{-4}$ and the fact that the molar absorption coefficient $\varepsilon_{vib}(\tilde{\nu})$ of higher overtones is much smaller, this energy transfer mechanism appears only significantly relevant in the regions of the second to fourth C–H overtones ν_{CH}^3 to ν_{CH}^5 with a strongly decreasing impact at higher overtones.

This is schematically illustrated in Figure 1b for CH₃,^{46,66} CH₂⁶⁷ and CH¹⁵ overtones and the emission bands of a series of chromium(III) complexes (Chart 1, Chart S1). We divided the aliphatic C–H modes in CH₂ and CH₃ modes (Figure 1b), as their overtone energies (different anharmonicity) and the number and orientation of C–H units differ, and as CH₂ units are often encountered in rigid cyclic structures, while CH₃ substituents are most often free rotors. This might have an additional effect on k_{nr} via the orientation factor κ (eq. 2). Interestingly, multiphonon relaxation pathways can also be thermally activated, when higher energy excited SF states that contribute to the non-radiative decay are thermally populated according to a Boltzmann distribution.¹⁰ In such cases, the emission intensity is temperature-dependent and activation barriers of a few hundred wavenumbers can be extracted by applying Arrhenius' law. These energy barriers roughly correspond to energy gaps between the lowest SF states.¹⁰ Additionally, changes of emission band shapes, band widths and band positions with temperature can modify the SOIs and hence k_{nr} .

In most cases reported so far, the CH moieties closest to the chromium center are the α -C–H units of the coordinating terminal aromatic heterocyclic donors (pyridine, quinoline, indazol, Chart 1, Chart S1), although methyl substituents at the α -position seem to play a role as well ([Cr(XMebipz)₂]³⁺,⁵³ N-heterocyclic carbene complexes,^{45,46} Chart 1a, Chart S1). Methylene units close to the chromium(III) center have not yet been considered, although these are present for example in the classical 1,2-ethylenediamine chromium(III) complexes.^{3,68}

In the present study, we investigate the influence of guanidine donors on the SF emission energy (nephelauxetic effect) and the effect of methylene groups close to the chromium(III) center on the non-radiative decay (see Figure 1b for estimated CH₂ overtones⁶⁷) found in the ligand 2,6-diguanidylpyridine (dgpy)⁶⁹ on the SF emission of chromium(III) in the complex [Cr(dgpy)₂]³⁺. Although this adaptive tridentate N-donor ligand had been successfully coordinated to the 3d metals manganese, iron, cobalt and nickel in various oxidation states,^{51,54–57} dgpy complexes with chromium(III) had not been reported so far (Chart 1b).

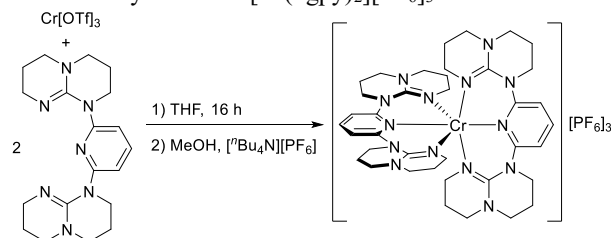
RESULTS AND DISCUSSION

Synthesis and Characterization of [Cr(dgpy)₂][PF₆]₃. The ligand dgpy was obtained by a literature procedure,⁶⁹ separated from the KBr by-product via extraction with toluene and carefully dried to avoid protonation of the basic guanidine sites (Figure S1), which would hamper complex formation. Coordination of dgpy to chromium(III) triflate in dry THF, salt metathesis with [*n*-Bu₄N][PF₆] and recrystallization gave [Cr(dgpy)₂][PF₆]₃ as orange crystals in 43 % yield (Scheme 1). The six-coordinate chromium(III) complex is stable under non-inert conditions (O₂, H₂O). Large but twinned crystals of [Cr(dgpy)₂][PF₆]₃×1.5 DMF were obtained by recrystallization from DMF/diethyl ether (Figure S2). SC-XRD confirmed the overall structure (Figure S3a), but twinning and disorder of the counter ions and in some of the terminal six-membered rings of the guanidine units precluded a detailed analysis of the bond lengths and angles. However, density functional theory (DFT) calculations

(B3LYP, TZVPP, ZORA, CPCM, D3BJ) typically describe the geometry of chromium(III) complexes well (Figure S3b).^{10,11,13,14} The metrical data for [Cr(dgpy)₂]³⁺ in its ⁴A₂ ground state are collected in Table S1. Remarkably, the Cr–N_{py} and Cr–N_{guanidine} distances are very similar, in spite of the different donor strengths of pyridine and guanidine. The N–Cr–N angles are with 87 – 94° and 173 – 179° close to values for an ideal octahedron.

The ATR IR spectrum of [Cr(dgpy)₂][PF₆]₃×1.5 DMF crystals confirms the presence of DMF ($\tilde{\nu}_{CO}$ = 1670 cm^{−1}) and PF₆[−] counter ions ($\tilde{\nu}_{PF}$ = 829, 554 cm^{−1}). The C–H vibrations of the ligand are observed at $\tilde{\nu}_{CH,pyridine}$ = 3119 cm^{−1} and $\tilde{\nu}_{CH2,guanidine}$ = 2960, 2876 cm^{−1} (Figure S4).⁷⁰ The ESI⁺ mass spectrum of [Cr(dgpy)₂][PF₆]₃ in MeCN shows characteristic peaks for the trication [Cr(dgpy)₂]³⁺ (m/z = 253) and the ion clusters {[Cr(dgpy)₂][PF₆]}²⁺ (m/z = 452) and {[Cr(dgpy)₂][PF₆]₂}⁺ (m/z = 1048) (Figure S5). In the cyclic voltammogram of [Cr(dgpy)₂][PF₆]₃ in [*n*-Bu₄N][PF₆]/MeCN, the complex cation [Cr(dgpy)₂]³⁺ is quasireversibly oxidized at $E_{p,ox}$ = 1.68 V and irreversibly reduced at $E_{p,red}$ = −1.56 V versus SCE (Figure S6a, 6b).

Scheme 1. Synthesis of [Cr(dgpy)₂][PF₆]₃.



To further elucidate the instability after reduction in the condensed phase, we turned to gas phase studies in the mass spectrometer. Electron transfer dissociation (ETD) spectra were obtained from the [Cr(dgpy)₂]³⁺ and {[Cr(dgpy)₂][PF₆]}²⁺ species (Figures S7, S8, Supporting Information). While the former is cleanly reduced to [Cr(dgpy)₂]²⁺ (m/z = 379) and [Cr(dgpy)₂]⁺ (m/z = 758), the ion cluster undergoes further reactions. After electron capture of {[Cr(dgpy)₂][PF₆]}²⁺ to give {[Cr(dgpy)₂][PF₆]}⁺ (m/z = 903), PF₅ is cleaved off to yield {[Cr(dgpy)₂F]}⁺ (m/z = 777) and finally dissociation of one dgpy ligand results in {[Cr(dgpy)F]}⁺ (m/z = 424). The fluoro ligands are presumably coordinated to the metal center in {[Cr(dgpy)₂F]}⁺ and {[Cr(dgpy)F]}⁺ with a dgpy ligand partially and fully dissociated, respectively. This sequence is reasonably described as an intermediate associative substitution reaction⁷¹ at chromium after (metal-centered⁷²) reduction. Analogous gas phase reactions were discussed for [Mn(dgpy)₂]ⁿ⁺ and PF₆[−] counter ions.⁷³ It is highly conceivable, that the reduced chromium(III) complex undergoes similar substitution reactions with PF₆[−] nucleophiles in solution. Collision-induced dissociation (CID) mass spectrometric experiments confirm the higher lability of reduced species and contact ion pairs with the counter ion (Figure S9, S10). All chromium species show unspecific fragmentation patterns, which in part prevents assignments, and hints at fragmentation of the dgpy skeleton. If the counter ion PF₆[−] is attached, the loss of PF₅ is the dominant fragmentation channel. The CID breakdown curves suggest an increasing lability in the series

$[\text{Cr}(\text{dgy})_2]^{3+} < [\text{Cr}(\text{dgy})_2]^{2+} < \{[\text{Cr}(\text{dgy})_2][\text{PF}_6]\}^{2+} < \{[\text{Cr}(\text{dgy})_2][\text{PF}_6]\}^+ \approx \{[\text{Cr}(\text{dgy})_2][\text{PF}_6]_2\}^+$. In the condensed phase (MeCN solution), $[\text{Cr}(\text{dgy})_2]^{3+}$ is stable in the presence of the comparably weakly coordinating anion PF_6^- , while $[\text{Cr}(\text{dgy})_2]^{2+}$ appears unstable possibly reacting with the counter ion (Figures S5–S10). To confirm the role of hexafluorophosphate in the irreversible reduction in solution, we turned to perchlorate as electrolyte in cyclic voltammetry experiments. Indeed, the reduction process becomes more reversible both in $\text{MeCN}/[n\text{-Bu}_4\text{N}][\text{ClO}_4]$ and in $\text{DMF}/[n\text{-Bu}_4\text{N}][\text{ClO}_4]$ with $E_{1/2} = -1.53$ V and -1.57 V, respectively (Figure S6c, 6d). Consequently, $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ is not the best choice as electrolyte for labile and highly charged redox intermediates.

Optical characterization of $[\text{Cr}(\text{dgy})_2][\text{PF}_6]_3$. UV/vis/NIR absorption, excitation and emission spectra of $[\text{Cr}(\text{dgy})_2][\text{PF}_6]_3$ in MeCN are depicted in Figure 2. Spin-allowed charge transfer ($^4\text{ILCT}$) and ligand field (^4MC admixed with CT character) absorption bands are discernable below 400 nm and at 466 nm/520 (sh) nm, respectively, according to time-dependent density functional theory (TD-DFT) calculations and charge transfer number analysis (Table S2, Figure S11). The spin-forbidden NIR absorption band pattern between 680 and 850 nm (Figure 2) was fitted using five Voigt functions with maxima at 712, 740, 752, 781 and 809 nm (14045, 13515, 13300, 12800 and 12360 cm^{-1} ; Figure S12). The molar absorption coefficients ϵ are below 0.5 $\text{M}^{-1} \text{cm}^{-1}$ due to the spin- and Laporte-forbidden⁷⁴ nature of these transitions. CASSCF(7,12)-NEVPT2 calculations on the ligandfield transitions at the FC geometry assign $^2\text{T}_1(3)$, $^2\text{E}(2)$, $^2\text{E}(1)$, $^2\text{T}_1(2)$ and $^2\text{T}_1(1)$ character to the spin- and Laporte-forbidden NIR absorption bands, respectively (Figure S13–S14, Tables S3, S4).

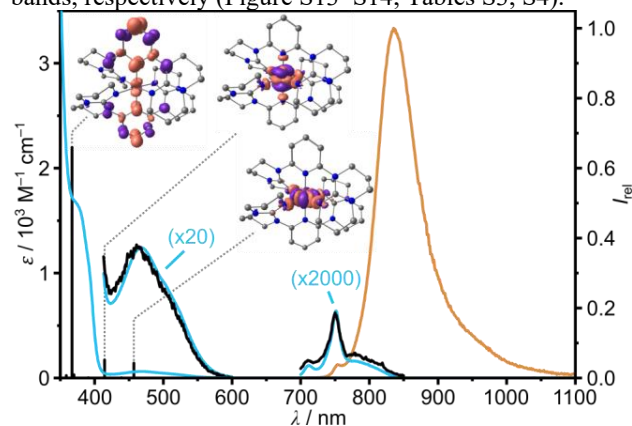


Figure 2. UV/vis/NIR absorption spectrum (blue), normalized excitation spectrum ($\lambda_{\text{em}} = 836$ nm and 875 nm for spin-allowed and spin-forbidden transitions, respectively, black) and normalized emission spectrum ($\lambda_{\text{exc}} = 468$ nm, orange) of $[\text{Cr}(\text{dgy})_2][\text{PF}_6]_3$ in deaerated MeCN at 293 K. The spin-forbidden and the low-energy spin-allowed absorption bands are scaled with the indicated factors. TD-DFT calculated oscillator strengths (black vertical bars) and difference electron densities of selected transitions.

Excitation at the ^4MC absorption maximum throughout the visible spectral region and at the ^2MC NIR bands (black excitation spectra in Figure 2) yields SF emission bands peaking at 754 nm (weak) and 835 nm (strong) with a full-width-at-half-maximum FWHM = 1010 cm^{-1} (orange emission

spectrum in Figure 2). This energy is below that of typical emissive polypyridine chromium(III) complexes, suggesting a stronger nephelauxetic effect^{35–37} of guanidine than pyridine donors (Figure 1).^{10–17,75} The stronger low-energy emission band possesses $^2\text{T}_1(1) \rightarrow ^4\text{A}_2$ character according to the CASSCF(7,12)-NEVPT2 calculations (Table S4). However, the numerical agreement between experimental and calculated energies is somewhat poorer than typically observed for polypyridine chromium(III) with this CASSCF method, even after scaling with an empirical scaling factor for the calculated SF energies^{10,11} (Figure S14). We attribute this to the effect of different donors, namely the four guanidines instead of pyridine donors. The experimental Stokes shift of 390 cm^{-1} (lowest absorption band at 809 nm, lowest emission band at 835 nm) is in the region typically observed for chromium(III) SF emitters with rather nested excited doublet states.

The PL lifetime of $\tau = 63$ μs at room temperature in MeCN is short (Figure S15) compared to that of benchmark molecular ruby complexes with millisecond lifetimes.^{10–21} Similarly, the PL quantum yield $\Phi = 0.5\%$ is comparably low.^{10–21} The resulting radiative rate constant $k_r = \Phi / \tau = 80 \text{ s}^{-1}$, however, is in the typical range of spin- and Laporte forbidden transitions in chromium(III) complexes.^{2,10–21} Hence, the low PL lifetime and quantum yield must be ascribed to efficient non-radiative decay pathways. Under air, the lifetime decreases marginally to 53 μs (Figure S15), suggesting only inefficient quenching of the doublet excited states by triplet oxygen.^{13,34} This inertness towards oxygen is based on the short excited state lifetime and the metal-centered nature of the excited state, hampering efficient wavefunction overlap for Dexter energy transfer.¹³

To elucidate thermally activated decay pathways such as bISC to ^4MC states or thermally activated multiphonon relaxation, temperature-dependent PL studies were performed. The emission band develops a vibrational fine structure in frozen butyronitrile ($n\text{-PrCN}$) at 77 K with maxima centered at 816, 834, 863, and 925 nm (12255, 11990, 11590 and 10810 cm^{-1} ; fitted with Voigt functions, Figure S16). Progressions of similar magnitude have been observed for $[\text{Cr}(\text{L}^X)_2]^{3+}$ ($X = \text{O}, \text{S}, \text{CH}_2, \text{NMe}$) and assigned to Cr–N vibrational modes.^{10–17} At 77 K, the PL lifetime increases by a factor of 5.7 to 360 μs (Figure S16) suggesting the presence of thermally activated decay pathways. However, millisecond lifetimes at 77 K as found for e.g. $[\text{Cr}(\text{L}^X)_2]^{3+}$ ($X = \text{O}, \text{S}$) are not achieved, suggesting efficient non-radiative decay even at 77 K.

To extract detailed kinetic information, temperature-dependent PL lifetime measurements were performed between 313 and 175 K in $n\text{-PrCN}$ (Figure 3). This solvent remains liquid in this temperature range and rigidochromic effects are not expected. Two kinetic regimes can be estimated from an Arrhenius plot. The activation energies and pre-exponential factors amount to $E_{a1} = 30 \text{ cm}^{-1}$, $E_{a2} = 2850 \text{ cm}^{-1}$ and $A_1 = 5.8 \times 10^3 \text{ s}^{-1}$, $A_2 = 2.7 \times 10^{10} \text{ s}^{-1}$, respectively. While the first process is essentially barrierless (small E_{a1}) but inefficient (small A_1), the second process is thermally activated (larger E_{a2}) but more efficient (larger A_2).

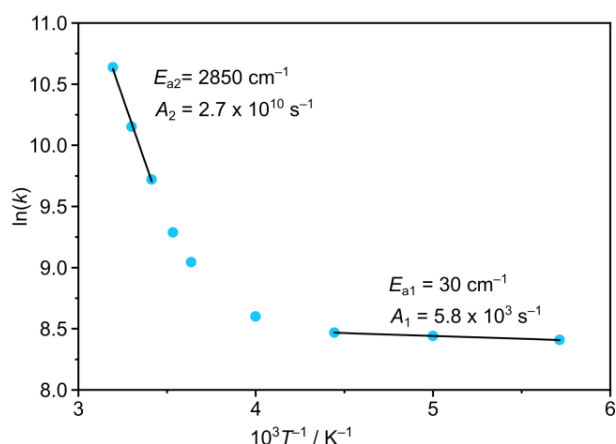


Figure 3. Arrhenius plot of the PL rate constants $\ln(k(T))$ vs. T^{-1} in the range $T = 175\text{--}313\text{ K}$ (blue) with two linear fits (black) according to $\ln(k) = \ln(A) + (-E_a/RT)$ and $k(T) = \alpha(T)^{-1}$. Measurements were performed in *n*-PrCN, which remains liquid in this temperature range.

Similarly, the complexes $[\text{Cr}(\text{L}^X)_2]^{3+}$ ($X = \text{O}, \text{S}$) show barriers of $370/3360\text{ cm}^{-1}$ and $1090/4320\text{ cm}^{-1}$ with pre-exponential factors of $1.80 \times 10^3/9.18 \times 10^9\text{ s}^{-1}$ and $4.65 \times 10^6/6.27 \times 10^{14}\text{ s}^{-1}$, respectively.¹⁰ The larger barriers were associated with thermally activated bISC to distorted ^4MC states, while the smaller ones were attributed to thermally activated energy transfer to C–H overtones by population of higher-energy SF states.¹⁰

In the present case, the barrier $E_{a2} = 2850\text{ cm}^{-1}$ might be assigned to thermally activated bISC as well. Compared to the barriers of $[\text{Cr}(\text{L}^X)_2]^{3+}$ ($X = \text{O}, \text{S}$), this barrier is lower by 510 and 1470 cm^{-1} , respectively. Hence, in $[\text{Cr}(\text{dgpy})_2]^{3+}$, bISC dominates the decay to a larger extent. A strongly distorted metal-centered state could be localized by TD-DFT geometry optimization (Table S1). Indeed, this geometry optimized ^4MC state has elongated Cr–N_{py} bonds up to 2.34 Å , a reduced intraligand N_{gua}–Cr–N_{guanidine} angle of 157° and a significant tilting of the pyridines with Cr–N_{py}–C_{para} of 160° as compared to Cr–N_{py} = 2.04 Å , N_{guanidine}–Cr–N_{guanidine} = 173° and Cr–N_{py}–C_{para} = 179° in the $^4\text{A}_2$ ground state. This optimized ^4MC state at 2.07 eV is lower by 0.64 eV than the respective FC state ($E_{\text{DFT,FC}} = 2.71\text{ eV}$) suggesting a major energy gain upon distortion. The energy lowering of the ^4MC state might be sufficient to enable thermally activated bISC from the ^2MC state(s) to the distorted ^4MC state(s). Furthermore, the large frequency factor $A_2 = 2.7 \times 10^{10}\text{ s}^{-1}$ suggests sufficient coupling of the doublet and quartet excited states.

To probe the second, nearly barrierless process, we focus on C–H oscillators of the dgpy ligand that are close to the metal center, i.e. guanidine ring-methylene units, which could contribute to the non-radiative excited state decay (d^6 dependency, eq. 2). The shortest Cr $\cdots$ CH₂ distances amount to $d_1 = 3.0\text{ Å}$ with the equatorial hydrogen atom of the CH₂ unit being closer to the metal than the axial one. The other five CH₂ groups possess Cr $\cdots$ CH₂ distances of $d_n = 4.4, 4.9, 5.4, 5.4$ and 4.7 Å ($n = 2\text{--}6$) and these will contribute less to k_{nr} (eq. 2).

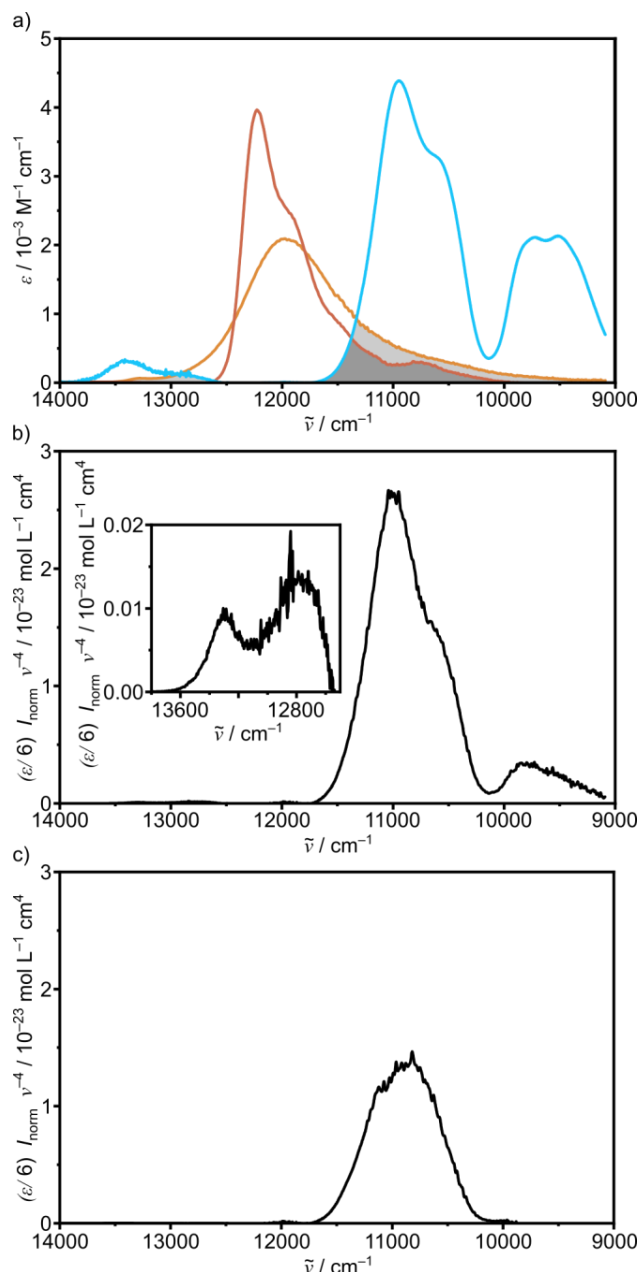


Figure 4. a) Emission spectra of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$ at 293 K (light orange, in MeCN) and 77 K (dark orange, in *n*-PrCN) and NIR absorption spectrum of *N*-deuterated 1,5,7-triazabicyclo[4.4.0]dec-5-ene (blue) in CD_2Cl_2 . Plots of the product of the extinction coefficients of *N*-deuterated 1,5,7-triazabicyclo[4.4.0]dec-5-ene (normalized to one CH_2 unit) in CD_2Cl_2 and the emission intensity (normalized to a unit area) of $[\text{Cr}(\text{dgpy})_2]^{3+}$, scaled with $\tilde{\nu}^{-4}$ in the overtone regions of ν_{CH^4} and ν_{CH^5} in MeCN b) at 293 K and c) at 77 K (eq. 3). The inset in b) shows a close-up of the ν_{CH^5} overtone region. While overtone spectra of ring CH_2 groups, e.g. cyclohexane, have been reported ($\nu_{\text{CH}^{2,3,4,5}} \approx 5700, 8300, 10800$ and 13100 cm^{-1}),⁶⁷ data for bicyclic guanidines are lacking. We chose the soluble 1,5,7-triazabicyclo[4.4.0]dec-5-ene as ligand and surrogate without interfering C–H modes of pyridine (Figure S17).⁷⁶ To eliminate the contribution of the N–H overtones of 1,5,7-triazabicyclo[4.4.0]dec-5-ene, we also

recorded the IR overtone spectrum of the *N*-deuterated derivative⁷⁷ in the spectral region of the $[\text{Cr}(\text{dgpy})_2]^{3+}$ emission band (Figure 4a, Figure S18). In fact, significant spectral overlap exists between the SF luminescence band of $[\text{Cr}(\text{dgpy})_2]^{3+}$ and the ν_{CH}^4 band of the *N*-deuterated model guanidine at 293 K (Figure 4a). Additionally, small spectral overlap of the weak higher energy emission is seen with the ν_{CH}^5 band around 13000 cm^{-1} . A combination band below 10000 cm^{-1} also contributes to the spectral overlap (Figure 4a).

As a measure of the SOI that is responsible for the energy transfer to individual CH_2 overtones, we plotted the product of the area-normalized emission spectrum of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$ at 293 K and the NIR overtone spectrum of *N*-deuterated 1,5,7-triazabicyclo[4.4.0]dec-5-ene (divided by 6 to account for the six CH_2 units of the bicyclic model) scaled with $\tilde{\nu}^{-4}$ (eq. 3, Figure 4b). Several C–H overtone regions contribute to the total SOI, namely the third and fourth C–H overtones ν_{CH}^4 and ν_{CH}^5 at around 11000 and 13400 cm^{-1} , respectively, in addition to a combination band at around 9800 cm^{-1} . At 77 K, however, the overlap between ν_{CH}^5 and the area-normalized emission vanishes due to depopulation of the higher SF states (Figure 4a). More importantly, the emission band sharpens at 77 K (FWHM = 540 cm^{-1}), which leads to a significantly smaller spectral overlap in the ν_{CH}^4 and combination mode regions (Figure 4c). The calculated SOIs for a single CH_2 moiety amount to 2.1×10^{-20} and $1.2 \times 10^{-20} \text{ M}^{-1} \text{ cm}^3$ at 293 and 77 K, respectively. The non-radiative rate constant k_{nr} of $[\text{Cr}(\text{dgpy})_2]^{3+}$ (four guanidines with six CH_2 units each) scales with the sum of the d^{-6} weighted SOI of a single CH_2 unit (eq. 2). Weighted summation over all six CH_2 units per guanidine with the respective $\text{Cr} \cdots \text{CH}_2$ distances multiplied by four to account for the four guanidines of the two dgpy ligands in

$[\text{Cr}(\text{dgpy})_2]^{3+}$ gives a factor $f = 4 \sum_{n=1}^{n=6} d_n^{-6} = 0.007$ with the closest CH_2 unit at a distance d_1 contributing 78% to f . Irrespective of inclusion of only the closest (d_1) or all CH_2 units ($4 \times (d_1 - d_6)$), the SOI increases by a factor of 1.75 at 293 K as compared to 77 K and hence k_{nr} should increase by a factor of 1.75 as well, based on the resonant energy transfer relaxation path. As the radiative rate constant $k_r = \Phi/\tau = 80 \text{ s}^{-1}$ should be temperature-independent,^{78–80} we can estimate $k_{\text{nr}}(293 \text{ K}) = 15800 \text{ s}^{-1}$ and $k_{\text{nr}}(77 \text{ K}) = 2700 \text{ s}^{-1}$. The experimental ratio of $k_{\text{nr}}(293 \text{ K}) / k_{\text{nr}}(77 \text{ K}) = 5.85$ is larger than the estimated increase via multiphonon relaxation only (factor of 1.75). The remaining contribution to excited state relaxation at increasing temperature hence stems from thermally activated bISC to ^4MC states. In the present complex, bISC is the dominant decay path at higher temperatures, while resonant energy transfer dominates at lower temperature (Figure 3).

The alternative assignment of the larger barrier E_{a2} to thermally activated resonant energy transfer to the higher-energy ν_{CH}^5 overtone (12600 – 13500 cm^{-1}) by thermal population of higher-energy SF states ($^2\text{T}_1(2)$, $^2\text{E}(1)$, $^2\text{E}(2)$ states at 12809, 13306, 13516 cm^{-1}) seems possible as well based on thermodynamics. However, the drastically different pre-ex-

ponential factors A_1 and A_2 (Figure 3) for both processes suggest different mechanisms for the two processes. This is further supported by the similar behavior of $[\text{Cr}(\text{L}^X)_2]^{3+}$ ($X = \text{O}, \text{S}$) complexes.¹⁰

SUMMARY AND CONCLUSIONS

This study details the thermally activated and non-activated relaxation pathways of the emissive doublet states in a chromium(III) complex $[\text{Cr}(\text{dgpy})_2]^{3+}$ coordinated with bicyclic guanidine and pyridine donor units (dgpy = 2,6-diguanidylpyridine). The guanidine donor shifts the spin-flip emission energy bathochromically as compared to pyridine donors (nephelauxetic effect). The radiative rate constant is small with $k_r = 80 \text{ s}^{-1}$ due to the spin- and Laporte-forbidden nature of the transition, typical for chromium(III) complexes. On the other hand, the non-radiative rate constant is with $k_{\text{nr}} = 15800 \text{ s}^{-1}$ at 293 K quite large for molecular rubies. Two temperature-dependent processes contribute to k_{nr} , namely thermally activated back-intersystem crossing to distorted metal-centered quartet states with elongated Cr–N_{py} bonds with an activation barrier of 2850 cm^{-1} and resonant energy transfer to the third and fourth vibrational overtones $\nu_{\text{CH}}^{4/5}$ and overtone combination bands of the CH_2 units. This energy transfer is a temperature-dependent process as well, due to spectral narrowing of the emission band at 77 K to 53 % of the original FWHM, which diminishes the spectral overlap with ν_{CH}^4 and combination modes, and depopulation of higher-energy doublet states, which reduces the spectral overlap with the ν_{CH}^5 overtone at lower temperature.

The dgpy ligand provides two non-radiative relaxation pathways, first by distortion of the coordination sphere with efficient back-intersystem crossing, which is facilitated by the flexible guanidine/pyridine units, and second by methylene oscillators close to the chromium(III) center, which enable resonant energy transfer. As the third C–H overtone and combination bands span a spectral region from 11500 – 9000 cm^{-1} (870 – 1110 nm), chromium(III) complexes with CH_2 units close to the metal center are not expected to strongly emit in this NIR spectral region (Figure 1b) and hence aliphatic units within the ligand coordination should be avoided when luminescence in this spectral region is targeted.

EXPERIMENTAL SECTION

General procedures. The ligand dgpy⁶⁹ and $\text{Cr}(\text{OTf})_3$ ¹⁰ were synthesized according to literature procedures. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene was *N*-deuterated according to a literature procedure.⁷⁷ All reagents were used as received from commercial suppliers (abcr, Acros Organics, Alfa Aesar, Thermo Fisher Scientific, Sigma-Aldrich and TCI) if not noted otherwise. Solvents were dried by refluxing over potassium (THF, toluene, C_6D_6), sodium (diethyl ether) or calcium hydride (MeCN, CD_2Cl_2) and distillation. Butyronitrile *n*-PrCN was purified according to a literature procedure.⁸¹ $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ for electrochemical experiments ($\geq 99\%$ for electrochemical analysis, Sigma-Aldrich) was dried at 80 °C and reduced pressure (10^{-3} mbar) for three days and stored under argon. Syntheses and handling of air-sensitive compounds were either conducted using Schlenk techniques or a glovebox (UniLab/Mbraun – Ar 5.0; $\text{O}_2 < 0.1 \text{ ppm}$; $\text{H}_2\text{O} < 0.1 \text{ ppm}$).

NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 400.13 MHz (^1H). Proton resonances are reported in ppm

versus the solvent signal as an internal standard (C_6D_6) = 7.16).⁸² (s) = singlet, (d) = doublet, (t) = triplet, (m) = multiplet.

IR spectra were recorded with a Bruker Alpha II FTIR spectrometer with an ATR unit containing a diamond crystal. The intensities were qualitatively indicated with weak (w), medium (m) and strong (s).

ESI⁺ mass spectra were measured on an Agilent 6545 HPLC-ESI-QTOF-MS spectrometer in MeCN.

ESI⁺ mass spectra for ETD and CID experiments were recorded using a Bruker amZon ETD 3D Paul trap mass spectrometer, which is operated at room temperature. The sample solution of $[Cr(dgpy)_2][PF_6]_3$ was prepared in dry and degassed MeCN with concentrations of 10^{-4} to 10^{-5} M. The sample solution was continuously infused into the spray chamber using a syringe pump. Nitrogen was used as nebulizer gas and dry gas. The mass spectrometer is equipped with a negative chemical ionization (nCI) module to allow for electron transfer dissociation/reduction (ETD/ETR) experiments. Fluoranthene radical anions are prepared via chemical ionization. These are transferred into the ion trap where they can interact/react with the stored ions. For ETD experiments, the target ion was isolated and stored in the ion trap for 300 ms to allow for enough time for the electron transfer reaction. Collision induced dissociation (CID) is used to induce fragmentation in a chosen precursor ion. Ions are stored in the 3D Paul trap (ion trap) of the mass spectrometer by a combination of DC voltage and radio frequency (RF). The trapped ions are accelerated by increasing the RF amplitude. Repeated collisions with the helium buffer gas transfer kinetic energy from the collisions into rotational-vibrational degrees of freedom. Internal vibrational redistribution leads to heating up of the stored ion and subsequently to fragmentation of the weakest bond.^{83,84} The full isotopic pattern of the respective chromium species was isolated prior to CID experiments. CID breakdown curves are recorded by step-wise increase of the excitation amplitude (E_{LAB}) from 0 to 3 V in 0.02 V steps. At each excitation amplitude, mass spectra were recorded for 300 ms. At each step mass spectra were recorded for a total of 18 s and averaged afterwards. Relative signal intensities are calculated according to eq. 4, with I_{abs}^P being the absolute intensity of the respective parent ion, and I_{abs}^{Fi} the absolute fragment intensities.

$$I_{rel}^P(E_{LAB}) = \frac{\sum_i I_{abs}^{Fi}(E_{LAB})}{\sum_i I_{abs}^{Fi}(E_{LAB}) + \sum_i I_{abs}^P(E_{LAB})} \quad (\text{eq. 4})$$

The instrument specific voltage applied as excitation amplitude, i.e., E_{LAB} , was corrected in two steps to consider the different masses and different charge states z of the investigated ions.

$$E_{COM} = E_{LAB} \times \frac{m_{He}}{m_{He} + m_{ion}} \quad (\text{eq. 5})$$

$$E_{COMz} = E_{COM} \times z \quad (\text{eq. 6})$$

The obtained intensities were fitted with a sigmoidal function. The obtained $E_{COMz}^{50\%}$ value is where half of the parent ions are fragmented and it can be used as a qualitative measure for the relative stabilities of ions of chemically similar structures.⁸⁵

$$I_{fit}^P(E_{COMz}) = \frac{A}{1 + e^{-B(E_{COMz} - E_{COMz}^{50\%})}} \quad (\text{eq. 7})$$

The parameter A describes the fitted intensity of the parent ion and the exponent the slope of the sigmoidal curve.

Electrochemical experiments were carried out on a BioLogic SP-200 voltammetric analyzer. The measurements were performed in a glovebox, using dry MeCN as the solvent. The working and counter electrodes consisted of platinum wire and 10 mM $Ag/AgNO_3$ (100 mM $[n-Bu_4N][ClO_4]$ in acetonitrile) was used as the reference electrode. 100 mM $[n-Bu_4N][PF_6]$ as supporting electrolyte and 1 mM of the sample were used. Cyclic voltammetry experiments were carried out at scan rates of 50–100 mV s⁻¹. Potentials were referenced relative to the ferrocenium/ferrocene couple. Potentials were converted to the saturated calomel electrode (SCE) according to the literature.⁸⁶

The **elemental analysis** was conducted by the central analytic service of the Department of Chemistry of the Johannes Gutenberg University Mainz using an Elementar vario EL Cube.

UV/vis/NIR absorption spectra were recorded with an Agilent Cary 5000 UV/vis/NIR spectrophotometer, using 1.00 cm quartz cells. When needed, 1.00 cm quartz cells with a Schott valve were used to maintain an inert atmosphere. For the measurement of the spin-forbidden absorption bands, a cuvette with a pathlength of 10.0 cm was used. The spin-forbidden NIR absorption bands were baseline corrected using a biexponential function (eq. 8) to model the tail of the spin-allowed absorption bands. Deconvolution of the baseline corrected spectrum was achieved with five Voigt functions using OriginPro 2024.

$$\varepsilon(\tilde{\nu}) = \varepsilon_0 + A_1 e^{\frac{\tilde{\nu} - \tilde{\nu}_0}{\tau_1}} + A_2 e^{\frac{\tilde{\nu} - \tilde{\nu}_0}{\tau_2}} \quad (\text{eq. 8})$$

Emission spectra and luminescence decay curves were recorded with a FLS1000 spectrometer from Edinburgh Instruments equipped with the cooled red and NIR sensitive photomultiplier detectors PMT-980 and N-G09 PMT-1700, together covering the entire spectral range between 200 and 1700 nm. A xenon arc lamp Xe2 (450 W) was used for excitation in steady-state measurements. Time-resolved luminescence experiments were performed in the multi-channel scaling mode employing a variable pulsed laser VPL-450 ($\lambda_{exc} = 451.3$ nm) as excitation source. The absolute luminescence quantum yield Φ was determined using an integrating sphere from Edinburgh Instruments. Relative uncertainty of Φ is estimated to be ± 10 %. Room temperature measurements were conducted in MeCN (Optima® LC/MS grade, Fisher Scientific). Low temperature measurements were conducted in purified butyronitrile n -PrCN using a liquid nitrogen cooled cryostat Optistat DN from Oxford Instruments. Deconvolution of the emission spectrum at 77 K was achieved with four Voigt functions using OriginPro 2024.

Intensity data for crystal structure determination of $[Cr(dgpy)_2][PF_6]_3$ were collected with a STOE IPDS-2T diffractometer from STOE & CIE GmbH with an Oxford cooling using Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The diffraction frames were integrated using the STOE X-Area⁸⁷ software package and were corrected for absorption with MULABS⁸⁸ of the PLATON software package.⁸⁹ The structures were solved with SHELXT⁹⁰ and refined by the full-matrix method based on F^2 using SHELXL⁹¹ of the SHELX⁹² software package and the ShelXle⁹³ graphical interface. 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-2448606.

Crystallographic data of $[Cr(dgpy)_2][PF_6]_3 \cdot 1.5DMF$: $C_{42}H_{64.50}CrF_{18}N_{15.50}O_{1.50}P_3$ (1303.50); monoclinic; Ia , $a = 35.485(7)$ Å, $b = 17.866(4)$ Å, $c = 16.787(3)$ Å, $\beta = 94.21(3)^\circ$; $V = 10614(4)$ Å³, $Z = 8$; density (calculated) = 1.631 g cm⁻³; $T = 120(2)$ K; $\mu = 0.423$ mm⁻¹; $F(000) = 5368$; crystal size $0.400 \times 0.280 \times 0.090$ mm³; $\theta = 2.433$ to 28.245 deg; $-47 \leq h \leq 46$, $-23 \leq k \leq 23$, $-18 \leq l \leq 22$; rfln collected = 75823; rfln unique = 23321 [$R(int) = 0.0968$]; completeness to $\theta = 25.242$ deg. = 99.9 %; semi empirical absorption correction from equivalents; max. and min. transmission 1.4293 and 0.6544; Data 23321; restraints 3430; parameters 1815; goodness-of-fit on $F^2 = 1.617$; final indices [$I > 2\sigma(I)$] $R_1 = 0.1230$, $wR_2 = 0.3515$; R indices (all data) $R_1 = 0.1431$, $wR_2 = 0.3775$; largest diff. peak and hole 3.142 and -1.018 e Å⁻³.

Density functional theory (DFT) and CASSCF-NEVPT2 calculations were carried out using the ORCA program package 5.0.3.^{94,95}

DFT calculations were performed using the B3LYP functional^{96,97} employing the RIJCOSX approximation^{98,99} and the SARC/J auxiliary basis.¹⁰⁰ Tight convergence criteria were chosen for DFT-

UKS calculations (keywords *tightscf* and *tightopt*). Relativistic effects were calculated at the zeroth order regular approximation (keyword *ZORA*) level.¹⁰⁰ The *ZORA* keyword automatically invokes relativistically adjusted basis sets. To account for solvent effects, a conductor-like screening model (keyword *CPCM*) modeling MeCN was used in all calculations.^{101,102} Geometry optimizations were performed using Ahlrichs' polarized valence triple- ζ basis set (def2-TZVPP).^{103,104} Atom-pairwise dispersion correction was performed with the Becke-Johnson damping scheme (keyword *D3BJ*).^{105,106} The energy of the electronic ground states (quartet and doublet) and the presence of energy minima were checked by numerical frequency calculations. Explicit counter ions and/or solvent molecules were not taken into account. TD-DFT calculations were performed at the same level of theory. Fifty vertical spin-allowed transitions were calculated. The assignment of the state characters has been done dividing the molecule into three fragments (metal center, two pyridine and two bis(guanidine) moieties) and calculating charge transfer (CT) numbers, as implemented in the TheoDore software package.^{107,108} Excited state geometry optimization of the ²MC state was done using DFT and setting the multiplicity to 2. Excited state geometry optimization of the lowest energy ⁴MC state was done using TD-DFT and the given state was selected according to the TD-DFT calculation at the initial geometry (keyword *iroot*). To prevent root flipping after a step during the optimization, the total overlap between the excited state wave functions was calculated and compared with the previous one (keyword *followiroot*). **CASSCF(7,12)-SC-NEVPT2** calculations of ground and excited state properties with respect to metal-centered (MC) states were performed using the complete-active-space self-consistent field method (CASSCF).^{109,110} To accelerate the calculation, the RI-JK approximation was used,^{111,112} with an automatically generated auxiliary basis (keyword *AutoAux*). To recover the missing dynamic electron correlation, the strongly contracted variant of N-electron valence perturbation theory to second order (SC-NEVPT2) was used.^{113,114} All electronic states are classified by irreducible representations of the *O* point group, despite the lower actual symmetry of the considered complex. To accurately model the ligand field, the active space was expanded to encompass the dominant bonding/antibonding orbitals formed between chromium and the ligand. In addition to the minimal active space of (3,5), two occupied Cr–N σ bonding orbitals and a second d shell¹¹⁵ were included in these calculations giving an active space of (7,12). 10 quartet and 10 doublet roots were calculated with this active space.

Synthesis of dgpy. The ligand dgpy was synthesized according to a modified literature procedure from 2,6-dibromopyridine and 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine using KO^tBu and Pd(OAc)₂/BINAP in toluene,⁶⁹ using Schlenk techniques and dry solvents to avoid protonation. The product dgpy was extracted from the beige crude product containing KBr with warm toluene (5×50 mL, 50 °C). The solvent was removed from the combined extracts under reduced pressure. The remaining beige solid was washed with dry diethyl ether (2×25 mL) and dried under reduced pressure to yield a beige powder. ¹H NMR (400 MHz, C₆D₆): δ /ppm = 7.91 (d, ³J = 8.0 Hz, 2H), 7.36 (t, ³J = 8.0 Hz, 1H), 3.83–3.80 (m, 4H), 3.53 (t, ³J = 5.7 Hz, 4H), 2.74 (t, ³J = 6.0 Hz, 4H), 2.58 (t, ³J = 6.5 Hz, 4H), 1.63–1.52 (m, 8H).

Synthesis of [Cr(dgpy)₂][PF₆]₃: To avoid protonation of the strongly basic dgpy ligand under ambient conditions, which would hamper the complexation of chromium(III), the complex synthesis was conducted in a glovebox. Cr[OTf]₃¹⁰ (141 mg, 0.28 mmol, 1.0 eq.) was dissolved in dry THF (20 mL). This solution was added dropwise to a solution of dgpy (200 mg, 0.57 mmol, 2.0 eq.) in dry THF (5 mL) yielding an orange-brown precipitate. The mixture was stirred for 16 h at 298 K. The reaction vessel was removed from the glovebox. The supernatant was decanted, the remaining solid was washed with THF (5×5 mL) and diethyl ether (5 mL) and

dried under air. The solid was dissolved in methanol (5 mL), yielding an orange solution. The complex solution was added dropwise to a solution of [*n*-Bu₄N][PF₆] (542 mg, 1.4 mmol, 5.0 eq.) in methanol (10 mL) yielding an orange to brown precipitate. The supernatant was decanted, washed with diethyl ether (5 mL) and dried under air. To ensure quantitative salt metathesis, the complex was dissolved in 5 mL of acetonitrile, containing [*n*-Bu₄N][PF₆] (542 mg, 1.4 mmol, 5.0 eq.) and crystallized via diethyl ether diffusion. The resulting orange crystals were washed with methanol (5×5 mL) and diethyl ether (5 mL), dried and recrystallized from DMF/diethyl ether, yielding large orange crystals (140 mg, 0.12 mmol; 43 % yield). The sample used for elemental analysis was recrystallized from MeCN/Et₂O. The isolated crystals were pulverized and dried under reduced pressure for three days. Elemental analysis: calcd (%) for C₃₈H₅₄CrF₁₈N₁₄P₃ (1193.84 g/mol): C, 38.23; H, 4.56; N, 16.43; found: C, 38.47; H, 4.85; N, 16.50. MS (MeCN/ESI⁺): calcd for {[Cr(dgpy)₂][PF₆]₂}⁺: *m/z* = 1048.334, found: *m/z* (%) = 1048.333 (28.6); calcd for {[Cr(dgpy)₂][PF₆]}²⁺: *m/z* = 451.684, found: *m/z* (%) = 451.684 (100); calcd for [Cr(dgpy)₂]³⁺: *m/z* = 252.801, found: *m/z* (%) = 252.801 (83.52). IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 3119 (w, CH), 2960 (w, CH), 2876 (w, CH), 1670 (w, C=O (DMF crystal solvate)), 1594 (s), 1504 (m), 1460 (m), 1432 (m), 1381 (m), 1328 (m), 1309 (m), 1208 (m), 1161 (m), 1070 (w), 1044 (w), 1028 (m), 877 (w), 829 (vs, PF), 754 (m), 719 (m), 554 (vs, PF), 427 (w). UV/vis/NIR (MeCN): λ / nm (ϵ / M⁻¹ cm⁻¹): 324 (10100), 380 (1200, sh), 393 (750, sh), 466 (60), 520 (40, sh), 712 (0.1), 751 (0.3), 800 (0.1, sh). Emission (MeCN, 293 K): λ / nm = 754, 835. Emission Lifetime (MeCN, 293 K): τ / μ s = 63 (deaerated); 53 (aerated). Emission (*n*-PrCN, 77 K): λ / nm = 816, 834, 863, 925. Quantum Yield (MeCN, 293 K): Φ / % = 0.5. CV (MeCN, 100 mM [*n*-Bu₄N][PF₆]): *E*_{p, red} / V vs. SCE = -1.56, *E*_{p, ox} / V vs. SCE = 1.68.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at [xx](http://www.xx). Analytical and spectroscopic data, results of quantum chemical calculations (PDF)
Cartesian coordinates of optimized geometries from quantum-chemical calculations (XYZ)

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Notes

The authors declare no conflict of interest.

ACKNOWLEDGMENTS

This work has been financially supported by the Deutsche Forschungsgemeinschaft (DFG) under grants INST 247/1018-1 and HE2778/10-2. Parts of this research were conducted using the supercomputer Elwetritsch and advisory services offered by the RPTU Kaiserslautern-Landau (<https://hpc.rz.rptu.de>), which is a member of the AHRP. We thank

REFERENCES

- (1) Morselli, G.; Reber, C.; Wenger, O. S. Molecular Design Principles for Photoactive Transition Metal Complexes: A Guide for “Photo-Motivated” Chemists. *J. Am. Chem. Soc.* **2025**, *147*, 11608–11624. DOI: 10.1021/jacs.5c02096.
- (2) Förster, C.; Heinze, K. The Photophysics and Applications of Molecular Rubies, *Adv. Inorg. Chem.* **2024**, *83*, 111–159. DOI: 10.1016/bs.adioch.2024.01.002.
- (3) 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 (Section Ed. V. W.-W. Yam) **2023**, 707–788. DOI: 10.1016/B978-0-12-823144-9.00063-7.
- (4) Förster, C.; Heinze, K. Bimolecular Reactivity of 3d Metal-Centered Excited States (Cr, Mn, Fe, Co), *Chem. Phys. Rev.* **2022**, *3*, 041302. DOI: 10.1063/5.0112531.
- (5) Kitzmann, W. R.; Ramanan, C.; Naumann, R.; Heinze, K. Molecular Ruby: Exploring the Excited State Landscape, *Dalton Trans.* **2022**, *51*, 6519–6525. DOI: 10.1039/D2DT00569G.
- (6) Wegeberg, C.; Wenger, O. S., Luminescent First-Row Transition Metal Complexes, *JACS Au* **2021**, *1*, 1860–1876. DOI: 10.1021/jacsau.1c00353.
- (7) Förster, C.; Heinze, K. Photophysics and photochemistry with Earth-abundant metals – fundamentals and concepts, *Chem. Soc. Rev.* **2020**, *49*, 1057–1070. DOI: 10.1039/c9cs00573k.
- (8) Wenger, O. S. Photoactive Complexes with Earth-Abundant Metals, *J. Am. Chem. Soc.* **2018**, *140*, 13522–13533. DOI: 10.1021/jacs.8b08822.
- (9) Kitzmann, W. R.; Moll, J.; Heinze, K. Spin-Flip Luminescence, *Photochem. Photobiol. Sci.* **2022**, *21*, 1309–1331. DOI: 10.1007/s43630-022-00186-3.
- (10) Reichenauer, F.; Naumann, R.; Förster, C.; Kitzmann, W. R.; Reponen, A.-P. M.; Feldmann, S.; Heinze, K. Bridge Editing of Spin-Flip Emitters gives Insight into Excited State Energies and Dynamics. *Chem. Sci.* **2024**, *15*, 20251–20262. DOI: 10.1039/D4SC05860G.
- (11) Reichenauer, F.; Zorn, D.; Naumann, R.; Förster, C.; Heinze, K. Factorizing the Nephelauxetic Effect in Heteroleptic Molecular Rubies. *Inorg. Chem.* **2024**, *63*, 23487–23496. DOI: 10.1021/acs.inorgchem.4c04167.
- (12) Wang, C.; Kitzmann, W. R.; Weigert, F.; Förster, C.; Wang, X.; Heinze, K.; Resch-Genger, U. Matrix Effects on Photoluminescence and Oxygen Sensitivity of a Molecular Ruby, *ChemPhotoChem* **2022**, *6*, e202100296. DOI: 10.1002/cptc.202100296.
- (13) Stein, L.; Wang, C.; Förster, C.; Resch-Genger, U.; Heinze, K. Bulky Ligands protect Molecular Ruby from Oxygen Quenching, *Dalton Trans.* **2022**, *51*, 17664–17670. DOI: 10.1039/d2dt02950b.
- (14) 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 $[\text{Cr}(\text{bpm})_2]^{3+}$ surpasses

- $[\text{Ru}(\text{bpy})_3]^{2+}$, *J. Am. Chem. Soc.* **2021**, *143*, 11843–11855. DOI: 10.1021/jacs.1c05971.
- (15) Wang, C.; Otto, S.; Dorn, M.; Kreidt, E.; Lebon, J.; Sršan, L.; Di Martino-Fumo, P.; Gerhards, M.; Resch-Genger, U.; Seitz, M.; Heinze, K. Deuterated Molecular Ruby with Record Luminescence Quantum Yield, *Angew. Chem. Int. Ed.* **2018**, *57*, 1112–1116. DOI: 10.1002/anie.201711350.
- (16) Otto, S.; Förster, C.; Wang, C.; Resch-Genger, U.; Heinze, K. A strongly luminescent chromium(III) complex acid, *Chem. Eur. J.* **2018**, *24*, 12555–12563. DOI: 10.1002/chem.201802797.
- (17) Otto, S.; Grabolle, M.; Förster, C.; Kreitner, C.; Resch-Genger, U.; Heinze, K. $[\text{Cr}(\text{ddpd})_2]^{3+}$: a molecular, water-soluble, highly NIR-emissive ruby analogue, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572–11576. DOI: 10.1002/anie.201504894.
- (18) Wang, C.; Li, H.; Bürgin, T. H.; Wenger, O. S. Cage escape governs photoredox reaction rates and quantum yields. *Nat. Chem.* **2024**, *16*, 1151–1159. DOI: 10.1038/s41557-024-01482-4.
- (19) 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*, 14181–14194. DOI: 10.1021/jacs.2c04465.
- (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. DOI: 10.1002/anie.202101158.
- (21) Jiménez, J.-R.; Doistau, B.; Cruz, C. M.; Besnard, C.; Cuerva, J. M.; Campaña, A. G.; Piguet, C. Chiral Molecular Ruby $[\text{Cr}(\text{dqp})_2]^{3+}$ with Long-Lived Circularly Polarized Luminescence, *J. Am. Chem. Soc.* **2019**, *141*, 13244–13252. DOI: 10.1021/jacs.9b06524.
- (22) Otto, S.; Scholz, N.; Behnke, T.; Resch-Genger, U.; Heinze, K. Thermo-Chromium: A Contactless Optical Molecular Thermometer, *Chem. Eur. J.* **2017**, *23*, 12131–12135. DOI: 10.1002/chem.201701726.
- (23) Otto, S.; Harris, J. P.; Heinze, K.; Reber, C. Molecular ruby under pressure, *Angew. Chem. Int. Ed.* **2018**, *57*, 11069–11073. DOI: 10.1002/anie.201806755.
- (24) Wang, C.; Otto, S.; Dorn, M.; Heinze, K.; Resch-Genger, U. Luminescent TOP Nanosensors for Simultaneously Measuring Temperature, Oxygen, and pH at a Single Excitation Wavelength, *Anal. Chem.* **2019**, *91*, 2337–2344. DOI: 10.1021/acs.analchem.8b05060.
- (25) Kalmbach, J.; Wang, C.; You, Y.; Förster, C.; Schubert, H.; Heinze, K.; Resch-Genger, U.; Seitz, M. Near-IR to Near-IR Upconversion Luminescence in Molecular Chromium Ytterbium Salts. *Angew. Chem. Int. Ed.* **2020**, *59*, 18804–18808. DOI: 10.1002/anie.202007200.
- (26) 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*, e202202238. DOI: 10.1002/anie.202202238.
- (27) Gabbani, A.; Poncet, M.; Pescitelli, G.; Carbonaro, L.; Krzystek, J.; Colacio, E.; Piguet, C.; Pineider, F.; Di Bari, L.; Jiménez, J.-R.; Zinna, F. Magnetic circularly polarized luminescence from spin-flip transitions in a molecular ruby. *Chem. Sci.* **2024**, *15*, 17217–17223. DOI: 10.1039/D4SC04718D.
- (28) Poncet, M.; Besnard, C.; Guénée, L.; Jiménez, J.-R.; Piguet, C. Tuning the circularly polarized luminescence in homoleptic and heteroleptic chiral Cr^{III} complexes. *Front. Chem.* **2024**, *12*, 1472943. DOI: 10.3389/fchem.2024.1472943.
- (29) Cheng, Y.; He, J.; Zou, W.; Chang, X.; Yang, Q.; Lu, W. Circularly polarized near-infrared phosphorescence of chiral chromium(III) complexes. *Chem. Commun.* **2023**, *59*, 1781–1784. DOI: 10.1039/d2cc06548g.
- (30) Dee, C.; Zinna, F.; Kitzmann, W. R.; Pescitelli, G.; Heinze, K.; Di Bari, L.; Seitz, M. Strong Circularly Polarized Luminescence of an Octahedral Chromium(III) Complex, *Chem. Commun.* **2019**, *55*, 13078–13081. DOI: 10.1039/c9cc06909g.
- (31) Sittel, S.; Neuner, J.; Grenz, J. M.; Förster, C.; Naumann, R.; Heinze, K. Gram-Scale Photocatalysis with a Stable and Recyclable Chromium(III) Photocatalyst in Acetonitrile and in Water. *Adv. Synth. Catal.* **2025**, *367*, e202500075. DOI: 10.1002/adsc.202500075.
- (32) Sittel, S.; Sell, A. C.; Hofman, K.; Wiedemann, C.; Nau, J. P.; Kerzig, C.; Manolikakes, G.; Heinze, K. Visible-Light Induced Fixation of SO_2 into Organic Molecules with Polypyridine Chromium(III) Complexes, *ChemCatChem* **2023**, *15*, e202201562. DOI: 10.1002/cctc.202201562.
- (33) Sittel, S.; Naumann, R.; Heinze, K. Molecular Rubies in Photoredox Catalysis, *Front. Chem.* **2022**, *10*, 887439. DOI: 10.3389/fchem.2022.887439.

- (34) Otto, S.; Nauth, A. M.; Ermilov, E.; Scholz, N.; Friedrich, A.; Resch-Genger, U.; Lochbrunner, S.; Opatz, T.; Heinze, K. Photo-Chromium: Sensitizer for Visible Light-Induced Oxidative C-H Bond Functionalization – Electron or Energy Transfer? *ChemPhotoChem* **2017**, *1*, 344–349. DOI: 10.1002/cptc.201700077.
- (35) Sinha, N.; Yaltseva, P.; Wenger, O. S. The Nephelauxetic Effect Becomes an Important Design Factor for Photoactive First-Row Transition Metal Complexes, *Angew. Chem. Int. Ed.* **2023**, *62*, e202303864. DOI: 10.1002/anie.202303864.
- (36) Figgis, B. N.; Hitchman, M. A. Ligand field theory and its applications. Wiley, Chichester (2000).
- (37) Lever, A. B. P.; Solomon, E. I. Ligand Field Theory and the Properties of Transition Metal Complexes in Inorganic Electronic Structure and Spectroscopy, 1999, Vol. I, (Ed. E. I. Solomon, A. B. P. Lever), 1–91, John Wiley & Sons, Inc.
- (38) Chong, J.; Besnard, C.; Cruz, C. M.; Piguet, C.; Jiménez, J.-R. Heteroleptic mer-[Cr(N(NN)(N)(CN))₃] complexes: synthetic challenge, structural characterization and photophysical properties, *Dalton Trans.* **2022**, *51*, 4297–4309. DOI: 10.1039/d2dt00126h.
- (39) Stein, L.; Förster, C.; Heinze, K. Luminescent Cyclometalated Chromium(III) Complexes, *Organometallics* **2024**, *43*, 1766–1774. DOI: 10.1021/acs.organomet.4c00075.
- (40) Stein, L.; Boden, P.; Naumann, R.; Förster, C.; Niedner-Schatteburg, G.; Heinze, K. The overlooked NIR luminescence of Cr(ppy)₃, *Chem. Commun.* **2022**, *58*, 3701–3704. DOI: 10.1039/D2CC00680D.
- (41) Cheng, Y.; Yang, Q.; He, J.; Zou, W.; Liao, K.; Chang, X.; Zou, C.; Lu, W. The energy gap law for NIR-phosphorescent Cr(III) complexes. *Dalton Trans.* **2023**, *52*, 2561–2565. DOI: 10.1039/D2DT02872G.
- (42) Sawicka, N.; Craze, C. J.; Horton, P. N.; Coles, S. J.; Richards, E.; Pope, S. J. A. Long-lived, near-IR emission from Cr(III) under ambient conditions, *Chem. Commun.* **2022**, *58*, 5733–5736. DOI: 10.1039/D2CC01434C.
- (43) 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. DOI: 10.1002/anie.202106398.
- (44) Morselli, G.; Eggenweiler, T. H.; Villa, M.; Prescimone, A.; Wenger, O. S. Pushing the Thermodynamic and Kinetic Limits of Near-Infrared Emissive Cr^{III} Complexes in Photocatalysis. *J. Am. Chem. Soc.* **2025**, *147*, 28226–28240. DOI: 10.1021/jacs.5c08541.
- (45) Jones, R. W.; Cowin, R. A.; Ivalo I. I.; Chekulaev, D.; Roseveare, T. M.; Rice, C. R.; Weinstein, J. A.; Elliott, P. I. P.; Scattergood, P. A. A Near-Infrared Luminescent Cr(III) N-Heterocyclic Carbene Complex, *Inorg. Chem.* **2024**, *63*, 8526–8530. DOI: 10.1021/acs.inorgchem.4c01270.
- (46) Sander, J.; Gauder, F.; Schickentanz, S. J.; Maulbetsch, T.; Kalmbach, J.; Zorn, D.; Naumann, R.; Förster, C.; Kunz, D.; Heinze, K. Excited State Dynamics of the Carbazolato-Carbene Chromium(III) Complex [Cr(bimca)]⁺. *Z. Anorg. Allg. Chem.* **2025**, accepted. DOI: 10.1002/zaac.202500149.
- (47) Kitzmann, W. R.; Hunger, D.; Reponen, A.-P. M.; Förster, C.; Schoch, R.; Bauer, M.; Feldmann, S.; van Slageren, J.; Heinze, K. Electronic Structure and Excited State Dynamics of the NIR-II Emissive Molybdenum(III) Analog to the Molecular Ruby. *Inorg. Chem.* **2023**, *62*, 15797–15808. DOI: 10.1021/acs.inorgchem.3c02186.
- (48) 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. DOI: 10.1039/D1SC02137K.
- (49) 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. DOI: 10.1021/jacs.0c02122.
- (50) König, A.; Naumann, R.; Förster, C.; Klett, J.; Heinze, K. A near-infrared-II luminescent and photoactive vanadium(II) complex with a 760 ns excited state lifetime. *J. Am. Chem. Soc.* **2025**, *147*, 20833–20842. DOI: 10.1021/jacs.5c04471.
- (51) 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**, *16*, 827–834. DOI: 10.1038/s41557-024-01446-8.
- (52) Harris, J. P.; Reber, C.; Colmer, H. E. 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. DOI: 10.1139/cjc-2016-0607.
- (53) Ye, Y.; Poncet, M.; Yaltseva, P.; Salcedo-Abraira, P.; Rodríguez-Diéguez, A.; Heredia Martín, J.; Cuevas-Contreras, L.; Cruz, C. M.; Doistau, B.; Piguet, C.; Wenger, O. S. Herrera, J. M.; Jiménez, J.-R. Modulating the spin–flip rates and emission energies through ligand design in chromium(III) molecular rubies. *Chem. Sci.* **2025**, *16*, 5205–5213. DOI: 10.1039/d4sc08021a.
- (54) East, N. R.; Dab, C.; Förster, C.; Heinze, K.; Reber, C. Coupled potential energy surfaces strongly impact the lowest-energy spin-flip transition in six-coordinate nickel(II) complexes. *Inorg. Chem.* **2023**, *62*, 9025–9034. DOI: 10.1021/acs.inorgchem.3c00779.
- (55) Pal, A. K.; Li, C.; Hanan, G. S.; Zysman-Colman, E. Blue-Emissive Cobalt(III) Complexes and Their Use in the Photocatalytic Trifluoromethylation of Polycyclic Aromatic Hydrocarbons. *Angew. Chem. Int. Ed.* **2018**, *57*, 8027–8031. DOI: 10.1002/anie.201802532.
- (56) Moll, J.; Förster, C.; König, A.; Carrella, L. M.; Wagner, M.; Panthöfer, M.; Möller, A.; Rentschler, E.; Heinze, K. Panchromatic Absorption and Oxidation of an Iron(II) Spin Crossover Complex. *Inorg. Chem.* **2022**, *61*, 1659–1671. DOI: 10.1021/acs.inorgchem.1c03511.
- (57) East, N. R.; Förster, C.; Carrella, L. M.; Rentschler, E.; Heinze, K. The full d3–d5 Redox Series of Mononuclear Manganese Complexes: Geometries and Electronic Structures of [Mn(dgpy)₂]^{III}. *Inorg. Chem.* **2022**, *61*, 14616–14625. DOI: 10.1021/acs.inorgchem.2c01680.
- (58) Englman, R.; Jortner, J. The energy gap law for radiationless transitions in large molecules. *Mol. Phys.* **1970**, *18*, 145–164. DOI: 10.1080/00268977000100171.
- (59) Wilson, J. S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Younus, M.; Khan, M. S.; Raithby, P. R.; Köhler, A.; Friend, R. H. The energy gap law for triplet states in Pt-containing conjugated polymers and monomers. *J. Am. Chem. Soc.* **2001**, *123*, 9412–9417. DOI: 10.1021/ja010986s.
- (60) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. Application of the energy gap law to the decay of charge-transfer excited states. *J. Am. Chem. Soc.* **1982**, *104*, 630–632. DOI: 10.1021/ja00366a051.
- (61) Caspar, J. V.; Meyer, T. J. Application of the energy gap law to non-radiative, excited-state decay. *J. Phys. Chem.* **1983**, *87*, 952–957. DOI: 10.1021/j100229a010.
- (62) Cummings, S. D.; Eisenberg, R. Tuning the Excited-State Properties of Platinum(II) Diimine Dithiolate Complexes. *J. Am. Chem. Soc.* **1996**, *118*, 1949–1960. DOI: 10.1021/ja951345y.
- (63) Ermolaev, V. L.; Sveshnikova, E. B. The application of luminescence-kinetic methods in the study of the formation of lanthanide ion complexes in solution, *Russ. Chem. Rev.* **1994**, *63*, 905–922. DOI: 10.1070/RC1994v063n11ABEH000125.
- (64) Kreidt, E.; Kruck, C.; Seitz, M. Nonradiative Deactivation of Lanthanoid Luminescence by Multiphonon Relaxation in Molecular Complexes, *Handbook on the Physics and Chemistry of Rare Earths*, chapter 300, Elsevier, **2018**, *53*, 35–79. DOI: 10.1016/bs.hpcr.2018.04.001.
- (65) Mishra, K.; Wu, Z.; Erker, C.; Müllen, K.; Basché, T. Suppressing non-radiative relaxation in a NIR single photon emitter: the impact of deuteration and temperature. *Chem. Sci.* **2025**, *16*, 90–97. DOI: 10.1039/D4SC05517A.
- (66) Nakagaki, R.; Hanazaki, I. Inequivalent methyl CH oscillators in methyl-substituted conjugated compounds as revealed by higher overtone spectra. *Chem. Phys.* **1982**, *72*, 93–99. DOI: 10.1016/0301-0104(82)87069-9.
- (67) Kjaergaard, H. K.; Henry, B. R. The relative intensity contributions of axial and equatorial CH bonds in the local mode overtone spectra of cyclohexane. *J. Chem. Phys.* **1992**, *96*, 4841–485. DOI: 10.1063/1.462774.
- (68) Kirk, A. D.; Porter, G. B. Luminescence of Chromium(III) Complexes. *J. Phys. Chem.* **1980**, *84*, 887–891. DOI: 10.1021/j100445a020.
- (69) Pal, A. K.; Zaccaroni, N.; Campagna, S.; Hanan, G. S. Near infrared emission from a mer-Ru(II) complex: consequences of strong σ-donation from a neutral, flexible ligand with dual binding modes. *Chem. Commun.* **2014**, *50*, 6846–6849. DOI: 10.1039/c3cc49880h.
- (70) Larkin, P. J. *Infrared and Raman Spectroscopy*; Elsevier Inc., 2018. 2nd ed., DOI: 10.1016/C2015-0-00806-1.
- (71) Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schönlé, J.; Zampese, J. A. The surprising lability of bis(2,2′:6′,2″-terpyridine)chromium(III) complexes. *Dalton Trans.* **2014**, *43*, 7227–7235. DOI: 10.1039/C4DT00200H.
- (72) Becker, P. M.; Förster, C.; Carrella, L. M.; Boden, P.; Hunger, D.; van Slageren, J.; Gerhards, M.; Rentschler, E.; Heinze, K. Spin Crossover and Long-lived Excited States in a Reduced Molecular Ruby. *Chem. Eur. J.* **2020**, *26*, 7199–7204. DOI: 10.1002/chem.202001237.

- (73) Huber, M.; Adela, A.; Berg, L.; Weber, P.; East, N. R.; Riehn, C.; Heinze, K.; Meyer, J. Gas-Phase Characterization of Redox-Active Manganese Complexes. *J. Am. Soc. Mass Spectrom.* **2024**, *35*, 2642–2649. DOI: 10.1021/jasms.4c00113.
- (74) Laporte, O.; Meggers, W. F. Some rules of spectral structure, *J. Opt. Soc. Am.* **1925**, *11*, 459–463. DOI: 10.1364/JOSA.11.000459.
- (75) Poncet, M.; Cuevas-Contreras, L.; Ye, Y.; Guénée, L.; Cruz, C. M.; Piguet, C.; Jiménez, J.-R. Exploring the Role of the Nephelauxetic Effect in Circularly Polarized Luminescence of Chiral Chromium(III) Complexes. *J. Am. Chem. Soc.* **2025**, *147*, 23827–23833. DOI: 10.1021/jacs.5c06196.
- (76) Brzezinski, B.; Schroeder, G.; Rybachenko, V. I.; Kozhevina, L. I.; Kovalenko, V. V. Study of 1,5,7-triazabicyclo[4,4,0]dec-5-ene protonation by vibrational spectroscopic methods. *J. Mol. Struct.* **2000**, *516*, 123–130. DOI: 10.1016/S0022-2860(99)00129-5.
- (77) Hjelmencrantz, A.; Berg, U. New approach to biomimetic transamination using bifunctional 1,3-proton transfer catalysis in thioxanthene di-oxide imines. *J. Org. Chem.* **2002**, *67*, 3585–3594. DOI: 10.1021/jo0106748.
- (78) Baryshnikov, G.; Minaev, B.; Ågren, H. Theory and Calculation of the Phosphorescence Phenomenon. *Chem. Rev.* **2017**, *117*, 6500–6537. DOI: aacs.chemrev.7b00060.
- (79) Minaev, B.; Baryshnikov, G.; Ågren, H. Principles of phosphorescent organic light emitting devices. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1719–1758. DOI: 10.1039/C3CP53806K.
- (80) Strickler, S. J.; Berg, R. A. Relationship between Absorption Intensity and Fluorescence Lifetime of Molecules. *J. Chem. Phys.* **1962**, *37*, 814–822. DOI: 10.1063/1.1733166.
- (81) van Duyne, R. P.; Reilley, C. N. Low-temperature electrochemistry. I. Characteristics of electrode reactions in the absence of coupled chemical kinetics. *Anal. Chem.* **1972**, *44*, 142–152. DOI: 10.1021/ac60309a026.
- (82) 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*, 2176–2179. DOI: 10.1021/om100106e.
- (83) McLuckey, S. A. Principles of collisional activation in analytical mass spectrometry. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 599–614. DOI: 10.1016/1044-0305(92)85001-Z.
- (84) Brendle, K.; Kordel, M.; Schneider, E.; Wagner, D.; Bräse, S.; Weis, P.; Kappes, M. M. Collision Induced Dissociation of Benzylpyridinium-Substituted Porphyrins: Towards a Thermometer Scale for Multiply Charged Ions? *J. Am. Soc. Mass Spectrom.* **2018**, *29*, 382–392. DOI: 10.1007/s13361-017-1835-4.
- (85) Zins, E.-L.; Pepe, C.; Schröder, D. Energy-dependent dissociation of benzylpyridinium ions in an ion-trap mass spectrometer. *J. Mass Spectrom.* **2010**, *45*, 1253–1260. DOI: 10.1002/jms.1847.
- (86) Pavlishchuk, V. V.; Addison, A. W. Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C. *Inorg. Chim. Acta* **2000**, *298*, 97–102. DOI: 10.1016/S0020-1693(99)00407-7.
- (87) STOE & Cie, X-Area; STOE & Cie GmbH: Darmstadt, Germany. <https://www.stoe.com/products/xarea/>.
- (88) Blessing, R. H. An empirical correction for absorption anisotropy. *Acta Crystallogr. Sect. A* **1995**, *51*, 33–38. DOI: 10.1107/S0108767394005726.
- (89) Spek, A. L. Structure validation in chemical crystallography. *Acta Crystallogr. Sect. D* **2009**, *65*, 148–155. DOI: 10.1107/S090744490804362X.
- (90) Sheldrick, G. M. SHELXT - integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8. DOI: 10.1107/S2053273314026370.
- (91) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8. DOI: 10.1107/S2053229614024218.
- (92) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122. DOI: 10.1107/S0108767307043930.
- (93) Hübschle, C. B.; Sheldrick, G. M.; Dittlich, B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284. DOI: 10.1107/S0021889811043202.
- (94) Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA quantum chemistry program package. *J. Chem. Phys.* **2020**, *152*, 224108. DOI: 10.1063/5.0004608.
- (95) Neese, F. Software update: The ORCA program system—Version 5.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2022**, *12*, e1606. DOI: 10.1002/wcms.1606.
- (96) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652. DOI: 10.1063/1.464913.
- (97) 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. DOI: 10.1016/0009-2614(89)87234-3.
- (98) 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*, 98–109. DOI: 10.1016/j.chemphys.2008.10.036.
- (99) Izsák, R.; Neese, F. An overlap fitted chain of spheres exchange method. *J. Chem. Phys.* **2011**, *135*, 144105. DOI: 10.1063/1.3646921.
- (100) 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*, 908–919. DOI: 10.1021/ct800047t.
- (101) 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*, 117–129. DOI: 10.1016/0301-0104(81)85090-2.
- (102) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem.* **1998**, *102*, 1995–2001. DOI: 10.1021/jp9716997.
- (103) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets for atoms Li to Kr. *J. Chem. Phys.* **1992**, *97*, 2571–2577. DOI: 10.1063/1.463096.
- (104) Schäfer, A.; Huber, C.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* **1994**, *100*, 5829–5835. DOI: 10.1063/1.467146.
- (105) 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*, 154104. DOI: 10.1063/1.3382344.
- (106) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465. DOI: 10.1002/jcc.21759.
- (107) Mai, S.; Plasser, F.; Dorn, J.; Fumanal, M.; Daniel, C.; González, L. Quantitative wave function analysis for excited states of transition metal complexes. *Coord. Chem. Rev.* **2018**, *361*, 74–97. DOI: 10.1016/j.ccr.2018.01.019.
- (108) Plasser, F. TheoDORE: A toolbox for a detailed and automated analysis of electronic excited state computations. *J. Chem. Phys.* **2020**, *152*, 84108. DOI: 10.1063/1.5143076.
- (109) Roos, B. O.; Taylor, P. R.; Sigbahn, P. E. A complete active space SCF method (CASSCF) using a density matrix formulated super-CI approach. *Chem. Phys.* **1980**, *48*, 157–173. DOI: 10.1016/0301-0104(80)80045-0.
- (110) Siegbahn, P. E. M.; Almlöf, J.; Heiberg, A.; Roos, B. O. The complete active space SCF (CASSCF) method in a Newton–Raphson formulation with application to the HNO molecule. *J. Chem. Phys.* **1981**, *74*, 2384–2396. DOI: 10.1063/1.441359.
- (111) Weigend, F.; Kattannek, M.; Ahlrichs, R. Approximated electron repulsion integrals: Cholesky decomposition versus resolution of the identity methods. *J. Chem. Phys.* **2009**, *130*, 164106. DOI: 10.1063/1.3116103.
- (112) Kossmann, S.; Neese, F. Comparison of two efficient approximate Hartree–Fock approaches. *Chem. Phys. Lett.* **2009**, *481*, 240–243. DOI: 10.1016/j.cplett.2009.09.073.
- (113) Angeli, C.; Cimiraglia, R.; Evangelisti, S.; Leininger, T.; Malrieu, J.-P. Introduction of n -electron valence states for multireference perturbation theory. *J. Chem. Phys.* **2001**, *114*, 10252–10264. DOI: 10.1063/1.1361246.
- (114) Angeli, C.; Cimiraglia, R.; Malrieu, J.-P. n -electron valence state perturbation theory: A spinless formulation and an efficient implementation of the strongly contracted and of the partially contracted variants. *J. Chem. Phys.* **2002**, *117*, 9138–9153. DOI: 10.1063/1.1515317.
- (115) Pierloot, K. Transition metals compounds: Outstanding challenges for multiconfigurational methods. *Int. J. Quantum Chem.* **2011**, *111*, 3291–3301. DOI: 10.1002/qua.23029.

Summary and Outlook

In 2015 the first *Molecular Ruby* $[\text{Cr}(\text{ddpd})_2]^{3+}$ was discovered.^[52] In the following years, additional complexes of this class were developed, their fundamental photophysical and electrochemical properties investigated and first applications described.^[87] This work aimed to establish *Molecular Rubies* as viable candidates for photoredox catalysis and to explore their strengths, peculiarities and associated challenges, utilizing catalytic experiments and numerous spectroscopic methods. Furthermore, novel chromium(III) complexes were developed, to gain deeper understanding of reduction potential- and emission energy tuning using rational design, guided by theoretical methods.

Molecular Rubies in Photoredox Catalysis

Prior to this work, *Molecular Rubies* had not been utilized as photoredox catalysts. The first application of $[\text{Cr}(\text{tpe})_2]^{3+}$ in a light-induced radical cation [4+2] cycloaddition was a great success. The chromium(III) complex outperformed its established noble-metal counterpart $[\text{Ru}(\text{bpz})_3]^{2+}$ due to superior photostability (Fig. 4.1a; section 3.2).^[181] Through a combination of photocatalytic experiments and spectroscopic techniques, oxygen was identified as a redox-shuttle in this net redox-neutral reaction. The need for a redox-shuttle was attributed to accumulation of the reduced complex $[\text{Cr}(\text{tpe})_2]^{2+}$ and the resulting increased rate of non-geminate back-ET to the oxidized organic substrate. While oxygen is a readily available oxidant, it can be detrimental in many reaction cycles, due to potential side-reactions. Thus, the slow reoxidation of $[\text{Cr}(\text{tpe})_2]^{2+}$ and the concomitant need for a suitable sacrificial oxidant was identified as a challenge associated with this catalyst.

After the encouraging results of the first study, $[\text{Cr}(\text{tpe})_2]^{3+}$ was used in the fixation of SO_2 into organic molecules, in two multi-component reactions (Fig. 4.1b; section 3.3).^[244] The photocatalytic syntheses of both the sulfone and sulfonamide products were successful, but once again, catalyst reoxidation was slow and impeded the reaction. Since conducting the reaction open to air proved detrimental in these reactions, the need for a suitable sacrificial oxidant aside from oxygen was underlined in this study. In addition to photocatalytic experiments, information on the reaction mechanism was gained via cyclic voltammetry, UV/vis/NIR absorption spectroscopy, *Stern-Volmer* analyses and laser flash photolysis. The latter provided valuable insight into the drastically different cage-escape yields of individual substrates. Said differences contributed to the success of the multi-component reactions, as undesired quenching of the ES photocatalyst by the wrong component was mostly unproductive

and thus less detrimental. Despite being advantageous in this case, there was no evident explanation for the observed differences. These results are in line with the general lack of predictability of cage-escape yields.^[139] At the same time they showcase the importance of deeper mechanistic understanding in the quest of maximizing reaction quantum yields Φ_R in the future (sections 1.3 and 1.4.3).^[229]

A promising tool for research on e.g. catalyst reoxidation speeds or cage-escape yields was developed via the addition of one or two trifluoromethyl groups to $[\text{Cr}(\text{tpe})_2]^{3+}$ in $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ and $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$, respectively (Fig. 4.1c, section 3.4).^[245] In most photocatalysts, the emission energy and the reduction potential are coupled and cannot be tuned independently. However, in this series of tripodal chromium(III) complexes, these properties are decoupled, owing to their spatial separation (metal-centered excited states vs. ligand-centered reduction). This decoupling was correctly predicted by quantum chemical calculations and observed experimentally via cyclic voltammetry and optical spectroscopy. While the geometries and emission energies of these complexes are almost identical, the introduction of each trifluoromethyl group shifts the reduction potential anodically by ca. 100 mV. The development of these compounds thus enables the assessment of cage-escape of a specific substrate or catalyst regeneration with a particular oxidant while changing only the thermodynamic driving force. Thus, this series of *Molecular Rubies* constitutes a tool for superior mechanistic research in the future. Furthermore, the high level of agreement between theoretical and experimental data could permit future *in silico* design of new tripodal chromium(III) compounds.

Fundamental mechanistic understanding is critical in the development of scalable photochemical reactions and thus for their more widespread application (section 1.4.3). However, there are numerous other challenges associated with the employed PC that need to be considered in this regard. Easy and scalable access from earth-abundant materials, very high levels of photostability, solubility and photocatalytic activity in organic solvents and water, simple irradiation setups and recyclability are requirements for a photocatalyst at larger scales – and $[\text{Cr}(\text{tpe})_2]^{3+}$ fulfills them (Fig. 4.1d; section 3.5).^[110] These desirable traits were demonstrated via simple, multigram syntheses of both ligand and complex, in photolysis experiments and in several photocatalytic transformations in both acetonitrile and water. The latter were partially conducted on a gram-scale, using a simple round-bottom flask as the reaction vessel. These achievements show that $[\text{Cr}(\text{tpe})_2]^{3+}$ can viably serve as a PC on at least a laboratory-scale. Future developments and optimizations could potentially permit further scaling. All in all, some of the most prevalent bottlenecks in photocatalysis were successfully addressed, using this chromium(III) complex.

Emission Energy Tuning and Assessment of Non-Radiative Decay Pathways

Most of the research conducted for this work was concerned with the application aspect of *Molecular Rubies*. However, understanding of their underlying properties

is by no means complete and plenty of knowledge can still be gained. Therefore, the emission properties of the newly synthesized complex $[\text{Cr}(\text{dgpy})_2]^{3+}$ were studied (Fig. 4.1e; section 3.6).^[246] In this compound, the more typical pyridine units were replaced with σ - and π -donating, saturated, cyclic guanidine-moieties. A bathochromic shift of the emission energy was observed relative to polypyridyl-complexes. This was attributed to the stronger *nephelauxetic effect* imposed by this ligand. Additionally, the quantum yield and excited-state lifetime of the complex are drastically lowered, compared to e.g. $[\text{Cr}(\text{ddpd})_2]^{3+}$ ($\Phi_{\text{p},0} = 13.7\% \rightarrow 0.5\%$; $\tau_0 = 1136 \mu\text{s} \rightarrow 63 \mu\text{s}$). Through a combination of theoretical methods and optical spectroscopy, two main non-radiative decay pathways were identified. Firstly, thermally activated bISC to the strongly distorted $^4\text{T}_2$ state depopulates the emissive ^2ES , which is facilitated by the flexible ligand. Secondly, intramolecular *Förster Resonance Energy Transfer* from the metal center to the C–H overtones of the ligand's guanidine moieties contributes to non-radiative decay. The efficiency of this process is enhanced through the high number of energy acceptors in the saturated ligand fragment (multiphonon-relaxation; section 1.3.3). Overall, while guanidine moieties succeed in red-shifting the emission energy of chromium(III) complexes, the introduction of saturated, highly flexible ligands proved detrimental to their emissive properties. The knowledge gained from these investigations will aid in future rational design of highly emissive chromium(III) complexes.

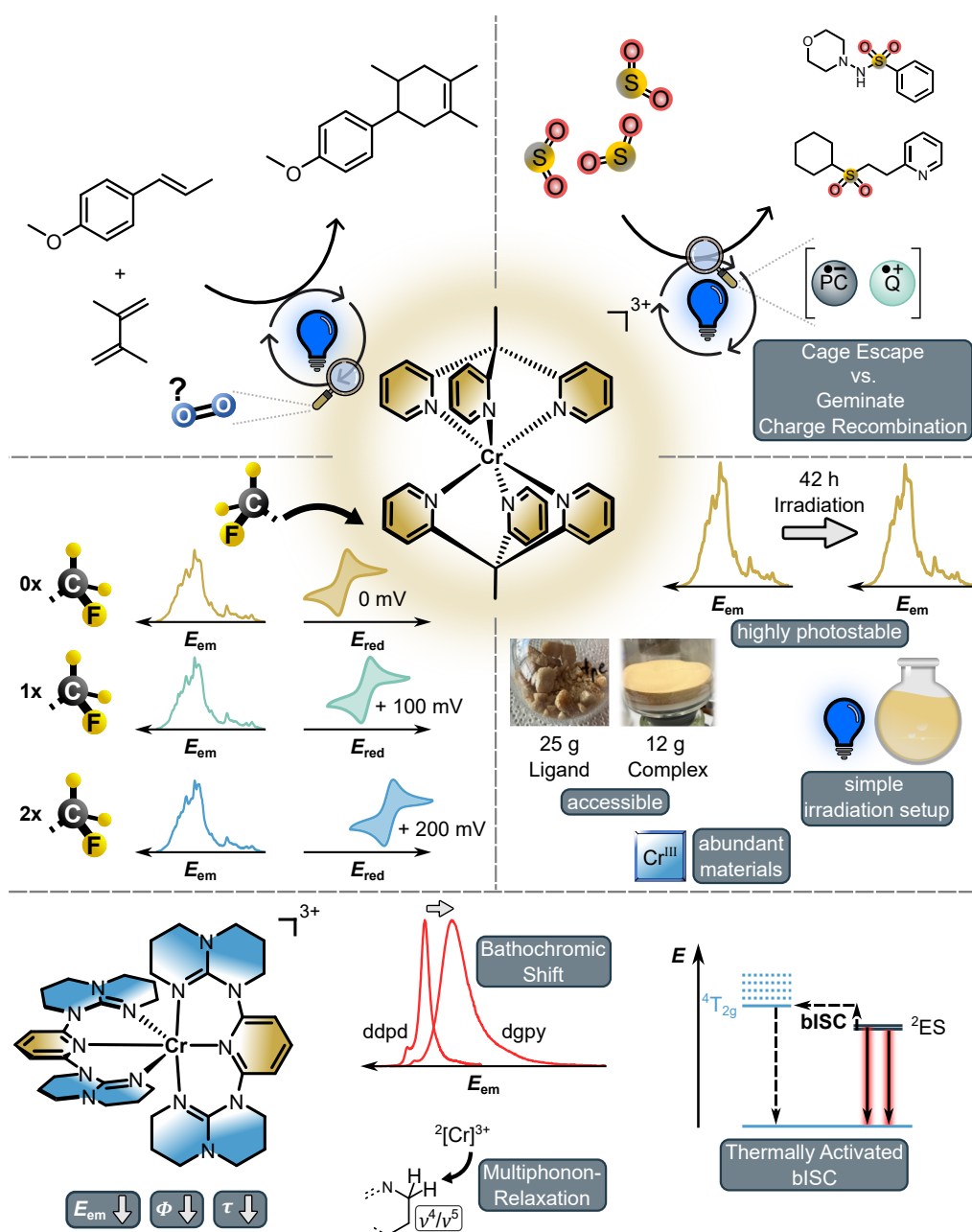


Fig. 4.1: Overview of the results of this work, including photocatalytic applications and reduction potential tuning of $[\text{Cr}(\text{tpe})_2]^{3+}$ as well as photophysical characterization of $[\text{Cr}(\text{dgpy})_2]^{3+}$. Single components of this figure were reused and adapted from published and submitted works and are licensed under CC BY-NC-ND 4.0 (<https://creativecommons.org/licenses/by-nc/4.0/>).^[110,181,244–246]

In summary, the *Molecular Ruby* $[\text{Cr}(\text{tpe})_2]^{3+}$ was successfully employed as a photo(redox) catalyst. Furthermore, new compounds were developed that permitted a deeper understanding of photo- and electrochemical properties of chromium(III) complexes. $[\text{Cr}(\text{tpe})_2]^{3+}$ was utilized in multiple photocatalytic applications and outcompeted the noble-metal TMC $[\text{Ru}(\text{bpz})_3]^{2+}$ due to superior photostability. Additionally, mechanistic investigations were conducted that not only yielded in-

formation on the investigated reactions, but on limitations of the catalytic system, namely the reoxidation of the reduced catalyst. Thus, critical knowledge for future approaches and optimizations was obtained. Furthermore, modifications to $[\text{Cr}(\text{tpe})_2]^{3+}$ permitted the independent tunability of reduction potentials in this type of complex, which should be utilized to gain deeper mechanistic understanding in the future. Due to its facile synthesis from cheap, abundant starting-materials, $[\text{Cr}(\text{tpe})_2]^{3+}$ is easily accessible on a multigram scale. The complex functions as a strongly oxidizing photocatalyst in organic solvents and water and its low extinction coefficient allows for the use of simple irradiation setups. Photophysical characterization of the complex $[\text{Cr}(\text{dgy})_2]^{3+}$ gave deep insight into the non-radiative decay pathways that dominate in chromium(III) complexes.

Future endeavours regarding $[\text{Cr}(\text{tpe})_2]^{3+}$ should be concerned with the identification of a suitable redox-shuttle/sacrificial oxidant (other than oxygen) for photocatalytic reactions in organic solvents. The results of this work have repeatedly shown that the slow reoxidation of the reduced catalyst can be a limiting factor. Additionally, research into the mechanistic aspects outlined above could be highly valuable and should be facilitated by the series of CF_3 -substituted tripodal complexes. While the anodic shift of the ground-state reduction potentials of these compounds is useful for mechanistic studies (and should also expand their available substrate scopes), it does make reoxidation of the respective $[\text{Cr}]^{2+}$ species even more challenging. Thus, to further increase the catalyst's excited-state reduction potential, a blue-shift of the emission energy could be desirable. However, this will most likely be a challenging task, as shifting the ES energies in chromium(III) complexes typically requires significant changes to the ligand scaffold (section 1.2.2) that could potentially compromise the numerous desirable traits of the $[\text{Cr}(\text{tpe})_2]^{3+}$ parent complex.

Molecular Rubies have advanced significantly since the development of their first representative $[\text{Cr}(\text{ddpd})_2]^{3+}$ ten years ago. Numerous applications have been realized, including multiple types of sensing and energy transfer. Through its many desirable properties, the complex $[\text{Cr}(\text{tpe})_2]^{3+}$ has extended their influence to the realm of photoredox catalysis research. The results presented in this thesis have proven the complex's ability to hold its own in competition with noble-metal catalysts. Thus, this work pushes forward the establishment of TMCs based on earth-abundant metals as part of the paradigm shift towards sustainable photochemistry.

References

- [1] *World Population Prospects 2024: Summary of Results*, United Nations, New York, **2024**.
- [2] *World Energy Outlook 2024*, IEA, Paris, **2024**.
- [3] M. K. H. Rabaia, M. A. Abdelkareem, E. T. Sayed, K. Elsaid, K.-J. Chae, T. Wilberforce, A. G. Olabi, *Sci. Total Environ.* **2021**, 754, 141989.
- [4] A. O. Ali, A. T. Elgohr, M. H. El-Mahdy, H. M. Zohir, A. Z. Emam, M. G. Mostafa, M. Al-Razgan, H. M. Kasem, M. S. Elhadidy, *Energy Convers. Manage.* **2025**, 26, 100952.
- [5] W. Kaim, B. Schwederski, *Bioanorganische Chemie: Zur Funktion chemischer Elemente in Lebensprozessen*, Vieweg+Teubner Verlag, Wiesbaden, **2005**.
- [6] M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, 81, 6898–6926.
- [7] R. E. Blankenship, *Plant Physiol.* **2010**, 154, 434–438.
- [8] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, 113, 5322–5363.
- [9] P.-T. Chou, Y. Chi, *Chem. Eur. J.* **2007**, 13, 380–395.
- [10] A. Carella, F. Borbone, R. Centore, *Front. Chem.* **2018**, 6, 481.
- [11] Y. Allamyradov, J. ben Yosef, B. Annamuradov, M. Ateyeh, C. Street, H. Whipple, A. O. Er, *Photochem* **2024**, 4, 434–461.
- [12] D. M. Arias-Rotondo, *Nat. Chem.* **2022**, 14, 716.
- [13] *CRC Handbook of Chemistry and Physics*, 97th ed., (Eds.: W. M. Haynes, D. R. Lide, T. J. Bruno), CRC Press, **2016**.
- [14] W. R. Kitzmann, M.-S. Bertrams, P. Boden, A. C. 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, 16597–16609.
- [15] C. Förster, K. Heinze, *Chem. Phys. Rev.* **2022**, 3, 041302.
- [16] C. B. Larsen, O. S. Wenger, *Chem. Eur. J.* **2018**, 24, 2039–2058.
- [17] O. Baslé, *Curr. Opin. Green Sust.* **2021**, 32, 100539.
- [18] Y. Zhang, Q. Wang, Z. Yan, D. Ma, Y. Zheng, *Beilstein J. Org. Chem.* **2021**, 17, 2520–2542.
- [19] L. H. M. de Groot, A. Ilic, J. Schwarz, K. Wärnmark, *J. Am. Chem. Soc.* **2023**, 146, 9369–9388.
- [20] P. Jin, C. Wang, *Phys. Chem. Chem. Phys.* **2025**, 27, 13793–13811.
- [21] S. Engl, O. Reiser, *Chem. Soc. Rev.* **2022**, 51, 5287–5299.
- [22] M. Dorn, N. R. East, C. Förster, W. R. Kitzmann, J. Moll, F. Reichenauer, T. Reuter, L. Stein, K. Heinze in *Comprehensive Inorganic Chemistry III*, pp. 707–788.

- [23] D. M. Arias-Rotondo, J. K. McCusker, *Chem. Soc. Rev.* **2016**, 45, 5803–5820.
- [24] G. Morselli, C. Reber, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, 147, 11608–11624.
- [25] *Visible Light Photocatalysis in Organic Chemistry*, 1. Auflage, (Eds.: C. R. J. Stephenson, T. P. Yoon, D. W. C. MacMillan), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2018**.
- [26] *Photochemistry and Photophysics of Coordination Compounds I*, (Eds.: V. Balzani, S. Campagna), Springer, Berlin, Heidelberg, **2007**.
- [27] A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, M. Chergui, *Angew. Chem. Int. Ed.* **2006**, 45, 3174–3176.
- [28] J. N. Demas, D. G. Taylor, *Inorg. Chem.* **1979**, 18, 3177–3179.
- [29] N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, J. K. McCusker, *Science* **1997**, 275, 54–57.
- [30] A. Soupart, I. M. Dixon, F. Alary, J.-L. Heully, *Theor. Chem. Acc.* **2018**, 137.
- [31] W. R. Kitzmann, K. Heinze, *Angew. Chem. Int. Ed.* **2023**, 62, e202213207.
- [32] T. J. Penfold, E. Gindensperger, C. Daniel, C. M. Marian, *Chem. Rev.* **2018**, 118, 6975–7025.
- [33] J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* **1983**, 105, 5583–5590.
- [34] D. W. Thompson, A. Ito, T. J. Meyer, *Pure Appl. Chem.* **2013**, 85, 1257–1305.
- [35] J. K. McCusker, *Science* **2019**, 363, 484–488.
- [36] M. Kaupp, *J. Comput. Chem.* **2007**, 28, 320–325.
- [37] T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard, M. E. Thompson, *J. Am. Chem. Soc.* **2009**, 131, 9813–9822.
- [38] T. Hofbeck, H. Yersin, *Inorg. Chem.* **2010**, 49, 9290–9299.
- [39] O. S. Wenger, *Chem. Eur. J.* **2019**, 25, 6043–6052.
- [40] C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, 49, 1057–1070.
- [41] G. Auböck, M. Chergui, *Nat. Chem.* **2015**, 7, 629–633.
- [42] A. Cannizzo, C. J. Milne, C. Consani, W. Gawelda, C. Bressler, F. van Mourik, M. Chergui, *Coord. Chem. Rev.* **2010**, 254, 2677–2686.
- [43] C. Wegeberg, O. S. Wenger, *JACS Au* **2021**, 1, 1860–1876.
- [44] B. M. Hockin, C. Li, N. Robertson, E. Zysman-Colman, *Catal. Sci. Technol.* **2019**, 9, 889–915.
- [45] T. Jin, N. Sinha, D. S. Wagner, A. Prescimone, D. Häussinger, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, 147, 4587–4594.
- [46] L. A. Büldt, O. S. Wenger, *Angew. Chem. Int. Ed.* **2017**, 56, 5676–5682.
- [47] P. Herr, C. Kerzig, C. B. Larsen, D. Häussinger, O. S. Wenger, *Nat. Chem.* **2021**, 13, 956–962.

- [48] S. Kronenberger, R. Naumann, C. Förster, N. R. East, J. Klett, K. Heinze, *Nat. Commun.* **2024**, *16*, 7850.
- [49] A. K. Pal, C. Li, G. S. Hanan, E. Zysman-Colman, *Angew. Chem. Int. Ed.* **2018**, *57*, 8027–8031.
- [50] A. Y. Chan, A. Ghosh, J. T. Yarranton, J. Twilton, J. Jin, D. M. Arias-Rotondo, H. A. Sakai, J. K. McCusker, D. W. C. MacMillan, *Science* **2023**, *382*, 191–197.
- [51] W. R. Kitzmann, J. Moll, K. Heinze, *Photochem. Photobiol. Sci.* **2022**, *21*, 1309–1331.
- [52] S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572–11576.
- [53] S. Otto, M. Dorn, C. Förster, M. Bauer, M. Seitz, K. Heinze, *Coord. Chem. Rev.* **2018**, *359*, 102–111.
- [54] Y. Tanabe, Sugano S, *J. Phys. Soc. Jpn.* **1954**, *9*, 753–766.
- [55] Y. Tanabe, Sugano S, *J. Phys. Soc. Jpn.* **1954**, *9*, 766–779.
- [56] L. S. Forster, *Chem. Rev.* **1990**, *90*, 331–353.
- [57] W. R. Kitzmann, C. Ramanan, R. Naumann, K. Heinze, *Dalton Trans.* **2022**, *51*, 6519–6525.
- [58] M. A. El-Sayed, *J. Chem. Phys.* **1963**, *38*, 2834–2838.
- [59] C. Wang, W. R. Kitzmann, F. Weigert, C. Förster, X. Wang, K. Heinze, U. Resch-Genger, *ChemPhotoChem* **2022**, *6*, e202100296.
- [60] R. Gauthier, P. Pinard, *Phys. Status Solidi A* **1970**, *3*, 995–1005.
- [61] T. H. Maiman, *Nature* **1960**, *187*, 493–494.
- [62] R. S. Quimby, W. M. Yen, *J. Appl. Phys.* **1980**, *51*, 1780–1782.
- [63] C. Degli Esposti, L. Bizzocchi, *J. Chem. Educ.* **2007**, *84*, 1316.
- [64] K. D. Barker, K. A. Barnett, S. M. Connell, J. W. Glaeser, A. J. Wallace, J. Wildsmith, B. J. Herbert, J. F. Wheeler, N. A. Kane-Maguire, *Inorg. Chim. Acta* **2001**, *316*, 41–49.
- [65] A. D. Kirk, G. B. Porter, *J. Phys. Chem.* **1980**, *84*, 887–891.
- [66] J. C. Barbour, A. J. I. Kim, E. deVries, S. E. Shaner, B. M. Lovaasen, *Inorg. Chem.* **2017**, *56*, 8212–8222.
- [67] J.-R. Jiménez, B. Doistau, C. Besnard, C. Piguet, *Chem. Commun.* **2018**, *54*, 13228–13231.
- [68] F. Reichenauer, C. Wang, C. Förster, P. Boden, N. Ugur, R. Báez-Cruz, J. Kalmbach, L. M. Carrella, E. Rentschler, C. Ramanan, G. Niedner-Schatteburg, M. Gerhards, M. Seitz, U. Resch-Genger, K. Heinze, *J. Am. Chem. Soc.* **2021**, *143*, 11843–11855.
- [69] S. Treiling, C. Wang, C. Förster, F. Reichenauer, J. Kalmbach, P. Boden, J. P. Harris, L. M. Carrella, E. Rentschler, U. Resch-Genger, C. Reber, M. Seitz, M. Gerhards, K. Heinze, *Angew. Chem. Int. Ed.* **2019**, *58*, 18075–18085.
- [70] F. Reichenauer, R. Naumann, C. Förster, W. R. Kitzmann, A.-P. M. Reponen, S. Feldmann, K. Heinze, *Chem. Sci.* **2024**, *15*, 20251–20262.

- [71] J.-R. Jiménez, B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *J. Am. Chem. Soc.* **2019**, *141*, 13244–13252.
- [72] L. Stein, P. Boden, R. Naumann, C. Förster, G. Niedner-Schatteburg, K. Heinze, *Chem. Commun.* **2022**, *58*, 3701–3704.
- [73] N. Sinha, J.-R. Jiménez, B. Pfund, A. Prescimone, C. Piguet, O. S. Wenger, *Angew. Chem. Int. Ed.* **2021**, *60*, 23722–23728.
- [74] C. Wang, S. Otto, M. Dorn, E. Kreidt, J. Lebon, L. Sršan, P. Di Martino-Fumo, M. Gerhards, U. Resch-Genger, M. Seitz, K. Heinze, *Angew. Chem. Int. Ed.* **2018**, *57*, 1112–1116.
- [75] L. Stein, C. Wang, C. Förster, U. Resch-Genger, K. Heinze, *Dalton Trans.* **2022**, *51*, 17664–17670.
- [76] S. Otto, N. Scholz, T. Behnke, U. Resch-Genger, K. Heinze, *Chem. Eur. J.* **2017**, *23*, 12131–12135.
- [77] S. Otto, J. P. Harris, K. Heinze, C. Reber, *Angew. Chem. Int. Ed.* **2018**, *57*, 11069–11073.
- [78] E. M. Kober, J. V. Caspar, R. S. Lumpkin, T. J. Meyer, *J. Phys. Chem.* **1986**, *90*, 3722–3734.
- [79] M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, J. L. Glasper, D. J. Robbins, *J. Chem. Soc. Perkin Trans. 2* **1984**, 1293–1301.
- [80] G. A. Parada, L. A. Fredin, M.-P. Santoni, M. Jäger, R. Lomoth, L. Hammarström, O. Johansson, P. Persson, S. Ott, *Inorg. Chem.* **2013**, *52*, 5128–5137.
- [81] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358.
- [82] P. Chen, T. J. Meyer, *Chem. Rev.* **1998**, *98*, 1439–1478.
- [83] M. Homocianu, *Microchem. J.* **2024**, *198*, 110166.
- [84] A. J. Lees, *Comments Inorganic Chem.* **1995**, *17*, 319–346.
- [85] Y. Ye, M. Poncet, P. Yaltseva, P. Salcedo-Abraira, A. Rodríguez-Diéguez, J. H. Martín, L. Cuevas-Contreras, C. M. Cruz, B. Doistau, C. Piguet, O. S. Wenger, J. M. Herrera, J.-R. Jiménez, *Chem. Sci.* **2025**, *16*, 5205–5213.
- [86] N. Sinha, P. Yaltseva, O. S. Wenger, *Angew. Chem. Int. Ed.* **2023**, *62*, e202303864.
- [87] C. Förster, K. Heinze, *Adv. Inorg. Chem.* **2024**, *83*, 111–159.
- [88] W. R. Kitzmann, D. Hunger, A.-P. M. Reponen, C. Förster, R. Schoch, M. Bauer, S. Feldmann, J. van Slageren, K. Heinze, *Inorg. Chem.* **2023**, *62*, 15797–15808.
- [89] M. Dorn, D. Hunger, C. Förster, R. Naumann, J. van Slageren, K. Heinze, *Chem. Eur. J.* **2023**, *29*, e202202898.
- [90] A. König, R. Naumann, C. Förster, J. Klett, K. Heinze, *J. Am. Chem. Soc.* **2025**, *147*, 20833–20842.
- [91] S. de Kreijger, F. Glaser, L. Troian-Gautier, *Chem Catal.* **2024**, *4*, 101110.
- [92] S. Neumann, C. Kerzig, O. S. Wenger, *Chem. Sci.* **2019**, *10*, 5624–5633.
- [93] C. Wang, H. Li, T. H. Bürgin, O. S. Wenger, *Nat. Chem.* **2024**, *16*, 1151–1159.

- [94] F. Draper, S. DiLuzio, H. J. Sayre, N. Le Pham, M. L. Coote, E. H. Doeven, P. S. Francis, T. U. Connell, *J. Am. Chem. Soc.* **2024**, *146*, 26830–26843.
- [95] F. Glaser, O. S. Wenger, *Chem. Sci.* **2023**, *14*, 149–161.
- [96] M. A. Cismesia, T. P. Yoon, *Chem. Sci.* **2015**, *6*, 5426–5434.
- [97] D. E. Yerien, S. Barata-Vallejo, E. W. Mora Flores, A. Postigo, *Catal. Sci. Technol.* **2020**, *10*, 5113–5128.
- [98] A. A. Lee, J. R. Swierk, *J. Am. Chem. Soc.* **2024**, *146*, 34900–34908.
- [99] B. Reiß, Q. Hu, E. Riedle, H.-A. Wagenknecht, *ChemPhotoChem* **2021**, *5*, 1009–1019.
- [100] L. Buzzetti, G. E. M. Crisenza, P. Melchiorre, *Angew. Chem. Int. Ed.* **2019**, *58*, 3730–3747.
- [101] O. Stern, M. Volmer, *Phys. Z.* **1919**, *20*, 183–188.
- [102] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 4th ed., Springer, New York, NY, **2010**.
- [103] N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075–10166.
- [104] B. Pfund, D. Gejsnæs-Schaad, B. Lazarevski, O. S. Wenger, *Nat. Commun.* **2024**, *15*, 4738.
- [105] J. D. Sakizadeh, R. Weiss, G. D. Scholes, B. Kudisch, *Annu. Rev. Phys. Chem.* **2025**, *76*, 203–229.
- [106] M. Smoluchowski, *Z. Phys. Chem.* **1918**, *92*, 129–168.
- [107] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, J. Michl, V. Balzani, *Handbook of Photochemistry*, 3rd ed., CRC Press, Boca Raton, **2006**.
- [108] M. Z. Hoffman, F. Bolletta, L. Moggi, G. L. Hug, *J. Phys. Chem. Ref. Data* **1989**, *18*, 219–543.
- [109] R. N. Motz, A. C. Sun, D. Lehnher, S. Ruccolo, *ACS Org. Inorg. Au* **2023**, *3*, 266–273.
- [110] S. Sittel, J. Neuner, J. M. Grenz, C. Förster, R. Naumann, K. Heinze, *Adv. Synth. Catal.* **2025**, *367*, e202500075.
- [111] N. A. Romero, D. A. Nicewicz, *J. Am. Chem. Soc.* **2014**, *136*, 17024–17035.
- [112] S. E. Braslavsky, *Pure Appl. Chem.* **2007**, *79*, 293–465.
- [113] T. H. Bürgin, F. Glaser, O. S. Wenger, *J. Am. Chem. Soc.* **2022**, *144*, 14181–14194.
- [114] D. Rehm, A. Weller, *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834–839.
- [115] I. Ahmad, Z. Anwar, S. A. Ali, K. A. Hasan, M. A. Sheraz, S. Ahmed, *J. Photochem. Photobiol. B* **2016**, *157*, 113–119.
- [116] J. N. Brønsted, *Z. Phys. Chem.* **1922**, *102*, 169–207.
- [117] N. Bjerrum, *Z. Phys. Chem.* **1924**, *108*, 82–100.
- [118] M. Schmitz, M.-S. Bertrams, A. C. Sell, F. Glaser, C. Kerzig, *J. Am. Chem. Soc.* **2024**, *146*, 25799–25812.

- [119] D. Genovese, M. Cingolani, E. Rampazzo, L. Prodi, N. Zaccheroni, *Chem. Soc. Rev.* **2021**, *50*, 8414–8427.
- [120] R. A. Marcus, *J. Chem. Phys.* **1956**, *24*, 966–978.
- [121] R. A. Marcus, *Angew. Chem. Int. Ed.* **1993**, *32*, 1111–1121.
- [122] E. J. Piechota, G. J. Meyer, *J. Chem. Educ.* **2019**, *96*, 2450–2466.
- [123] P. J. Larkin, *Infrared and Raman Spectroscopy*, Elsevier, **2018**.
- [124] J. W. Tucker, C. R. J. Stephenson, *J. Org. Chem.* **2012**, *77*, 1617–1622.
- [125] N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, J. L. Dempsey, *J. Chem. Educ.* **2018**, *95*, 197–206.
- [126] O. R. Luca, J. L. Gustafson, S. M. Maddox, A. Q. Fenwick, D. C. Smith, *Org. Chem. Front.* **2015**, *2*, 823–848.
- [127] H. Roth, N. Romero, D. Nicewicz, *Synlett* **2016**, *27*, 714–723.
- [128] D. Kim, T. S. Teets, *Chem. Phys. Rev.* **2022**, *3*, 021302.
- [129] E. Speckmeier, T. G. Fischer, K. Zeitler, *J. Am. Chem. Soc.* **2018**, *140*, 15353–15365.
- [130] A. Singh, K. Teegardin, M. Kelly, K. S. Prasad, S. Krishnan, J. D. Weaver, *J. Organomet. Chem.* **2015**, *776*, 51–59.
- [131] J.-H. Shon, S. Sittel, T. S. Teets, *ACS Catal.* **2019**, *9*, 8646–8658.
- [132] J. Konzal, M. Murley, A. Wolter, L. Camou, A. Oberbroeckling, M. Dekker, G. Wagner, K. Jennejohn, M. Peters, N. Hayes, C. Franklin, S. Tobin, E. Collier, I. MacKenzie, *Chem. Eur. J.* **2025**, *31*, e202403543.
- [133] D. L. Ashford, C. R. K. Glasson, M. R. Norris, J. J. Concepcion, S. Keinan, M. K. Brennaman, J. L. Templeton, T. J. Meyer, *Inorg. Chem.* **2014**, *53*, 5637–5646.
- [134] E. J. Piechota, G. J. Meyer, *J. Chem. Educ.* **2024**, *101*, 2954.
- [135] T. P. Silverstein, *J. Chem. Educ.* **2012**, *89*, 1159–1167.
- [136] L. H. Gade, *Koordinationschemie*, 1st ed., Wiley-VCH, Weinheim, **1998**.
- [137] A. Devaquet, *Pure Appl. Chem.* **1975**, *41*, 455–473.
- [138] N. S. Hush, *Coord. Chem. Rev.* **1985**, *64*, 135–157.
- [139] M. J. Goodwin, J. C. Dickenson, A. Ripak, A. M. Deetz, J. S. McCarthy, G. J. Meyer, L. Troian-Gautier, *Chem. Rev.* **2024**, *124*, 7379–7464.
- [140] A. Ripak, S. de Kreijger, B. Elias, L. Troian-Gautier, *STAR Protoc.* **2023**, *4*, 102312.
- [141] S. Neumann, O. S. Wenger, C. Kerzig, *Chem. Eur. J.* **2021**, *27*, 4115–4123.
- [142] L. Capaldo, D. Ravelli, *Eur. J. Org. Chem.* **2020**, *2020*, 2783–2806.
- [143] M. Schmittel, A. Burghart, *Angew. Chem. Int. Ed.* **1997**, *36*, 2550–2589.
- [144] D. L. Dexter, *J. Chem. Phys.* **1953**, *21*, 836–850.
- [145] F. Strieth-Kalthoff, M. J. James, M. Teders, L. Pitzer, F. Glorius, *Chem. Soc. Rev.* **2018**, *47*, 7190–7202.

- [146] S. Dutta, J. E. Erchinger, F. Strieth-Kalthoff, R. Kleinmans, F. Glorius, *Chem. Soc. Rev.* **2024**, 53, 1068–1089.
- [147] M. C. DeRosa, R. J. Crutchley, *Coord. Chem. Rev.* **2002**, 233–234, 351–371.
- [148] A. A. Ghogare, A. Greer, *Chem. Rev.* **2016**, 116, 9994–10034.
- [149] M. Prein, W. Adam, *Angew. Chem. Int. Ed.* **1996**, 35, 477–494.
- [150] T. Förster, *Ann. Phys.* **1948**, 437, 55–75.
- [151] E. Wigner, *Nachr. Akad. Wiss. Goettingen Math. Phys.* **1927**, 1927, 375–381.
- [152] D. Guo, T. E. Knight, J. K. McCusker, *Science* **2011**, 334, 1684–1687.
- [153] H. Sahoo, *J. Photochem. Photobiol. C* **2011**, 12, 20–30.
- [154] D. L. Andrews, R. H. Lipson, *Molecular photophysics and spectroscopy*, 2nd ed., IOP Publishing, Bristol, UK, **2021**.
- [155] G. Ciamician, *Science* **1912**, 36, 385–394.
- [156] E. Paterno, G. Chieffi, *Gazz. Chim. Ital.* **1909**, 39, 341–361.
- [157] G. Büchi, C. G. Inman, E. S. Lipinsky, *J. Am. Chem. Soc.* **1954**, 76, 4327–4331.
- [158] M. Fréneau, N. Hoffmann, *J. Photochem. Photobiol. C* **2017**, 33, 83–108.
- [159] P. Bayer, R. Pérez-Ruiz, A. Jacobi von Wangelin, *ChemPhotoChem* **2018**, 2, 559–570.
- [160] T. J. Meyer, *Acc. Chem. Res.* **1989**, 22, 163–170.
- [161] F. Teplý, *Collect. Czech. Chem. Commun.* **2011**, 76, 859–917.
- [162] M. A. Ischay, M. E. Anzovino, J. Du, T. P. Yoon, *J. Am. Chem. Soc.* **2008**, 130, 12886–12887.
- [163] D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, 322, 77–80.
- [164] J. M. R. Narayanam, J. W. Tucker, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2009**, 131, 8756–8757.
- [165] C. G. Thomson, A.-L. Lee, F. Vilela, *Beilstein J. Org. Chem.* **2020**, 16, 1495–1549.
- [166] J. Clayden, N. Greeves, S. G. Warren, *Organische Chemie*, 2nd ed., Springer, Berlin, **2017**.
- [167] T. Noël, E. Zysman-Colman, *Chem. Catal.* **2022**, 2, 468–476.
- [168] H. E. Bonfield, T. Knauber, F. Lévesque, E. G. Moschetta, F. Susanne, L. J. Edwards, *Nat. Commun.* **2020**, 11, 804.
- [169] V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta* **2000**, 298, 97–102.
- [170] J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, 40, 102–113.
- [171] *Visible Light-Active Photocatalysis: Nanostructured Catalyst Design, Mechanisms, and Applications*, 1. Auflage, (Ed.: S. Ghosh), Wiley-VCH, Weinheim, **2018**.
- [172] B. König, *Chemical Photocatalysis*, 2nd ed., de Gruyter, Berlin, **2020**.
- [173] *Emerging Trends in Photoredox Synthetic Transformation*, 1st ed., (Eds.: M. Sen, D. Ray), Springer, Singapore, **2025**.

- [174] T. Huang, P. Du, Y.-M. Lin, *Chin. J. Chem.* **2025**, *43*, 2566–2587.
- [175] N. Sinha, N. Kumar, T. Sharma, N. Thakur, R. Jain, *Chem. Eur. J.* **2025**, *31*, e202500365.
- [176] P. M. Becker, C. Förster, L. M. Carrella, P. Boden, D. Hunger, J. van Slageren, M. Gerhards, E. Rentschler, K. Heinze, *Chem. Eur. J.* **2020**, *26*, 7199–7204.
- [177] C. C. Scarborough, S. Sproules, T. Weyhermüller, S. DeBeer, K. Wieghardt, *Inorg. Chem.* **2011**, *50*, 12446–12462.
- [178] C. C. Scarborough, K. M. Lancaster, S. DeBeer, T. Weyhermüller, S. Sproules, K. Wieghardt, *Inorg. Chem.* **2012**, *51*, 3718–3732.
- [179] M. Wang, T. Weyhermüller, K. Wieghardt, *Eur. J. Inorg. Chem.* **2015**, *2015*, 3246–3254.
- [180] A. M. McDaniel, H.-W. Tseng, N. H. Damrauer, M. P. Shores, *Inorg. Chem.* **2010**, *49*, 7981–7991.
- [181] S. Sittel, R. Naumann, K. Heinze, *Front. Chem.* **2022**, *10*, 887439.
- [182] G. Morselli, T. H. Eggenweiler, M. Villa, A. Prescimone, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, *147*, 28226–28240.
- [183] S. M. Stevenson, M. P. Shores, E. M. Ferreira, *Angew. Chem. Int. Ed.* **2015**, *54*, 6506–6510.
- [184] S. Lin, M. A. Ischay, C. G. Fry, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, *133*, 19350–19353.
- [185] R. F. Higgins, S. M. Fatur, S. G. Shepard, S. M. Stevenson, D. J. Boston, E. M. Ferreira, N. H. Damrauer, A. K. Rappé, M. P. Shores, *J. Am. Chem. Soc.* **2016**, *138*, 5451–5464.
- [186] Y. Yang, Q. Liu, L. Zhang, H. Yu, Z. Dang, *Organometallics* **2017**, *36*, 687–698.
- [187] S. M. Stevenson, R. F. Higgins, M. P. Shores, E. M. Ferreira, *Chem. Sci.* **2017**, *8*, 654–660.
- [188] F. J. Sarabia, Q. Li, E. M. Ferreira, *Angew. Chem. Int. Ed.* **2018**, *57*, 11015–11019.
- [189] F. J. Sarabia, E. M. Ferreira, *Org. Lett.* **2017**, *19*, 2865–2868.
- [190] S. Otto, A. M. Nauth, E. Ermilov, N. Scholz, A. Friedrich, U. Resch-Genger, S. Lochbrunner, T. Opatz, K. Heinze, *ChemPhotoChem* **2017**, *1*, 344–349.
- [191] U. Basu, S. Otto, K. Heinze, G. Gasser, *Eur. J. Inorg. Chem.* **2019**, *2019*, 37–41.
- [192] C. Wang, F. Reichenauer, W. R. Kitzmann, C. Kerzig, K. Heinze, U. Resch-Genger, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202238.
- [193] N. R. East, C. Förster, L. M. Carrella, E. Rentschler, K. Heinze, *Inorg. Chem.* **2022**, *61*, 14616–14625.
- [194] N. R. East, R. Naumann, C. Förster, C. Ramanan, G. Diezemann, K. Heinze, *Nat. Chem.* **2024**, *16*, 827–834.
- [195] T. Huang, P. Du, X. Cheng, Y.-M. Lin, *J. Am. Chem. Soc.* **2024**, *146*, 24515–24525.
- [196] J. N. Miller, J. K. McCusker, *Chem. Sci.* **2020**, *11*, 5191–5204.
- [197] A. Gualandi, M. Marchini, L. Mengozzi, M. Natali, M. Lucarini, P. Ceroni, P. G. Cozzi, *ACS Catal.* **2015**, *5*, 5927–5931.

- [198] D. A. Nagib, M. E. Scott, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2009**, *131*, 10875–10877.
- [199] M. D. Woodhouse, J. K. McCusker, *J. Am. Chem. Soc.* **2020**, *142*, 16229–16233.
- [200] S. Kaufhold, N. W. Rosemann, P. Chábera, L. Lindh, I. Bolaño Losada, J. Uhlig, T. Pascher, D. Strand, K. Wärnmark, A. Yartsev, P. Persson, *J. Am. Chem. Soc.* **2021**, *143*, 1307–1312.
- [201] J. Beaudelot, S. Oger, S. Peruško, T.-A. Phan, T. Teunens, C. Moucheron, G. Evano, *Chem. Rev.* **2022**, *122*, 16365–16609.
- [202] A. Hossain, A. Bhattacharyya, O. Reiser, *Science* **2019**, *364*, eaav9713.
- [203] R. H. Viradiya, A. Choudhary, M. Morja, K. H. Chikhliya, *Chem. Eng. Process. Tech.* **2024**, *9*, 1095.
- [204] C. Sandoval-Pauker, G. Molina-Aguirre, B. Pinter, *Polyhedron* **2021**, *199*, 115105.
- [205] J.-M. Kern, J.-P. Sauvage, *J. Chem. Soc. Chem. Commun.* **1987**, 546–548.
- [206] M. Pirtsch, S. Paria, T. Matsuno, H. Isobe, O. Reiser, *Chem. Eur. J.* **2012**, *18*, 7336–7340.
- [207] D. B. Bagal, G. Kachkovskyi, M. Knorn, T. Rawner, B. M. Bhanage, O. Reiser, *Angew. Chem. Int. Ed.* **2015**, *54*, 6999–7002.
- [208] A. Call, C. Casadevall, F. Acuña-Parés, A. Casitas, J. Lloret-Fillol, *Chem. Sci.* **2017**, *8*, 4739–4749.
- [209] S. Shanmugam, J. Xu, C. Boyer, *J. Am. Chem. Soc.* **2015**, *137*, 9174–9185.
- [210] C. Grundke, R. C. Silva, W. R. Kitzmann, K. Heinze, K. T. de Oliveira, T. Opatz, *J. Org. Chem.* **2022**, *87*, 5630–5642.
- [211] Z. Zhang, D. Slak, T. Krebs, M. Leuschner, N. Schmickler, E. Kuchuk, J. Schmidt, L. I. Domenianni, J. B. Kleine Büning, S. Grimme, P. Vöhringer, A. Gansäuer, *J. Am. Chem. Soc.* **2023**, *145*, 26667–26677.
- [212] Y. Zhang, J. L. Petersen, C. Milsmann, *J. Am. Chem. Soc.* **2016**, *138*, 13115–13118.
- [213] N. Sinha, C. Wegeberg, D. Häussinger, A. Prescimone, O. S. Wenger, *Nat. Chem.* **2023**, *15*, 1730–1736.
- [214] L. A. Büldt, X. Guo, A. Prescimone, O. S. Wenger, *Angew. Chem. Int. Ed.* **2016**, *55*, 11247–11250.
- [215] J. Fajardo, A. T. Barth, M. Morales, M. K. Takase, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2021**, *143*, 19389–19398.
- [216] Y. J. Jang, H. An, S. Choi, J. Hong, S. H. Lee, K.-H. Ahn, Y. You, E. J. Kang, *Org. Lett.* **2022**, *24*, 4479–4484.
- [217] A. Aydogan, R. E. Bangle, A. Cadranel, M. D. Turlington, D. T. Conroy, E. Cauët, M. L. Singleton, G. J. Meyer, R. N. Sampaio, B. Elias, L. Troian-Gautier, *J. Am. Chem. Soc.* **2021**, *143*, 15661–15673.
- [218] A. Ilic, J. Schwarz, C. Johnson, L. H. M. de Groot, S. Kaufhold, R. Lomoth, K. Wärnmark, *Chem. Sci.* **2022**, *13*, 9165–9175.

- [219] J.-L. Tu, H. Gao, M. Luo, L. Zhao, C. Yang, L. Guo, W. Xia, *Green Chem.* **2022**, *24*, 5553–5558.
- [220] H. D. Burrows, T. J. Kemp, *Chem. Soc. Rev.* **1974**, *3*, 139–165.
- [221] W.-D. Wang, A. Bakac, J. H. Espenson, *Inorg. Chem.* **1995**, *34*, 6034–6039.
- [222] L. Capaldo, D. Merli, M. Fagnoni, D. Ravelli, *ACS Catal.* **2019**, *9*, 3054–3058.
- [223] J. W. Beatty, J. J. Douglas, K. P. Cole, C. R. J. Stephenson, *Nat. Commun.* **2015**, *6*, 7919.
- [224] P. Püllmann, D. Homann, T. A. Karl, B. König, M. J. Weissenborn, *Angew. Chem. Int. Ed.* **2023**, *62*, e202307897.
- [225] K. P. Cole, J. J. Douglas, T. Hammerstad, C. R. J. Stephenson, *Org. Process Res. Dev.* **2023**, *27*, 399–408.
- [226] K. C. Harper, E.-X. Zhang, Z.-Q. Liu, T. Grieme, T. B. Towne, D. J. Mack, J. Griffin, S.-Y. Zheng, N.-N. Zhang, S. Gangula, J.-L. Yuan, R. Miller, P.-Z. Huang, J. Gage, M. Diwan, Y.-Y. Ku, *Org. Process Res. Dev.* **2022**, *26*, 404–412.
- [227] D. Ravelli, S. Protti, P. Neri, M. Fagnoni, A. Albini, *Green Chem.* **2011**, *13*, 1876–1884.
- [228] L. Buglioni, F. Raymenants, A. Slattery, S. D. A. Zondag, T. Noël, *Chem. Rev.* **2022**, *122*, 2752–2906.
- [229] S. B. Beil, S. Bonnet, C. Casadevall, R. J. Detz, F. Eisenreich, S. D. Glover, C. Kerzig, L. Næsborg, S. Pullen, G. Storch, N. Wei, C. Zeymer, *JACS Au* **2024**, *4*, 2746–2766.
- [230] S. Cañellas, M. Nuño, E. Speckmeier, *Nat. Commun.* **2024**, *15*, 307.
- [231] B. Pijper, L. M. Saavedra, M. Lanzi, M. Alonso, A. Fontana, M. Serrano, J. E. Gómez, A. W. Kleij, J. Alcázar, S. Cañellas, *JACS Au* **2024**, *4*, 2585–2595.
- [232] P. Kusuma, P. M. Pattison, B. Bugbee, *Hortic. Res.* **2020**, *7*, 56.
- [233] S. D. A. Zondag, D. Mazzarella, T. Noël, *Annu. Rev. Chem. Biomol. Eng.* **2023**, *14*, 283–300.
- [234] E. E. Callard-Langdon, A. Steven, R. J. Kahan, *ChemCatChem* **2023**, *15*, e202300537.
- [235] M. A. Green, *Prog. Photovolt: Res. Appl.* **2012**, *20*, 954–959.
- [236] M. Zhang, P. Roth, *Curr. Opin. Chem. Eng.* **2023**, *39*, 100897.
- [237] E. Kayahan, M. Jacobs, L. Braeken, L. C. Thomassen, S. Kuhn, T. van Gerven, M. E. Leblebici, *Beilstein J. Org. Chem.* **2020**, *16*, 2484–2504.
- [238] J. G. H. Hermens, M. L. Lepage, A. Kloekhorst, E. Keller, R. Bloem, M. Meijer, B. L. Feringa, *React. Chem. Eng.* **2022**, *7*, 2280–2284.
- [239] N. C. Neyt, D. L. Riley, *React. Chem. Eng.* **2021**, *6*, 1295–1326.
- [240] F. Wang, H. Duan, *Chem Catal.* **2022**, *2*, 644–646.
- [241] S. Mishra, B. Sundaram, *Mater. Today Proc.* **2024**, *102*, 393–409.
- [242] C. G. Bochet, *Chimia* **2019**, *73*, 720–723.
- [243] E. C. Constable, C. E. Housecroft, M. Neuburger, J. Schönle, J. A. Zampese, *Dalton Trans.* **2014**, *43*, 7227–7235.

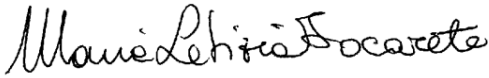
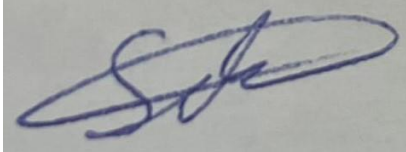
- [244] S. Sittel, A. C. Sell, K. Hofmann, C. Wiedemann, J. P. Nau, C. Kerzig, G. Manolikakes, K. Heinze, *ChemCatChem* **2023**, *15*, e202201562.
- [245] S. Sittel, D. Zorn, A. König, J. M. Grenz, C. Förster, R. Naumann, K. Heinze, *Chem. Eur. J.* **2025**, submitted.
- [246] S. Sittel, R. Naumann, C. Förster, M. E. Huber, J. Meyer, K. Heinze, *Inorg. Chem.* **2025**, submitted.
- [247] D. Kim, V. Q. Dang, T. S. Teets, *Chem. Sci.* **2024**, *15*, 77–94.
- [248] C. Russo, F. Brunelli, G. C. Tron, M. Giustiniano, *J. Org. Chem.* **2023**, *88*, 6284–6293.
- [249] S. Fukuzumi, K. Ohkubo, *Org. Biomol. Chem.* **2014**, *12*, 6059–6071.

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Authorization

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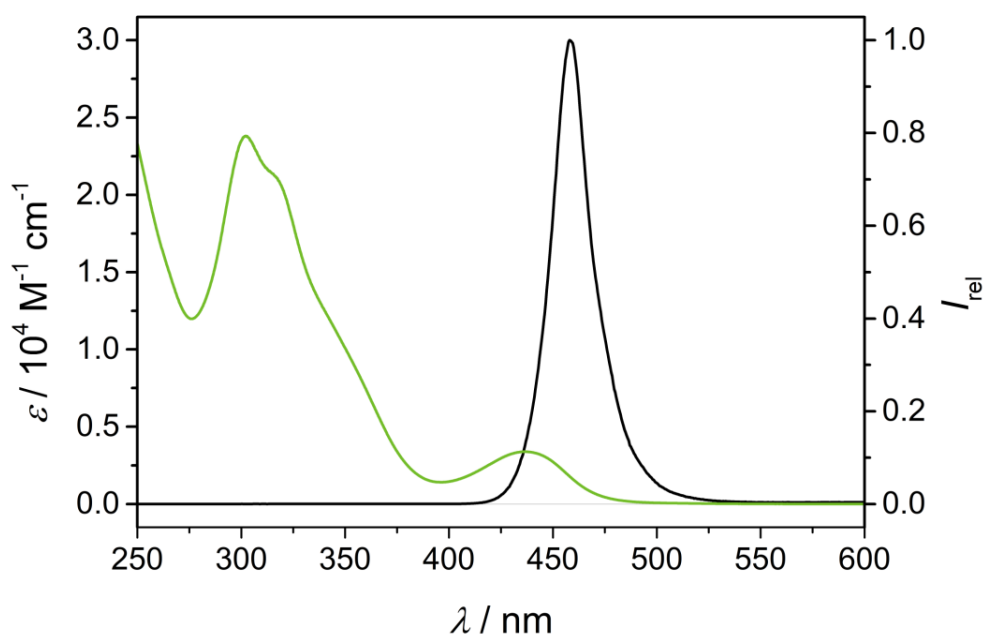
6.1 Supporting Information: Molecular Rubies in Photoredox Catalysis

Supplementary Material

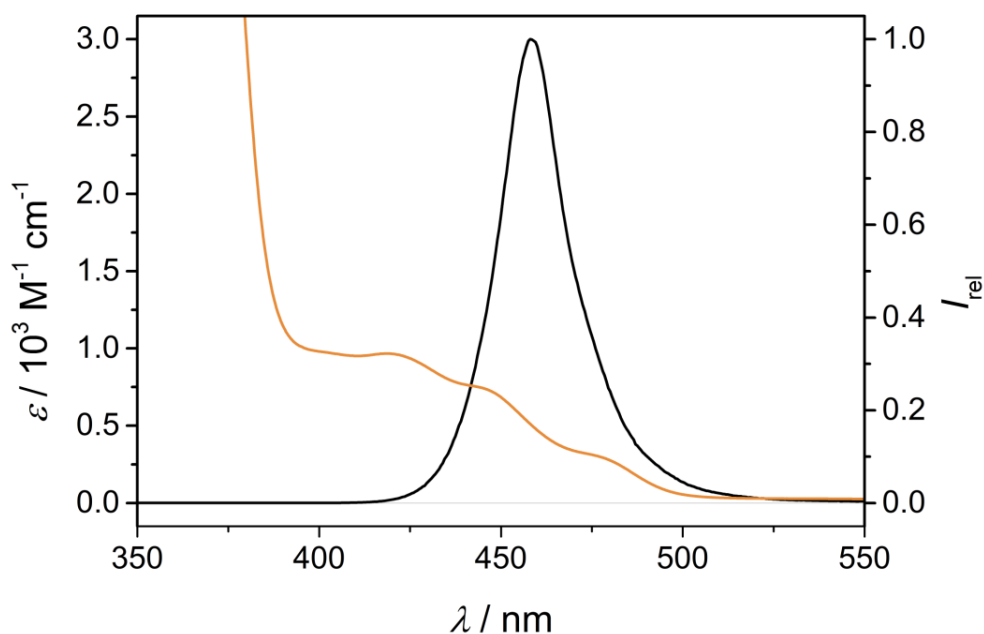
Static unrestricted Kohn-Sham orbitals Density Functional Theory Calculations were performed using the quantum computing suite ORCA 4.0.1 or 4.2.1.¹ Geometry optimization was performed using unrestricted Kohn-Sham orbitals DFT and the B3LYP functional² in combination with Ahlrichs' split-valence triple- ζ basis set def2-TZVPP for all atoms.^{3,4} Tight convergence criteria were chosen for DFT-UKS calculations (keywords *tightscf* and *tightopt*). All DFT-UKS 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 (*COSX*).^{5,6} The zero order relativistic approximation was used to describe relativistic effects in all calculations (keyword *ZORA*).^{7,8} Grimme's empirical dispersion correction D3(BJ) was employed (keyword *D3BJ*).^{9,10} To account for solvent effects, a conductor-like screening model (keyword *CPCM* acetonitrile) modeling acetonitrile was used in all calculations.¹¹ A numerical frequency calculation confirmed that the optimized geometry corresponds to a minimum structure. Explicit counter ions and/or solvent molecules were neglected.

Table 1. Cartesian coordinates of the DFT-optimized geometry of $^2[\text{Cr}(\text{tpe})_2]^{3+}$.

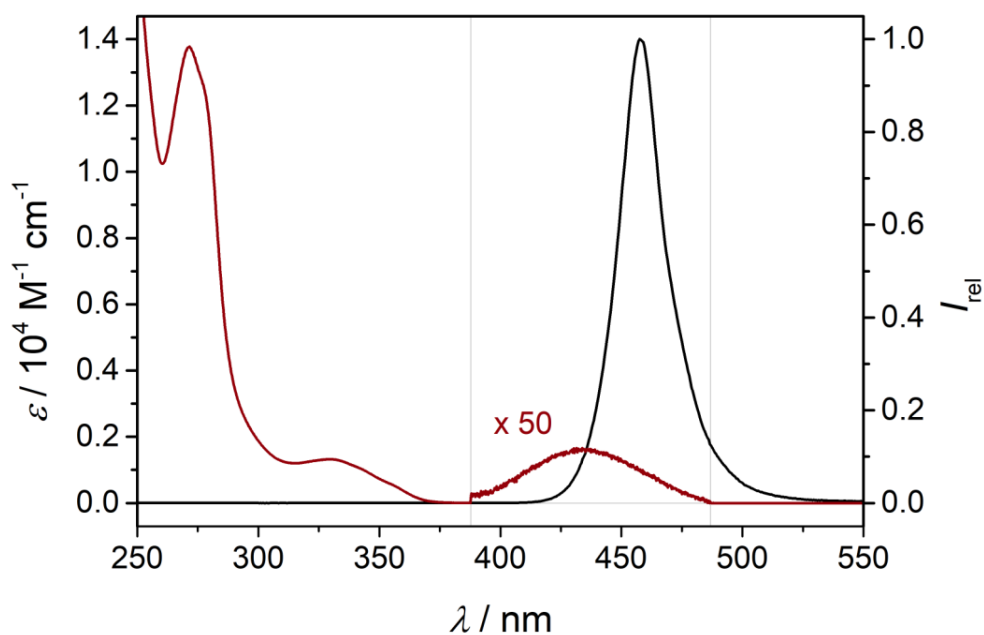
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7	0.062359835	-2.044531336	0.102885816
7	2.044921340	-0.050287185	0.127906904
7	-0.020940073	-0.000768895	2.047243369
6	-0.079570266	0.000681051	4.801326253
6	1.731309206	-1.741336056	1.902580068
6	4.164236534	0.744984198	-0.625736222
6	4.024408325	-0.889061171	1.119616290
6	4.792774220	-0.081350948	0.292805943
6	2.787047451	0.733882059	-0.675459833
6	0.798228954	-0.829842003	2.724118222
6	-0.914398178	0.848723048	4.090411545
6	-0.855388035	0.818215979	2.713956431
6	0.780674028	-0.842079227	4.111192335
6	2.582402438	-2.598976269	2.836705444
6	0.877028209	-2.645427978	0.991680281
6	0.925429936	-4.030273196	1.061321066
6	0.133698219	-4.794718417	0.215625970
6	-0.699835853	-4.161074170	-0.692799913
6	-0.707378217	-2.783152178	-0.717871272
6	2.640738409	-0.863447934	1.020763863
7	-0.062216957	2.044504348	-0.102405852
7	-2.045376961	0.050045880	-0.127178227
7	0.019710265	0.001600761	-2.046906283
6	0.075387120	-0.000693751	-4.801037322
6	-1.732482921	1.742226132	-1.900865005
6	-4.164446088	-0.744039087	0.628414917
6	-4.025406353	0.892164266	-1.114948946
6	-4.793446275	0.084358791	-0.287943862
6	-2.787173395	-0.734372077	0.676239311
6	-0.800239828	0.830443149	-2.723090031
6	0.911262273	-0.848249963	-4.090785144
6	0.853611058	-0.817307911	-2.714282404
6	-0.784235920	0.842139024	-4.110206478
6	-2.583875138	2.600237299	-2.834350076
6	-0.877184317	2.645893124	-0.990543079
6	-0.924883825	4.030770094	-1.060083849
6	-0.132113863	4.794744346	-0.214935923
6	0.701790105	4.160578331	0.692796209
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6	-2.641602026	0.864674037	-1.018405320



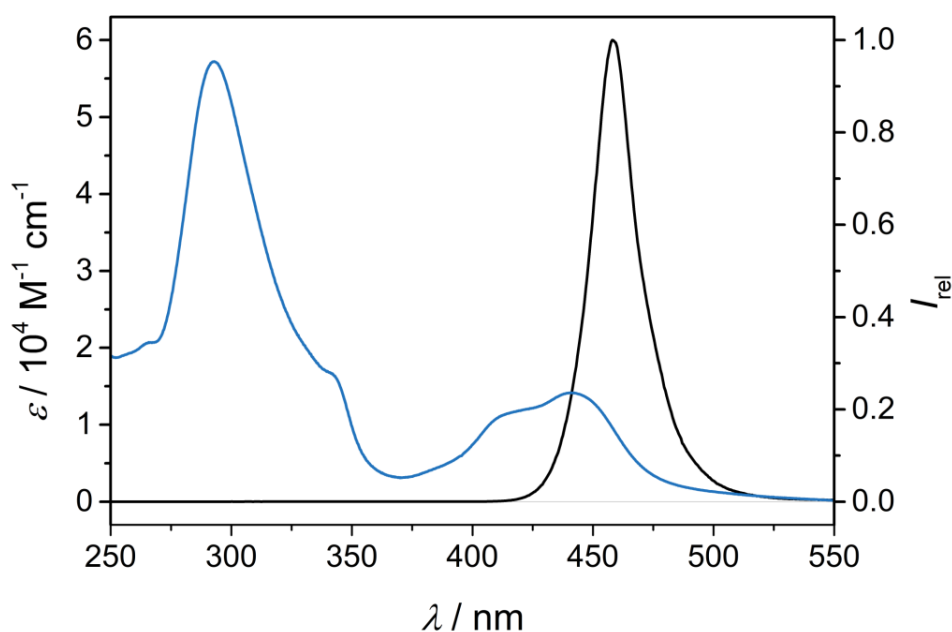
Supplementary Figure 1. UV/Vis spectrum of $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ (0.1 mM) in acetonitrile (green) and emission spectrum of the Aldrich[®] Micro Photochemical Reactor, blue LED lights (black).



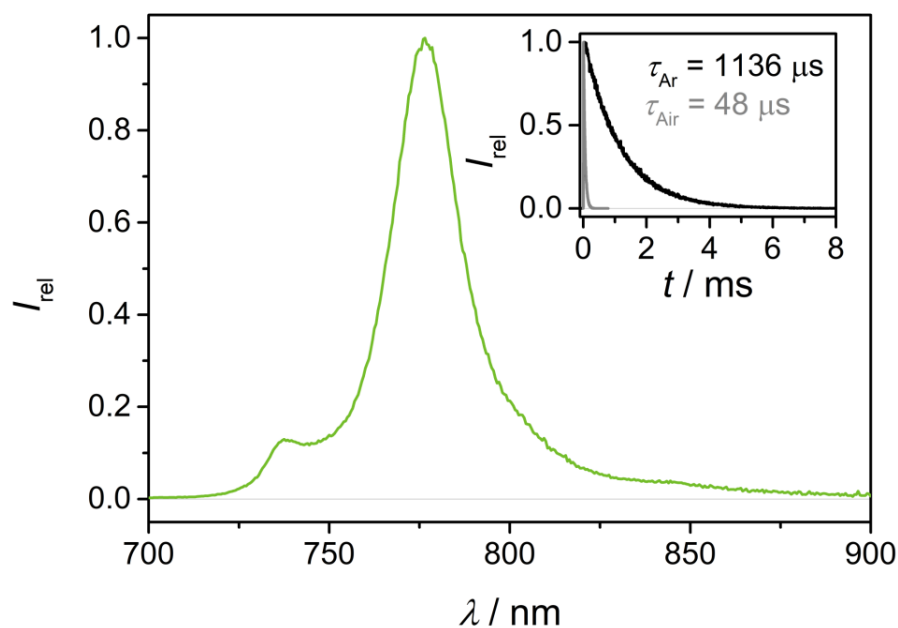
Supplementary Figure 2. UV/Vis spectrum of $[\text{Cr}(\text{dmcbpy})_3][\text{BF}_4]_3$ (1 mM) in acetonitrile (orange) and emission spectrum of the Aldrich[®] Micro Photochemical Reactor, blue LED lights (black).



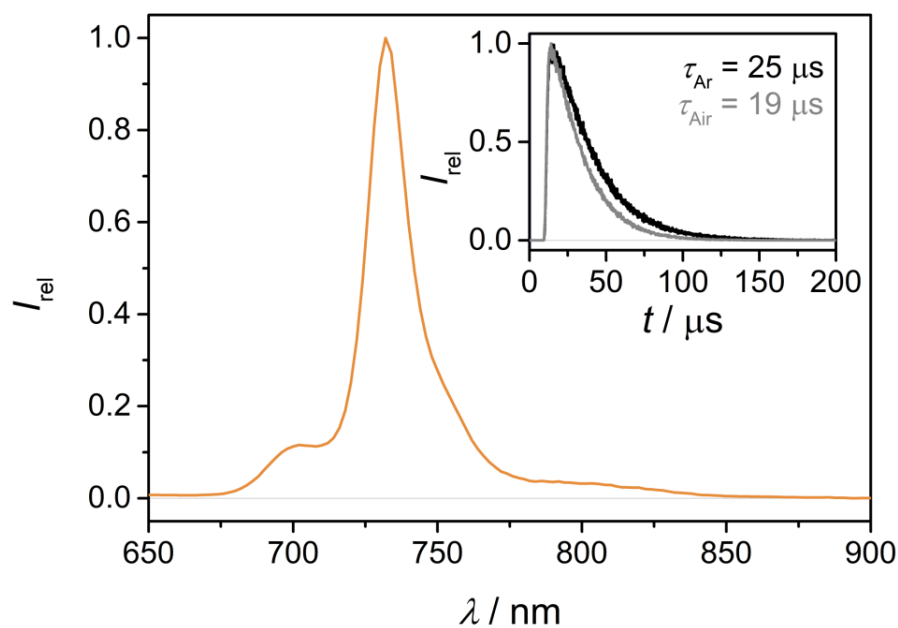
Supplementary Figure 3. UV/Vis spectrum of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (1 mM) in acetonitrile (red) and emission spectrum of the Aldrich® Micro Photochemical Reactor, blue LED lights (black).



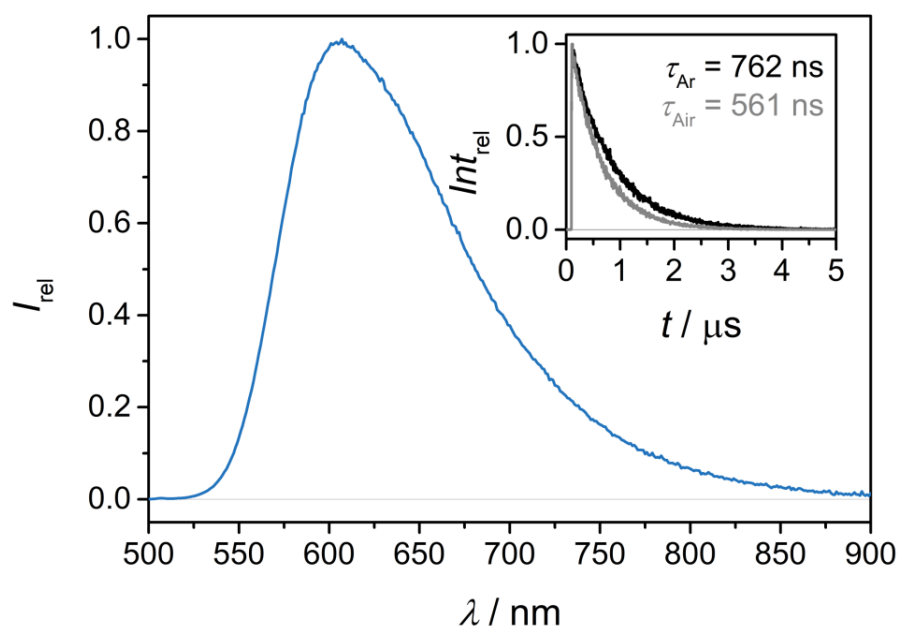
Supplementary Figure 4. UV/Vis spectrum of $[\text{Ru}(\text{bpz})_3][\text{PF}_6]_2$ (0.01 mM) in acetonitrile (blue) and emission spectrum of the Aldrich® Micro Photochemical Reactor, blue LED lights (black).



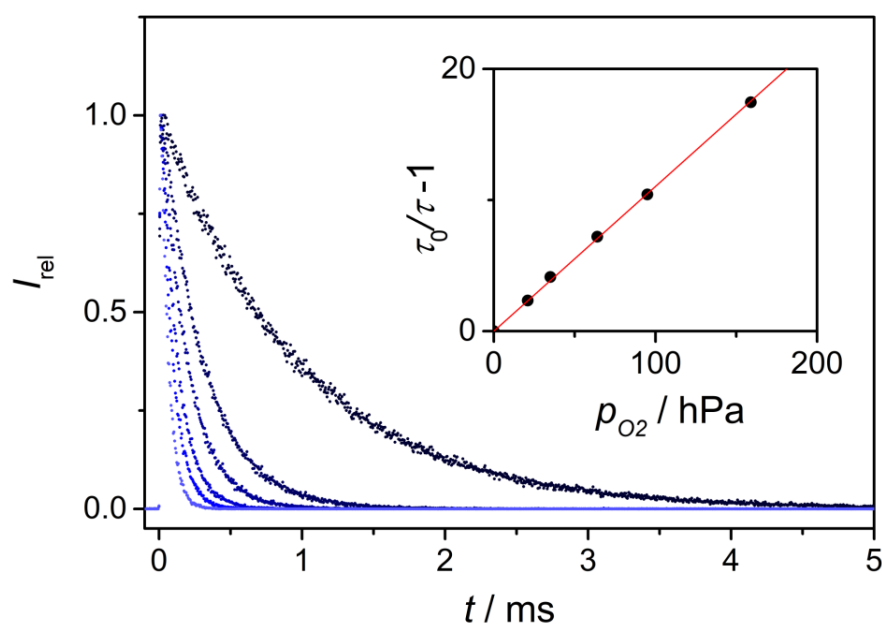
Supplementary Figure 5. Emission spectrum of $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ (0.1 mM) in acetonitrile after excitation at 435 nm. Inset: emission decay curves under deaerated (black) and aerated (grey) conditions.



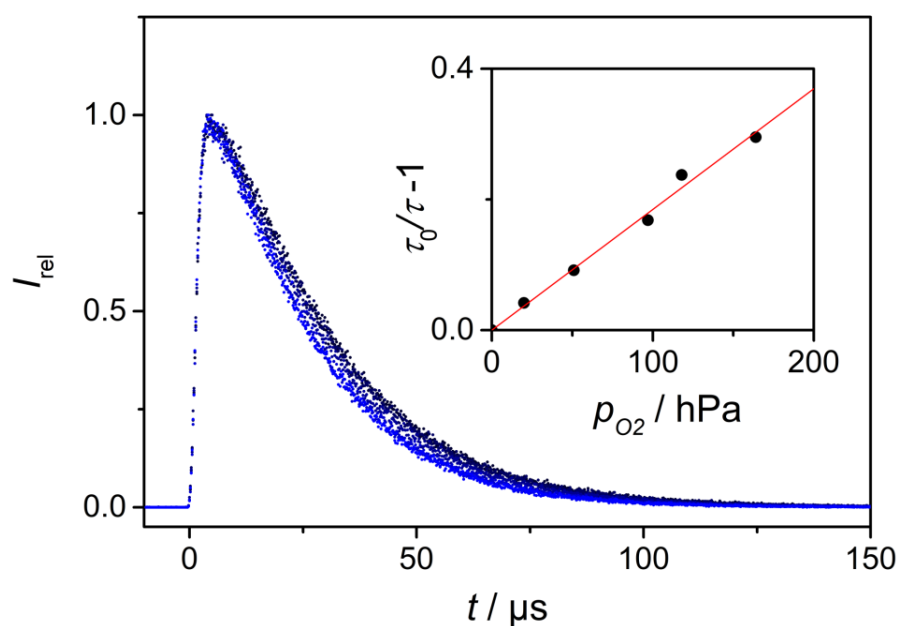
Supplementary Figure 6. Emission spectrum of $[\text{Cr}(\text{dmcipy})_3][\text{BF}_4]_3$ (1 mM) in acetonitrile after excitation at 480 nm. Inset: emission decay curves under deaerated (black) and aerated (grey) conditions.



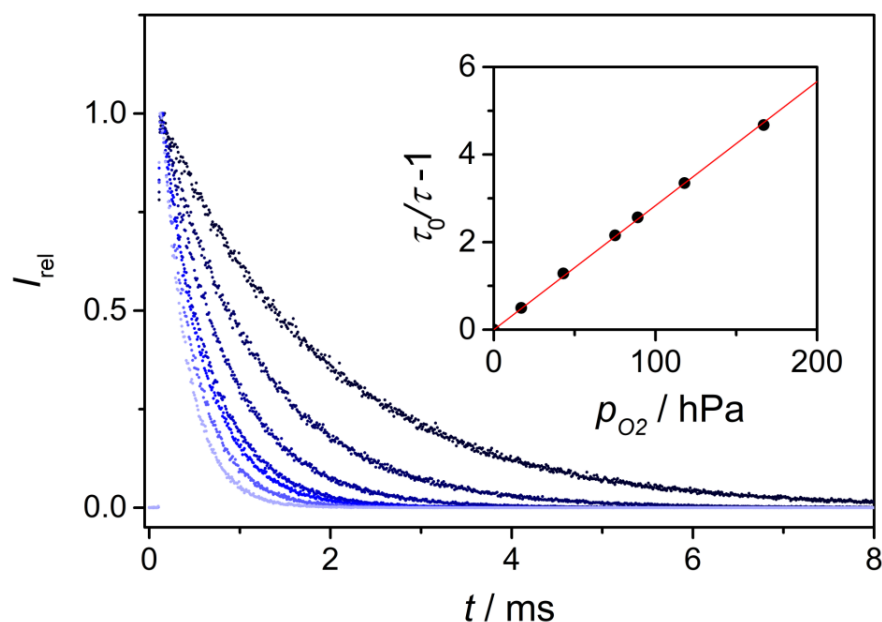
Supplementary Figure 7. Emission spectrum of $[\text{Ru}(\text{bpz})_3][\text{PF}_6]_2$ (0.01 mM) in acetonitrile after excitation at 440 nm. Inset: emission decay curves under deaerated (black) and aerated (grey) conditions.



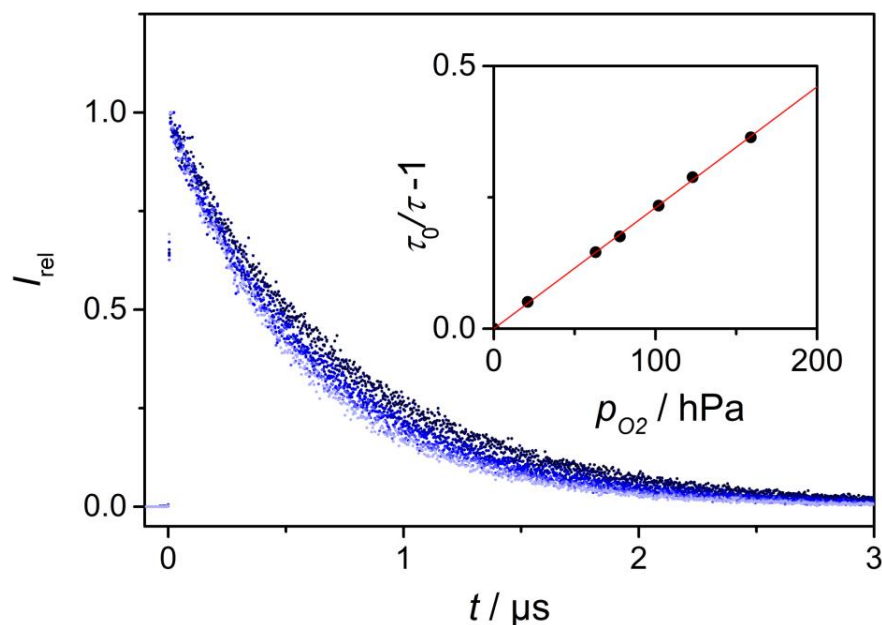
Supplementary Figure 8. Quenching of $[\text{Cr}(\text{ddpd})_2]^{3+}$ by oxygen. Main plot, emission decay traces recorded at 776 nm following excitation (435 nm, 2 μs pulse duration) of a $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ (0.1 mM) solution in deaerated acetonitrile with variable oxygen partial pressure p_{O_2} (0 hPa, 21 hPa, 35 hPa, 64 hPa, 95 hPa, 159 hPa). Inset, corresponding Stern-Volmer plot with best-fit function overlaid on the data.



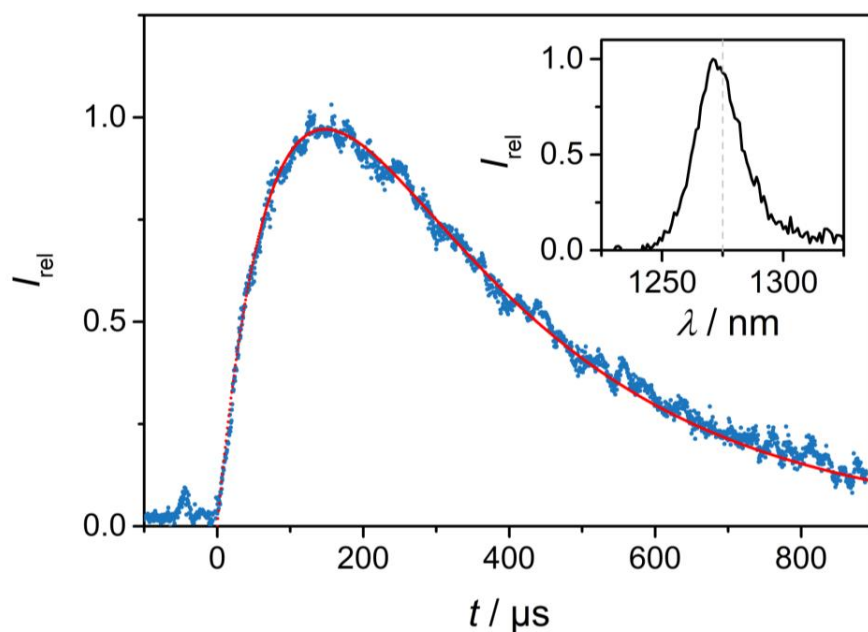
Supplementary Figure 9. Quenching of $[\text{Cr}(\text{dmcbpy})_3]^{3+}$ by oxygen. Main plot, emission decay traces recorded at 733 nm following excitation (480 nm, 2 μs pulse duration) of a $[\text{Cr}(\text{dmcbpy})_3][\text{BF}_4]_3$ (0.5 mM) solution in deaerated acetonitrile with variable oxygen partial pressure p_{O_2} (0 hPa, 20 hPa, 51 hPa, 97 hPa, 118 hPa, 164 hPa). Inset, corresponding Stern-Volmer plot with best-fit function overlaid on the data.



Supplementary Figure 10. Quenching of $[\text{Cr}(\text{tpe})_2]^{3+}$ by oxygen. Main plot, emission decay traces recorded at 742 nm following excitation (435 nm, 2 μs pulse duration) of a $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (1 mM) solution in deaerated acetonitrile with variable oxygen partial pressure p_{O_2} (0 hPa, 17 hPa, 43 hPa, 75 hPa, 89 hPa, 118 hPa, 167 hPa). Inset, corresponding Stern-Volmer plot with best-fit function overlaid on the data.



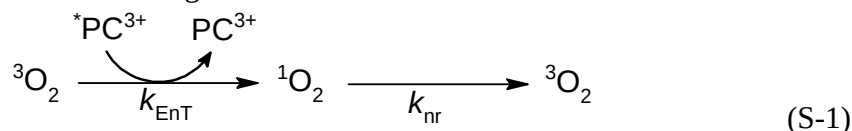
Supplementary Figure 11. Quenching of $^*[\text{Ru}(\text{bpz})_3]^{2+}$ by oxygen. Main plot, emission decay traces recorded at 606 nm following laser excitation (440 nm) of a $[\text{Ru}(\text{bpz})_3][\text{PF}_6]_2$ (0.01 mM) solution in deaerated acetonitrile with variable oxygen partial pressure p_{O_2} (0 hPa, 21 hPa, 63 hPa, 78 hPa, 102 hPa, 123 hPa, 159 hPa). Inset, corresponding Stern-Volmer plot with best-fit function overlaid on the data.



Supplementary Figure 12. $^1\text{O}_2$ emission upon excitation of 1 mM $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ in air-saturated acetonitrile with a xenon-lamp at 355 nm. Main plot, decay trace of the emission at 1275 nm (blue) with the best-fit function (red dots) overlaid on the data. Inset, corresponding emission spectrum. For further explanations, see text.

Kinetic modeling of the $^1\text{O}_2$ decay trace (Supplementary Figure 12)

$^1\text{O}_2$ forms via Dexter energy transfer from $^*\text{PC}^{3+}$ to $^3\text{O}_2$ and decays mainly via non-radiative relaxation with the radiative relaxation neglected:



The processes follow second- (pseudo-first-order with $[^3\text{O}_2]$ constant) and first-order kinetics, respectively, so that the rate law for the $^1\text{O}_2$ concentration $[^1\text{O}_2]$ can be written as:

$$\frac{d[^1\text{O}_2]}{dt} = k_{\text{EnT}}[^3\text{O}_2][^*\text{PC}^{3+}] - k_{\text{nr}}[^1\text{O}_2] \quad (\text{S-2})$$

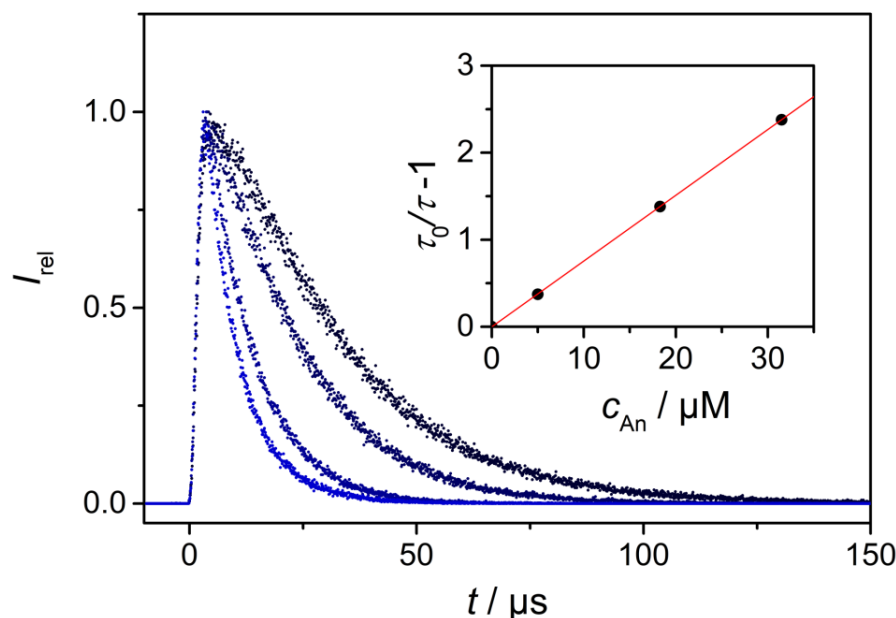
For the first-order decay of the emissive $^*\text{PC}^{3+}$ with the rate constant k_{lum} and the initial concentration $[^*\text{PC}^{3+}]_0$ the integrated rate law equals:

$$[^*\text{PC}^{3+}] = [^*\text{PC}^{3+}]_0 e^{-k_{\text{lum}}t} \quad (\text{S-3})$$

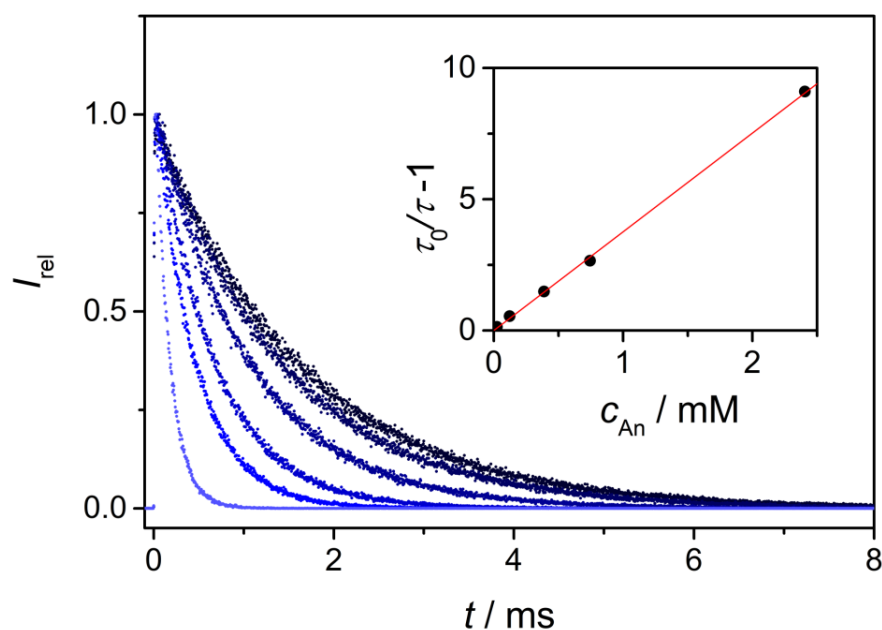
Insertion of S-3 into S-2 and subsequent integration gives the integrated rate law of $[^1\text{O}_2]$:

$$[^1\text{O}_2] = \left(\frac{[^*\text{PC}^{3+}]_0 \cdot k_{\text{EnT}} \cdot [^3\text{O}_2]}{k_{\text{lum}} + k_{\text{EnT}} \cdot [^3\text{O}_2] - k_{\text{nr}}} \right) \cdot (e^{-k_{\text{nr}}t} - e^{-(k_{\text{lum}} + k_{\text{EnT}} \cdot [^3\text{O}_2])t}) \quad (\text{S-4})$$

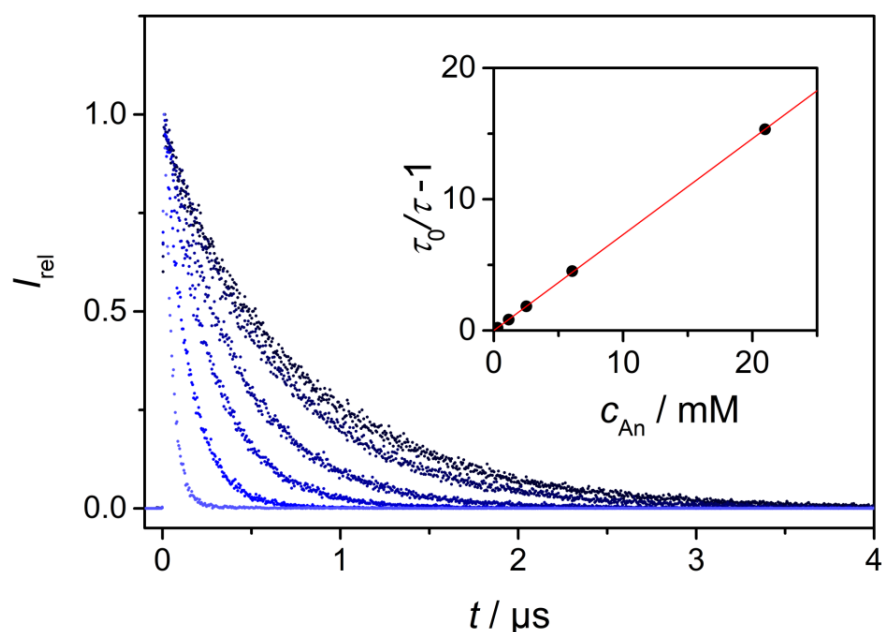
The constants $k_{\text{EnT}} [^3\text{O}_2]$ and $(k_{\text{lum}} + k_{\text{EnT}} [^3\text{O}_2])$ can be calculated from the independently determined lifetimes of $^*[\text{Cr}(\text{tpe})_2]^{3+}$ in deaerated (1965 μs) and air-saturated acetonitrile (304 μs). As k_{nr} is known from the literature¹² ($k_{\text{nr}} = 1.2 \times 10^4 \text{ s}^{-1}$) the scaling factor $[^*\text{PC}^{3+}]_0$ remains as the only degree of freedom in the fit overlapped on the data in Supplementary Figure 12.



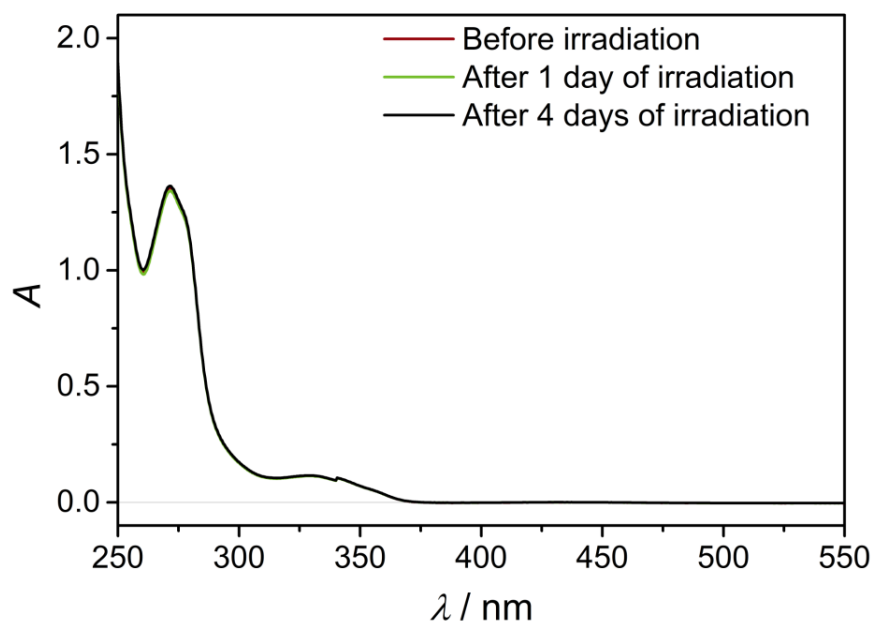
Supplementary Figure 13. Reductive quenching of $^*[\text{Cr}(\text{dmcbpy})_3]^{3+}$ by $t\text{An}$. Main plot, emission decay traces recorded at 733 nm following excitation (480 nm, 2 μs pulse duration) of a $[\text{Cr}(\text{dmcbpy})_3][\text{BF}_4]_3$ (0.5 mM) solution in deaerated acetonitrile with variable amounts of $t\text{An}$ (0 mM, 5.0 mM, 18.3 mM, 31.5 mM). Inset, corresponding Stern-Volmer plot with best-fit function overlaid on the data.



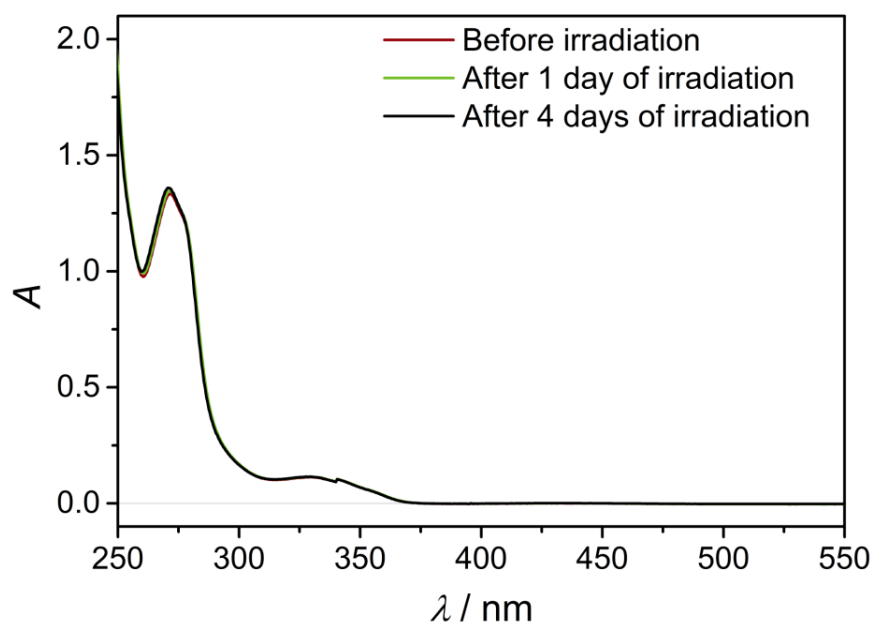
Supplementary Figure 14. Reductive quenching of $^*\text{[Cr(tpe)}_2\text{]}^{3+}$ by $t\text{An}$. Main plot, emission decay traces recorded at 742 nm following excitation (435 nm, 2 μs pulse duration) of a $[\text{Cr(tpe)}_2][\text{BF}_4]_3$ (1 mM) solution in deaerated acetonitrile with variable amounts of $t\text{An}$ (0 mM, 0.02 mM, 0.12 mM, 0.39 mM, 0.74 mM, 2.41 mM). Inset, corresponding Stern-Volmer plot with best-fit function overlaid on the data.



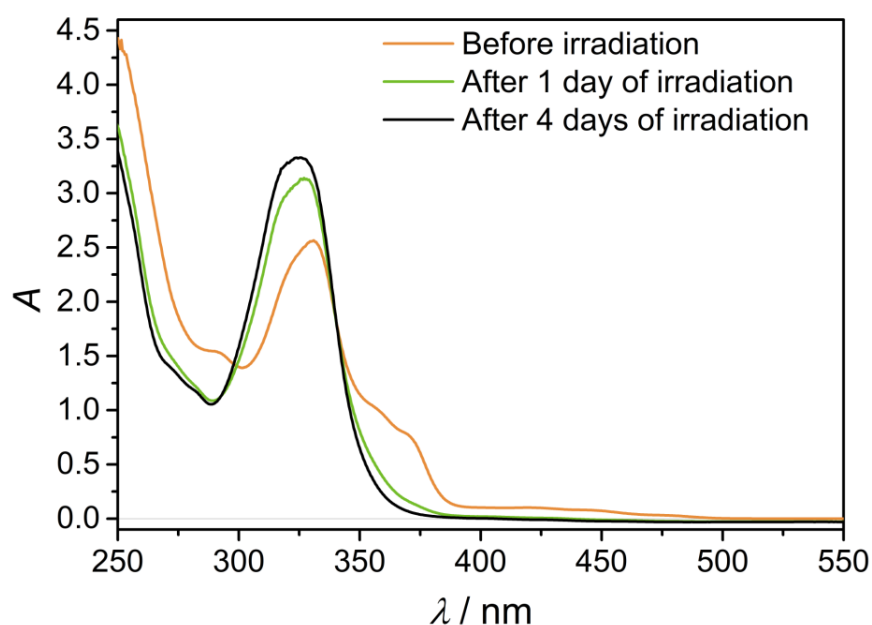
Supplementary Figure 15. Reductive quenching of $^*\text{[Ru(bpz)}_3\text{]}^{2+}$ by $t\text{An}$. Main plot, emission decay traces recorded at 606 nm following laser excitation (440 nm) of a $[\text{Ru(bpz)}_3][\text{PF}_6]_2$ (0.01 mM) solution in deaerated acetonitrile with variable amounts of $t\text{An}$ (0 mM, 0.3 mM, 1.2 mM, 2.5 mM, 6.1 mM, 21 mM). Inset, corresponding Stern-Volmer plot with best-fit function overlaid on the data.



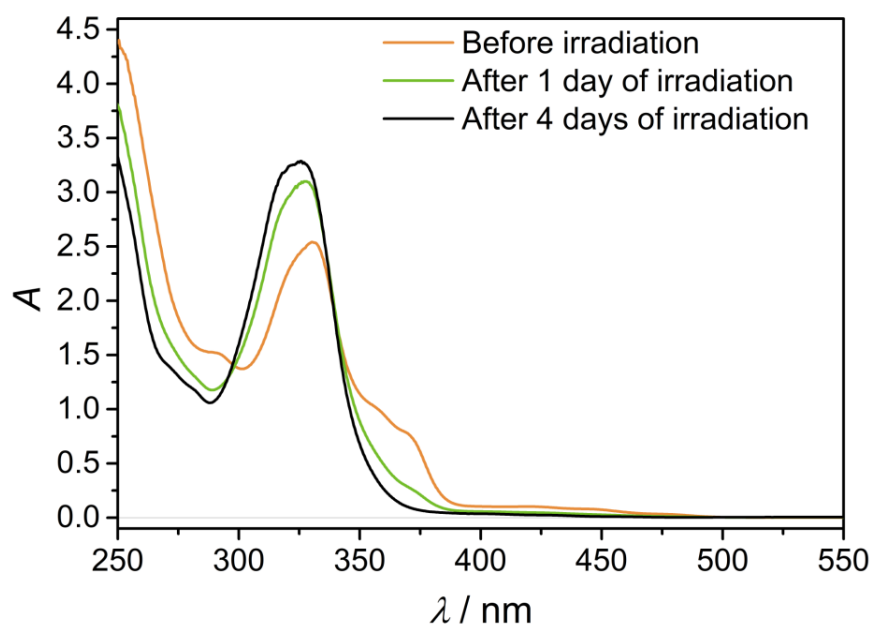
Supplementary Figure 16. UV/Vis spectra of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ in deaerated acetonitrile before (red), after 1 day (green) and after 4 days (black) of irradiation (460 nm).



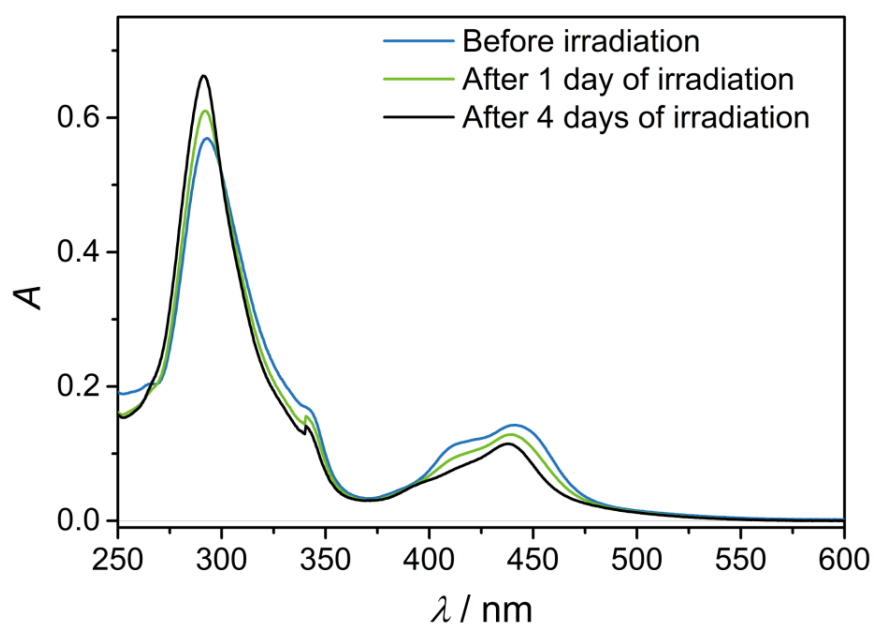
Supplementary Figure 17. UV/Vis spectra of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ in aerated acetonitrile before (red), after 1 day (green) and after 4 days (black) of irradiation (460 nm).



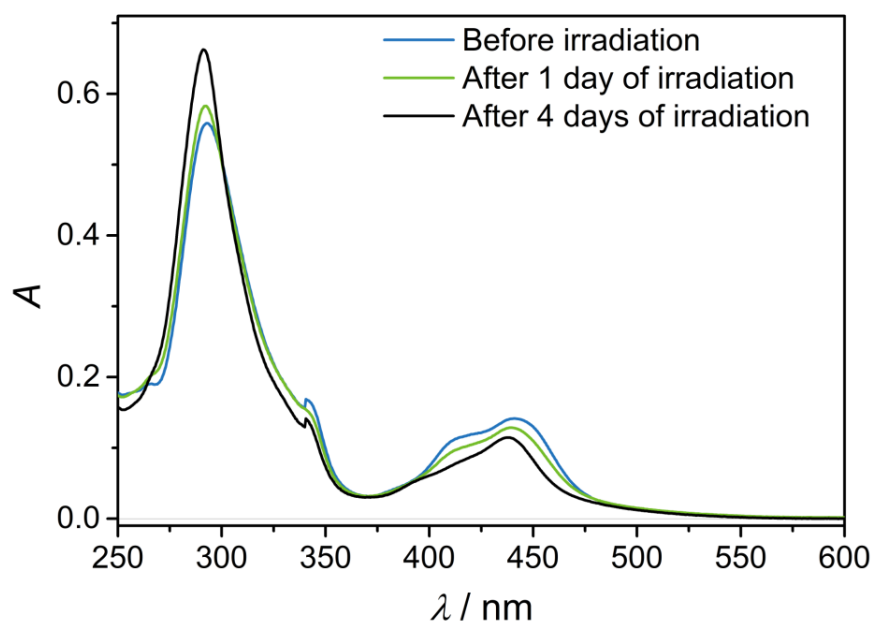
Supplementary Figure 18. UV/Vis spectra of $[\text{Cr}(\text{dmcbpy})_3][\text{BF}_4]_3$ in deaerated acetonitrile before (orange), after 1 day (green) and after 4 days (black) of irradiation (460 nm).



Supplementary Figure 19. UV/Vis spectra of $[\text{Cr}(\text{dmcbpy})_3][\text{BF}_4]_3$ in aerated acetonitrile before (orange), after 1 day (green) and after 4 days (black) of irradiation (460 nm).

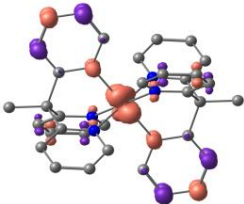
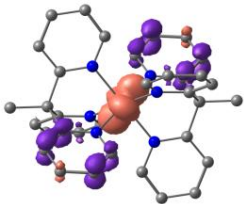
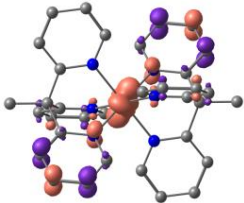
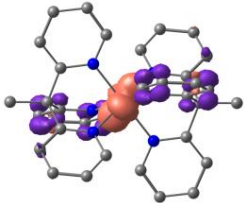
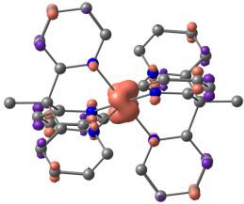
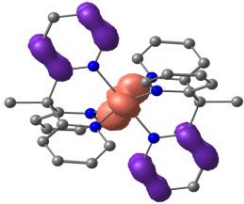
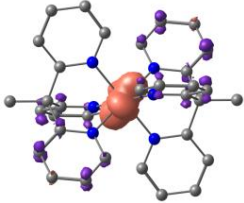
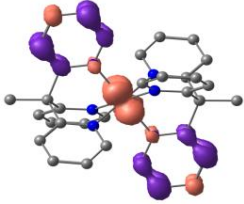
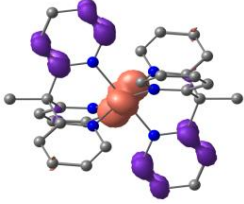


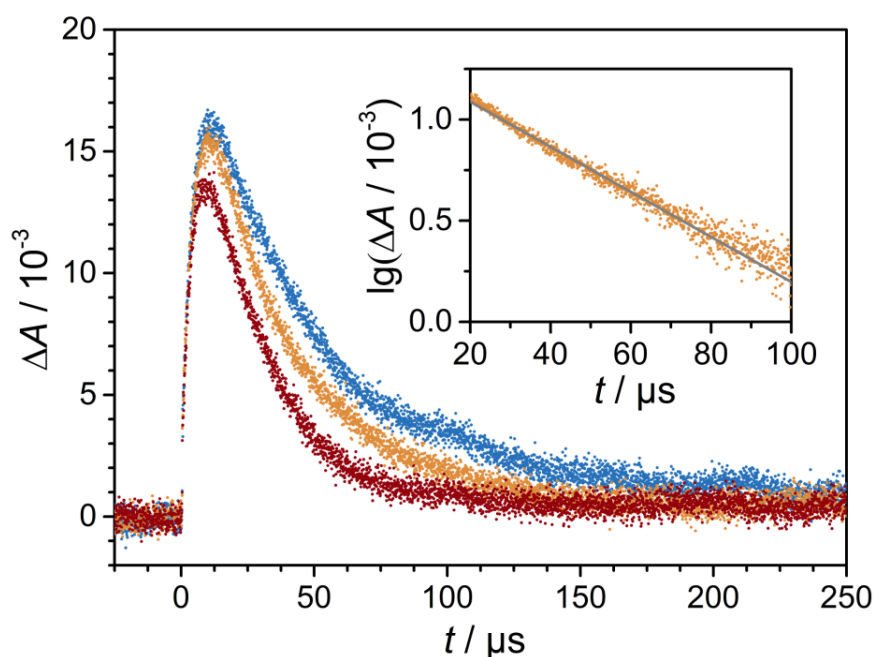
Supplementary Figure 20. UV/Vis spectra of $[\text{Ru}(\text{bpz})_3][\text{PF}_6]_2$ in deaerated acetonitrile before (blue), after 1 day (green) and after 4 days (black) of irradiation (460 nm).



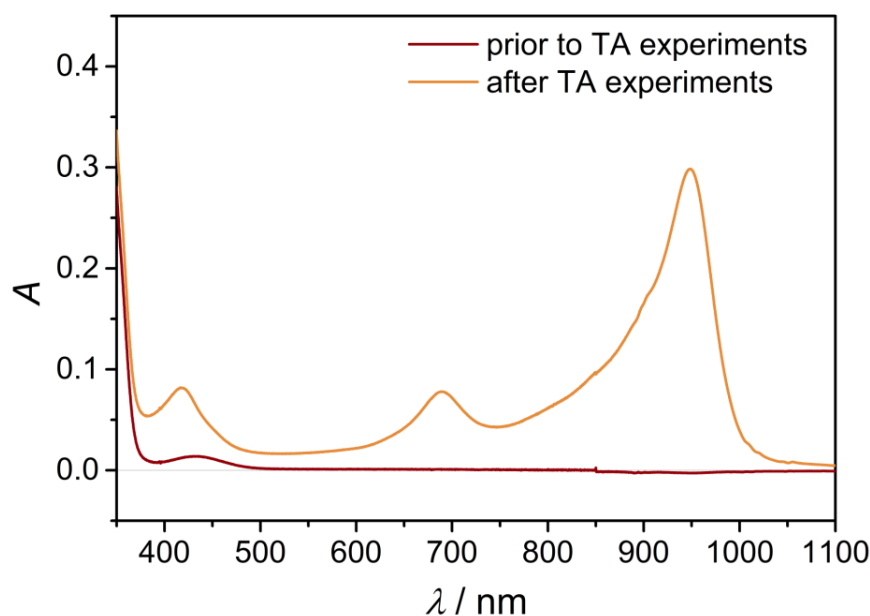
Supplementary Figure 21. UV/Vis spectra of $[\text{Ru}(\text{bpz})_3][\text{PF}_6]_2$ in aerated acetonitrile before (blue), after 1 day (green) and after 4 days (black) of irradiation (460 nm).

Supplementary Table 2. TD-DFT (CPCM(acetonitrile)-UB3LYP-D3BJ-ZORA/def2-TZVPP) calculated lowest-energy spin-allowed transitions for the quartet ground state¹³ and the lowest doublet state. Hydrogen atoms omitted. Difference electron densities plotted with an isosurface value of 0.004 a.u.; purple = electron depletion; orange = electron gain. Transition dipole moments given in parentheses. Other low-energy transitions possess oscillator strengths below 10^{-8} , and hence these are not given.

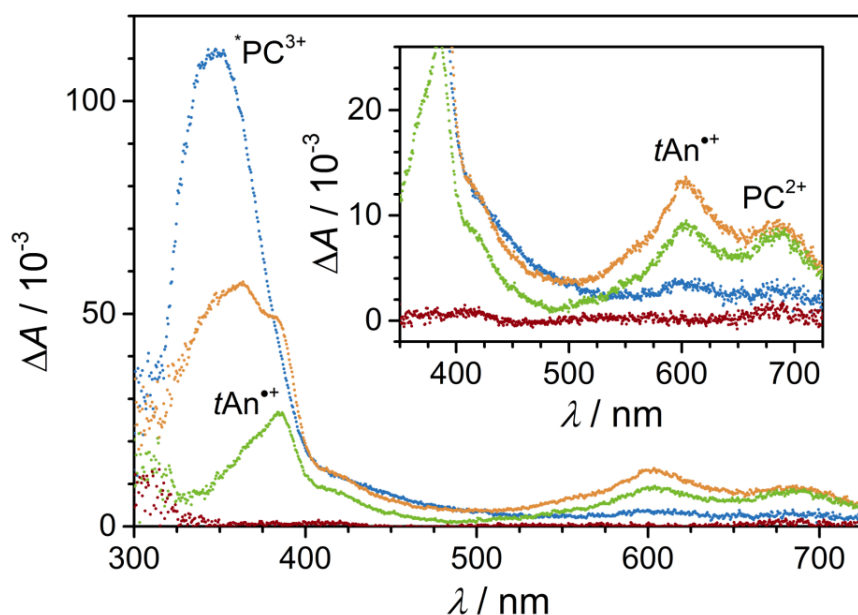
quartet ground state: transitions with LMCT/ILCT character			lowest doublet state: transitions with LMCT/ILCT character		
#7	326 nm (0.0044)		#9	375 nm (0.0016)	
#8	326 nm (0.0043)		#10	373 nm (0.0034)	
#9	322 nm (0.0027)		#13	372 nm (0.0021)	
			#14	345 nm ($<<0.001$)	
			#15	345 nm (0.0045)	
			#16	345 nm ($<<0.001$)	



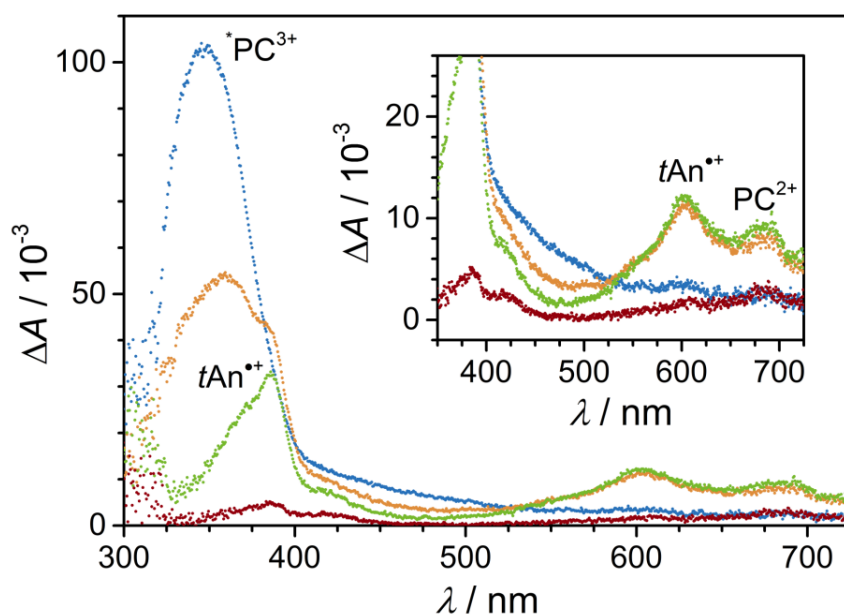
Supplementary Figure 22. Repeated (eight times) measurement of the decay of $t\text{An}^{\bullet+}$ (detection at 606 nm) following laser excitation at 355 nm of a $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (0.35 mM) solution in *deaerated* acetonitrile quenched by 0.1 M $t\text{An}$. Main plot, experimental decay traces for the first (blue), the third (orange) and the eighth (red) iteration. Inset: corresponding linearization of a first-order process for the third iteration (orange) with best-fit function (gray line) overlaid on the data.



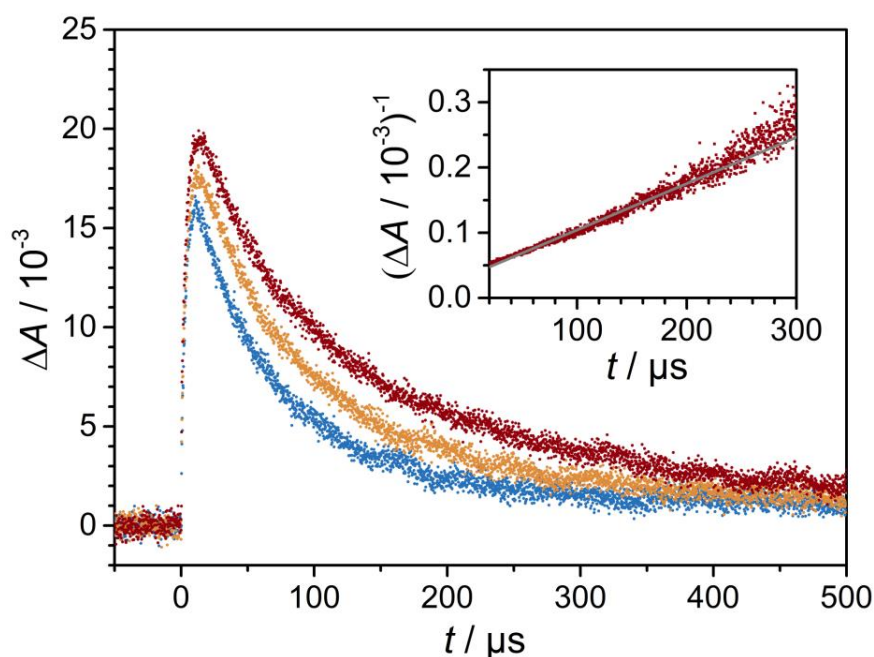
Supplementary Figure 23. UV/Vis/NIR spectrum of the solution (Figure 22) prior to (red) and after (orange) TA experiments.



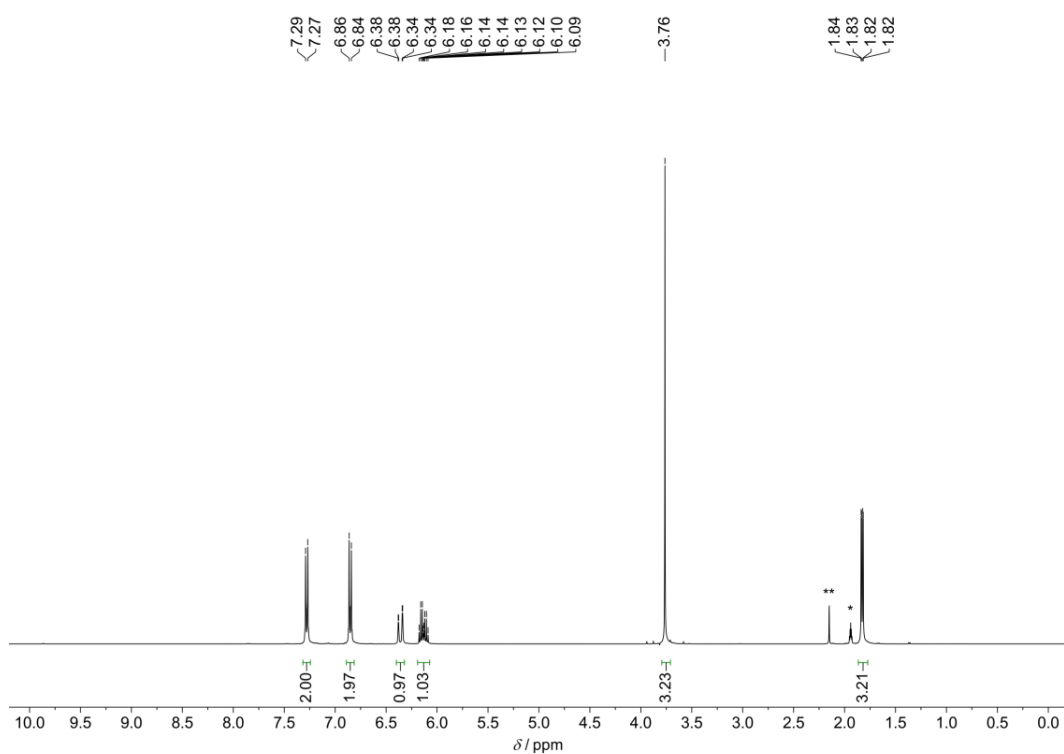
Supplementary Figure 24. ns-TA spectra illustrating the evolution and the decay of $^*\text{PC}^{3+}$ (345 nm), $t\text{An}^{\bullet+}$ (385 nm, 606 nm) and PC^{2+} (690 nm) following laser excitation at 355 nm of a $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (0.35 mM) solution in *deaerated* acetonitrile with 0.1 M $t\text{An}$ and 0.5 M **DMB**. The transient absorption spectra are time-integrated over 100 ns and taken at a time delay of 50 ns (blue), 5 μs (orange), 50 μs (green) and 500 μs (red) relative to the excitation pulse.



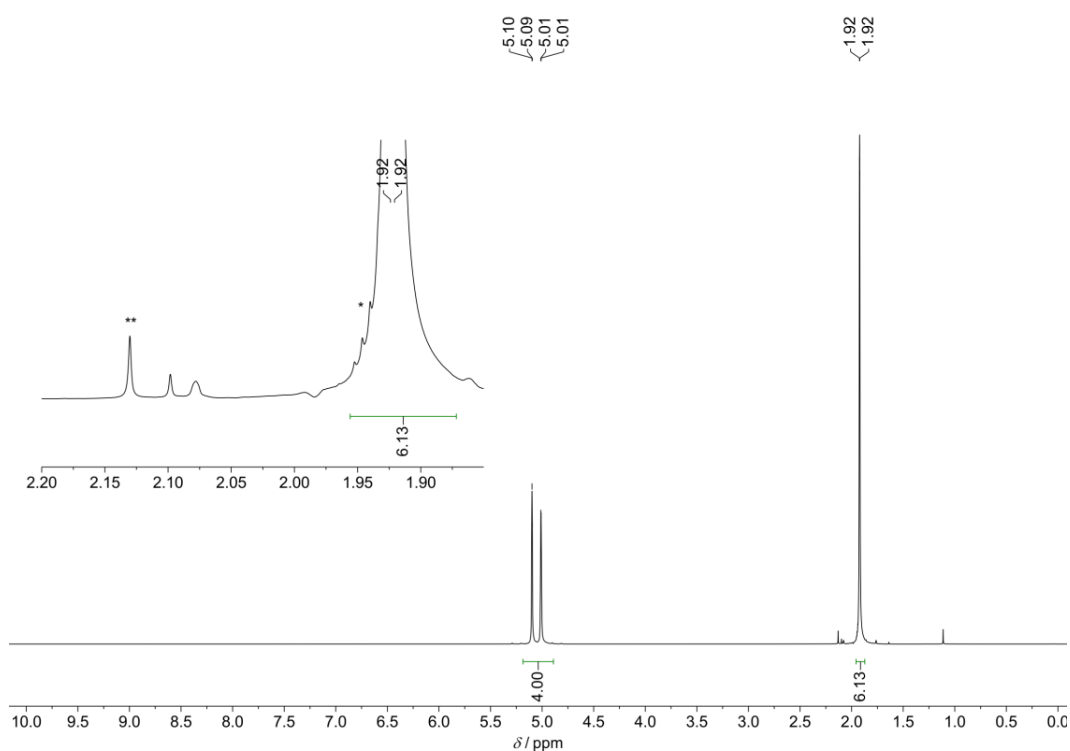
Supplementary Figure 25. ns-TA spectra illustrating the evolution and the decay of $^*\text{PC}^{3+}$ (345 nm), $t\text{An}^{\bullet+}$ (385 nm, 606 nm) and PC^{2+} (690 nm) following laser excitation at 355 nm of a $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (0.35 mM) solution in *air-saturated* acetonitrile with 0.1 M $t\text{An}$ and 0.5 M **DMB**. The transient absorption spectra are time-integrated over 100 ns and taken at a time delay of 50 ns (blue), 5 μs (orange), 50 μs (green) and 500 μs (red) relative to the excitation pulse.



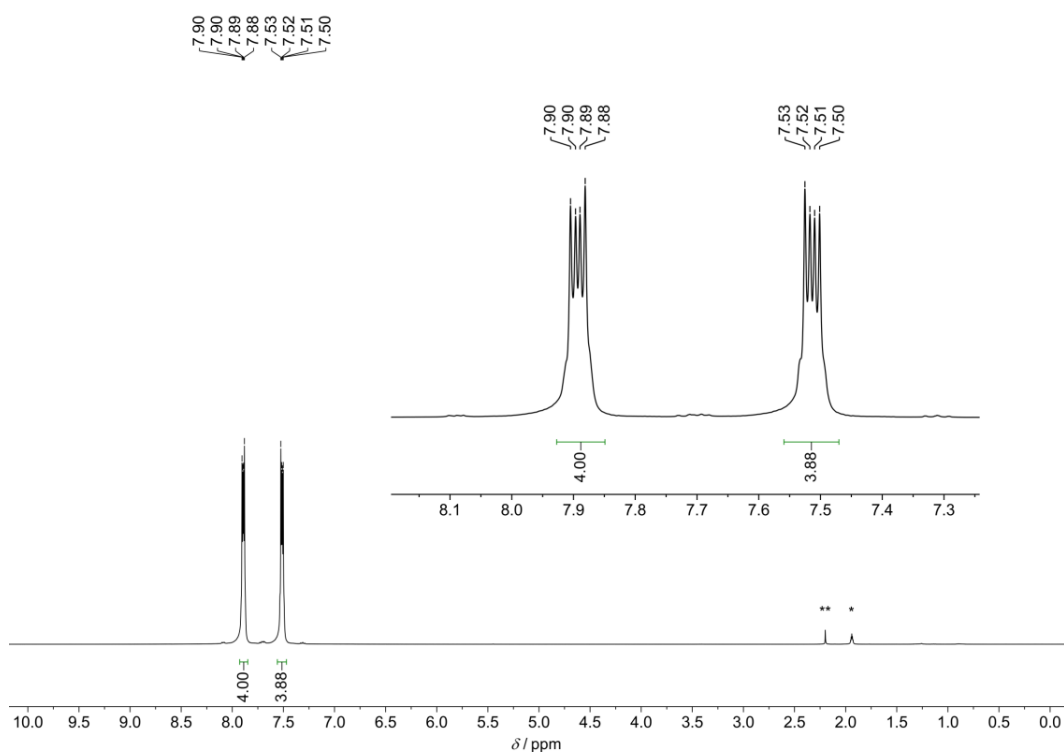
Supplementary Figure 26. Repeated (eight times) measurement of the decay of $t\text{An}^{\bullet+}$ (detection at 606 nm) following laser excitation at 355 nm of a $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (0.35 mM) solution in *air-saturated* acetonitrile quenched by 0.1 M $t\text{An}$. Main plot, experimental decay traces for the first (blue), the third (orange) and the eighth (red) iteration. Inset: corresponding linearization of a second-order process for the eighth iteration (red) with best-fit function (gray line) overlaid on the data.



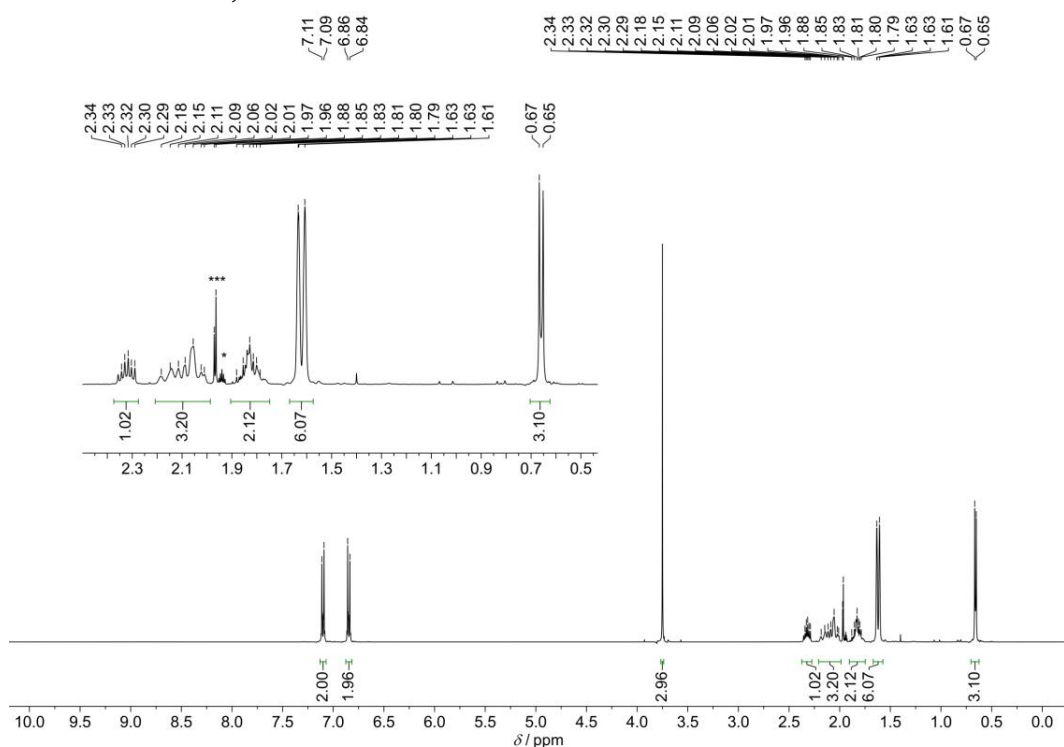
Supplementary Figure 27. ^1H NMR spectrum of **tAn** in CD_3CN . * denotes acetonitrile solvent resonance, ** denotes water resonance.



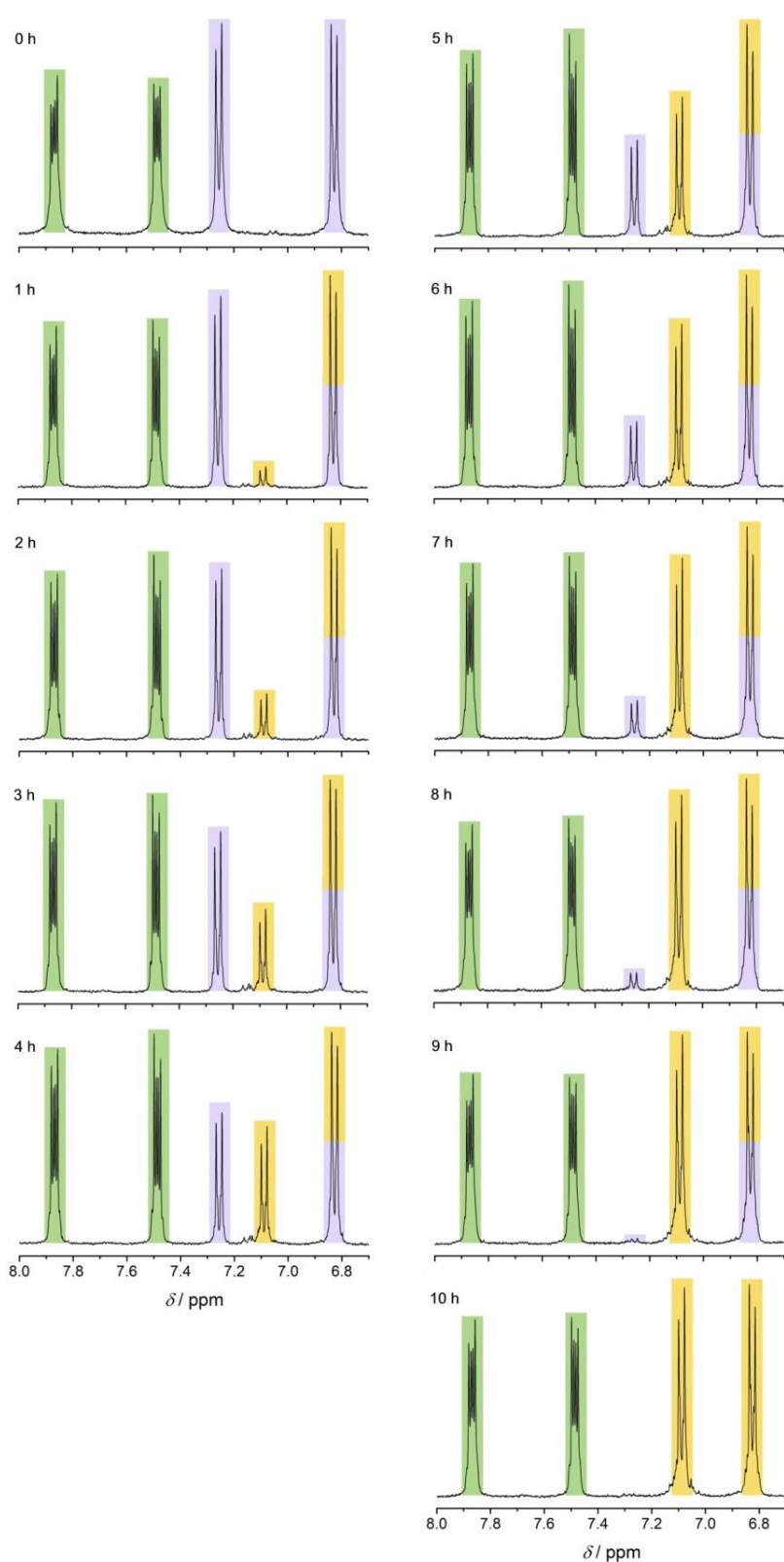
Supplementary Figure 28. ^1H NMR spectrum of **DMB** in CD_3CN . * denotes acetonitrile solvent resonance, ** denotes water resonance.



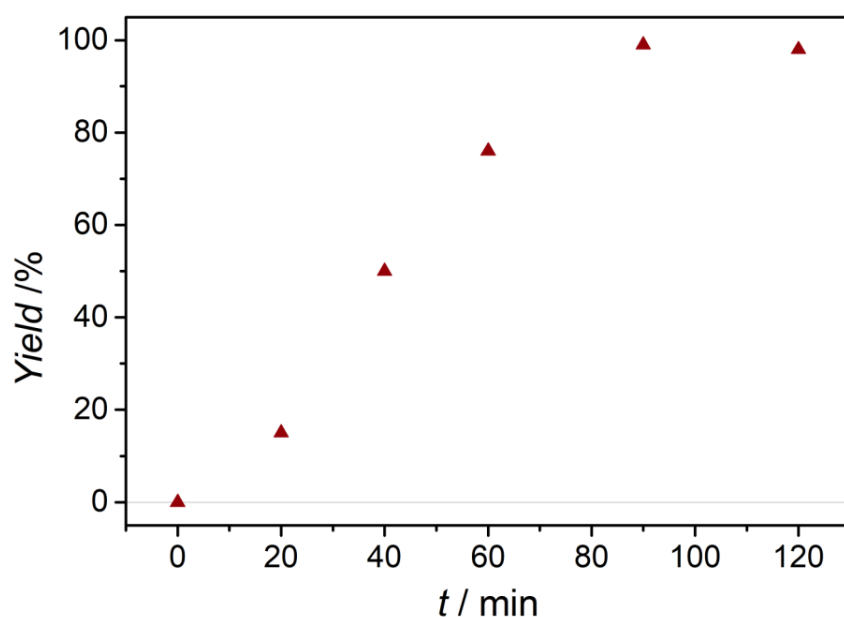
Supplementary Figure 29. ^1H NMR spectrum of **naphthalene** in CD_3CN . * denotes acetonitrile solvent resonance, ** denotes water resonance.



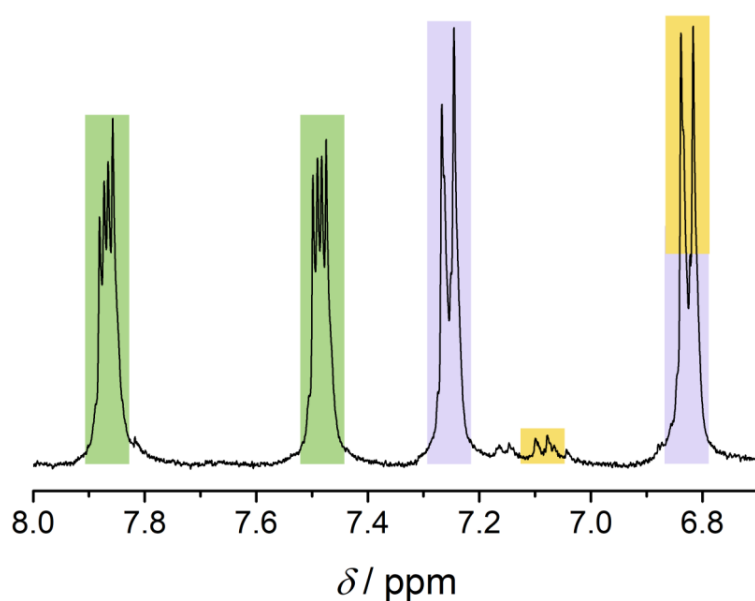
Supplementary Figure 30. ^1H NMR spectrum of the isolated product **DAP** in CD_3CN . * denotes acetonitrile solvent resonance, *** denotes a resonance of an unknown impurity.



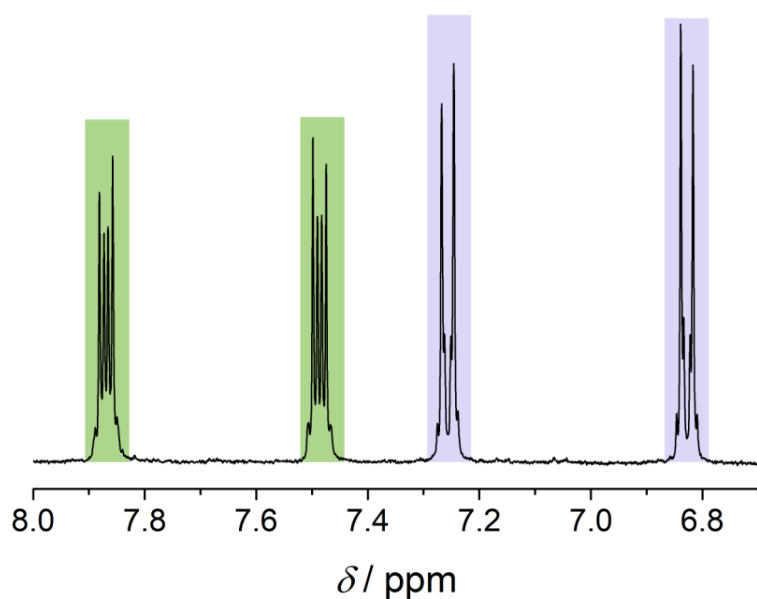
Supplementary Figure 31. Exemplary partial ^1H NMR spectra of the reaction using 100 mM *t*An (purple), 500 mM DMB and 0.2 mM $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ in acetonitrile with naphthalene (green) as internal standard with 460 nm light excitation. Product resonances of DAP highlighted in yellow.



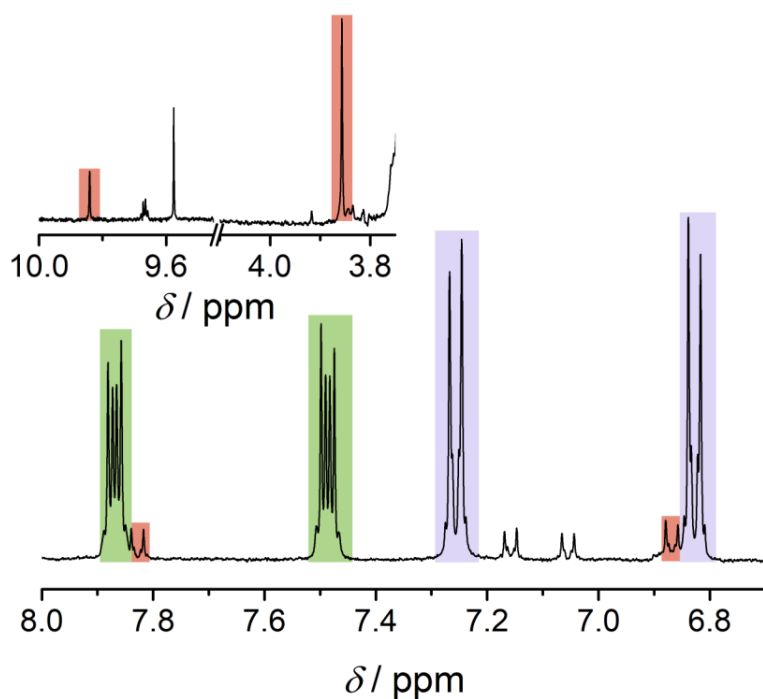
Supplementary Figure 32. Conversion vs. times plot of the photoredox catalyzed radical cation Diels–Alder cycloaddition of 100 mM **tAn** and 500 mM **DMB** using $[\text{Cr}(\text{tpe})_2]^{3+}$ (5 mM) in CH_3CN with 460 nm light excitation.



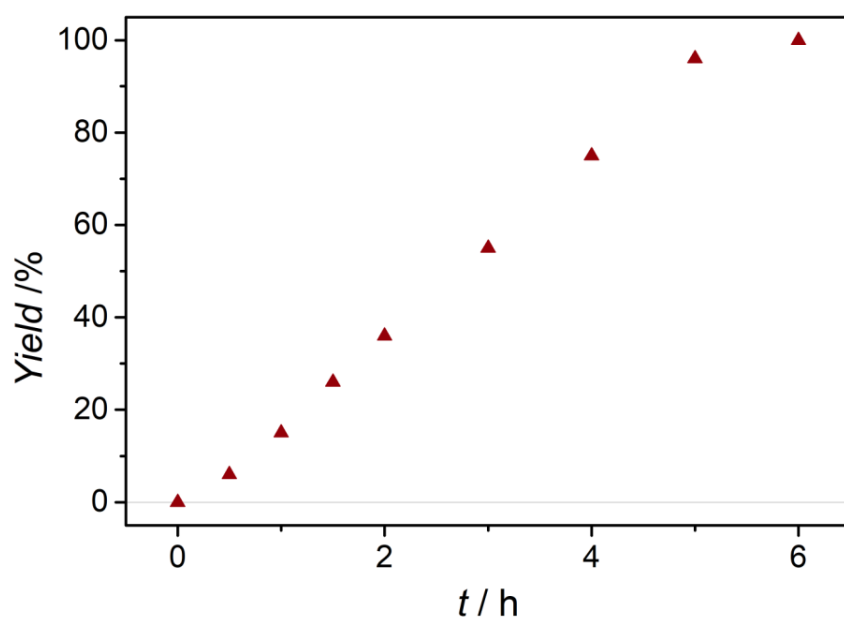
Supplementary Figure 33. Partial ^1H NMR spectrum of the reaction mixture 100 mM **tAn** (purple), 500 mM **DMB** and 1 mM $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ in acetonitrile in the absence of air with 460 nm light excitation after 4 h using naphthalene (green) as internal standard. Product resonances of DAP highlighted in yellow.



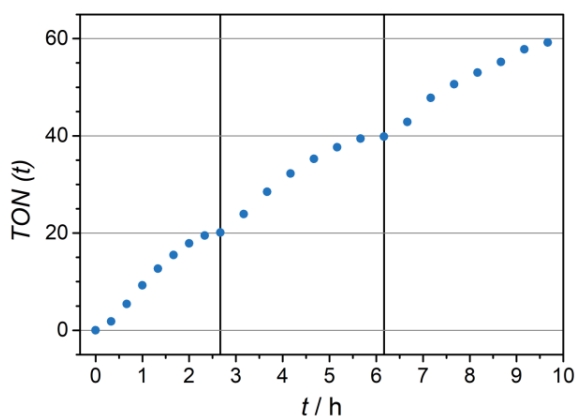
Supplementary Figure 34. Partial ^1H NMR spectrum of the reaction mixture 100 mM **tAn** (purple), 500 mM **DMB** and 1 mM $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ in acetonitrile in the presence of air in the dark after 24 h using naphthalene (green) as internal standard.



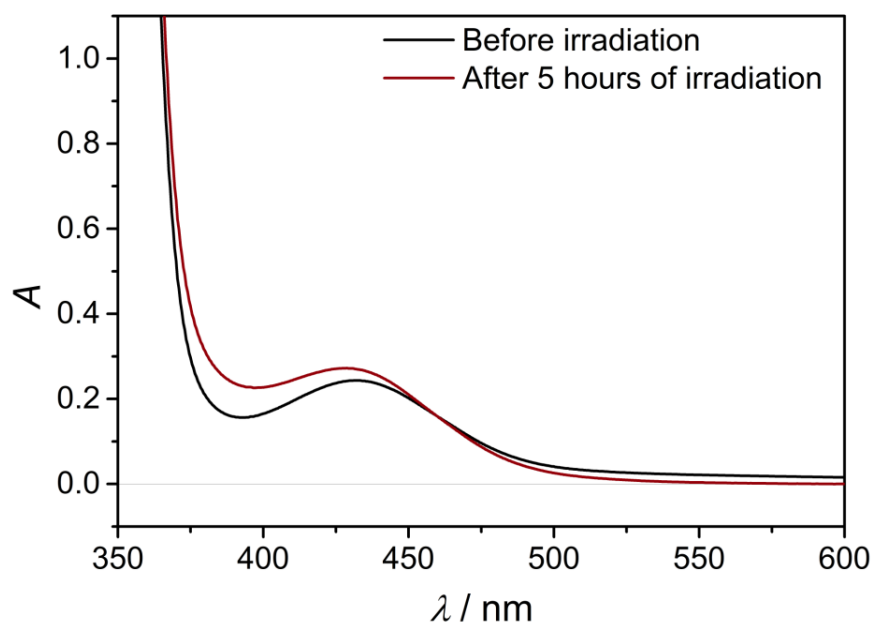
Supplementary Figure 35. Partial ^1H NMR spectrum of the reaction mixture 100 mM **tAn** (purple) and 500 mM **DMB** without a photocatalyst in acetonitrile in the presence of air with 460 nm light excitation after 24 h using naphthalene (green) as internal standard. The weak resonances highlighted in red are assigned to 4-anisaldehyde.



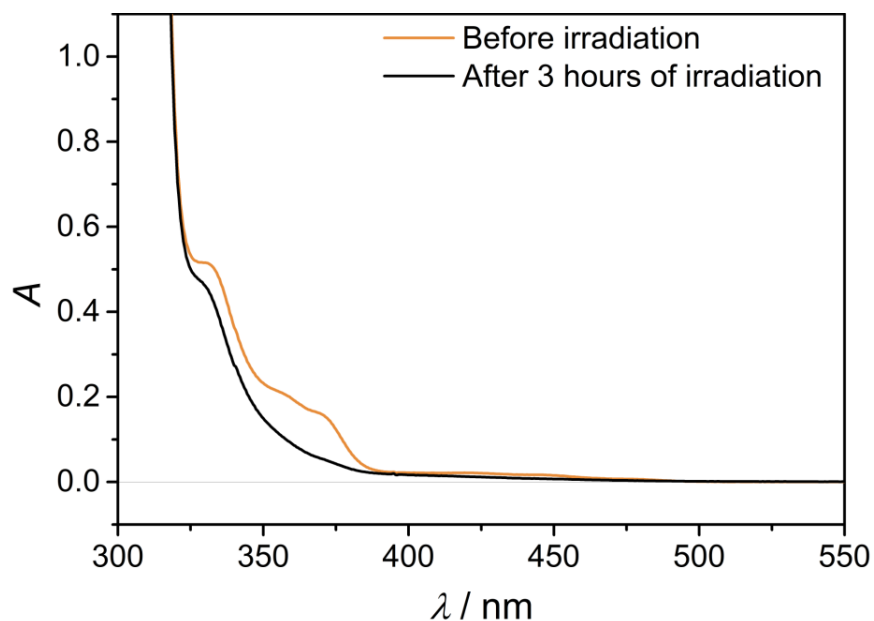
Supplementary Figure 36. Conversion vs. times plot of the photoredox catalyzed radical cation Diels-Alder cycloaddition of 100 mM **tAn** and 500 mM **DMB** using $[\text{Cr}(\text{tpe})_2]^{3+}$ (1 mM) in CH_3CN with 460 nm light excitation.



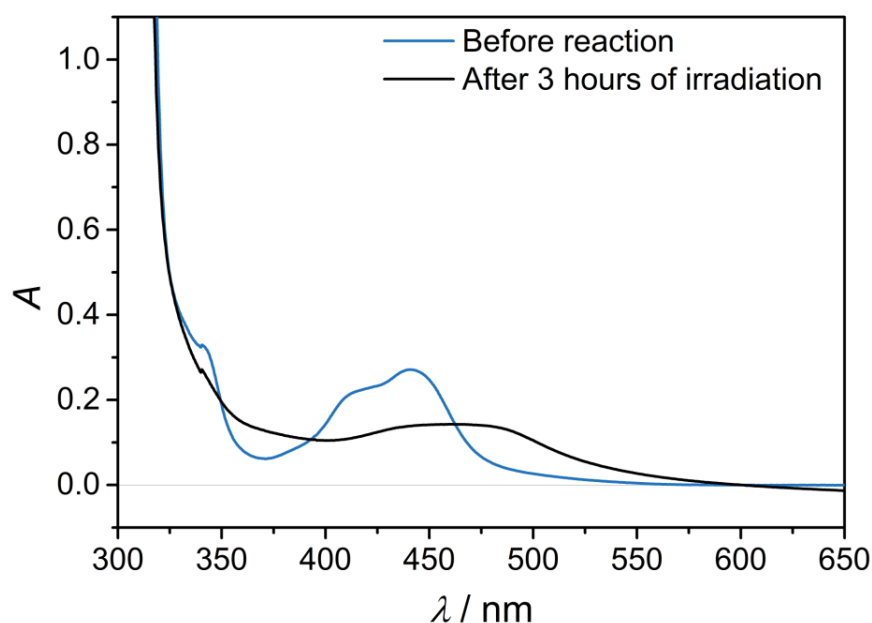
Supplementary Figure 37. Conversion vs. times plot of the photoredox catalyzed radical cation Diels-Alder cycloaddition of 100 mM **tAn** and 500 mM **DMB** using $[\text{Cr}(\text{tpe})_2]^{3+}$ (5 mM) in CH_3CN with 460 nm light excitation. After full consumption of **tAn**, further **tAn** and **DMB** was added to replace the converted material (two times indicated by thick vertical lines). Due to the large number of samples withdrawn from the reaction mixture, a total volume of 4 mL was used, so that the upper part of the vial was less illuminated which accounts for the slower reaction as compared to the experiment shown in Supplementary Figure 32.



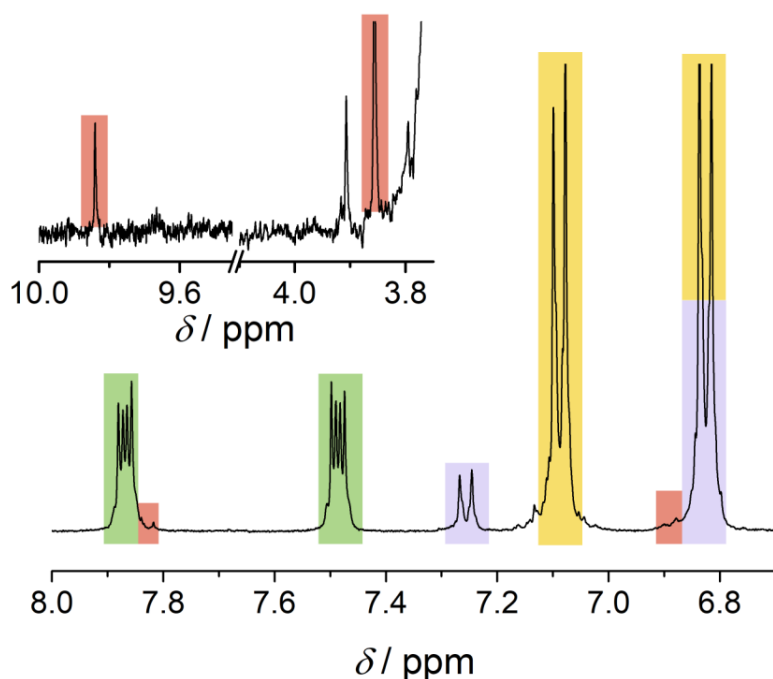
Supplementary Figure 38. UV/Vis spectra of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (5 mM) in aerated acetonitrile before (red) and after 5 h (black) irradiation (460 nm) in the presence of *tAn* (100 mM) and **DMB** (500 mM). The slight blue shift of the absorption maximum might arise from the consumption of *tAn* and thus a change in the high energy part of the spectrum.



Supplementary Figure 39. UV/Vis spectra of $[\text{Cr}(\text{dmc bpy})_3][\text{BF}_4]_3$ (1 mM) in aerated acetonitrile before (orange) and after 3h (black) irradiation (460 nm) in the presence of *tAn* (100 mM) and **DMB** (500 mM). The spectrum was recorded after ca. 10 fold dilution.



Supplementary Figure 40. UV/Vis spectra of $[\text{Ru}(\text{bpz})_3][\text{PF}_6]_2$ (1 mM) in aerated acetonitrile before (blue) and after 3h (black) irradiation (460 nm) in the presence of **tAn** (100 mM) and **DMB** (500 mM). The spectrum was recorded after ca. 100 fold dilution.



Supplementary Figure 41. Partial ^1H NMR spectrum of the reaction using 100 mM **tAn** (purple), 500 mM **DMB** and 5 mM $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ in acetonitrile using naphthalene (green) as internal standard with 460 nm light excitation after 8.5 h. Product resonances of DAP highlighted in yellow. Resonances of 4-anisaldehyde highlighted in red.

References

- 1 Neese, F. (2012) The ORCA program system. *WIREs Comput. Mol. Sci.* 2, 73–78.
- 2 a) Becke, A. D. (1993) Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 98, 5648–5652. b) Lee, C.; Yang, W.; Parr, R. G. (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* 37, 785–789. c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. (1989) Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* 157, 200–206.
- 3 Weigend, F.; Ahlrichs, R. (2005) 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.* 7, 3297–3305.
- 4 Weigend, F. (2006) Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* 8, 1057–1065.
- 5 Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. (200) Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A ‘chain-of-spheres’ algorithm for the Hartree–Fock exchange. *Chem. Phys.* 356, 98–109.
- 6 Izsák, R.; Neese, F. (2011) An overlap fitted chain of spheres exchange method. *J. Chem. Phys.* 135, 144105.
- 7 Pantazis, D. A.; Chen, X.-Y.; Landis, C. R.; Neese, F. (2008) All-Electron Scalar Relativistic Basis Sets for Third-Row Transition Metal Atoms. *J. Chem. Theory Comput.* 4, 908–919.
- 8 a) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. (1993) Relativistic regular two-component Hamiltonians. *J. Chem. Phys.* 99, 4597–4610; b) van Wüllen, C. (1998) Molecular density functional calculations in the regular relativistic approximation: Method, application to coinage metal diatomics, hydrides, fluorides and chlorides, and comparison with first-order relativistic calculations. *J. Chem. Phys.* 109, 392–399.
- 9 Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. (2010) A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* 132, 154104.
- 10 Grimme, S.; Ehrlich, S.; Goerigk, L. (2011) Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* 32, 1456–1465.
- 11 Barone, V.; Cossi, M. (1998) Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* 102, 1995–2001.
- 12 Hasebe, N.; Suzuki, K.; Horiuchi, H.; Suzuki, H.; Yoshihara, T.; Okutsu, T.; Tobita, S. (2015) Absolute Phosphorescence Quantum Yields of Singlet Molecular Oxygen in Solution Determined Using an Integrating Sphere Instrument. *Anal. Chem.* 87, 2360–2366.
- 13 Treiling, S., Wang, C., Förster, C., Reichenauer, F., Kalmbach, J., Boden, P., Harris, J. P., Carrella, L., Rentschler, E., Resch-Genger, U., Reber, C., Seitz, M., Gerhards, M., Heinze, K. (2019) Luminescence and Light-driven Energy and Electron Transfer from an Exceptionally Long-lived Excited State of a Non-innocent Chromium(III) Complex. *Angew. Chem. Int. Ed.* 58, 18075–18085.

6.2 Supporting Information: Visible-Light Induced Fixation of SO₂ into Organic Molecules with Polypyridine Chromium(III) Complexes

ChemCatChem

Supporting Information

Visible-Light Induced Fixation of SO₂ into Organic Molecules with Polypyridine Chromium(III) Complexes

Steven Sittel⁺, [REDACTED]
[REDACTED]

Experimental Details

General. The photocatalysts $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$, $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ and $[\text{Cr}(\text{bpmp})_2][\text{OTf}]_3$ were prepared according to literature procedures.^[1-3] 1,4-Diazabicyclo[2.2.2]octane bis(sulfur dioxide) and SO_2 solution in CH_3CN were prepared according to literature procedures.^[4-6] Diphenyliodonium salts (98 %, Alpha Aesar), 4-aminomorpholine (97 %, Sigma-Aldrich), 2-vinylpyridine (97 %, Sigma-Aldrich), 1,4-diazabicyclo[2.2.2]octane (ReagentPlus® ≥ 99 %, Sigma-Aldrich) were obtained from commercial suppliers and used without further purification. Potassium cyclohexyltrifluoroborate for spectroscopic measurements was obtained commercially (95 %, Sigma-Aldrich) and purified by recrystallizing from acetone three times and subsequent washing with acetonitrile and diethylether. Cobaltocene was obtained from FisherSci (98%) and sublimed before use. Acetonitrile used for electrochemical measurements (HPLC gradient grade, VWR Chemicals) was dried by distillation over CaH_2 before use. The electrolytes used for these measurements were $[\text{tBu}_4\text{N}][\text{PF}_6]$ (for electrochemical analysis, ≥ 99.0 %, Sigma-Aldrich), which was used as received or $[\text{tBu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$, which was synthesized according to a literature procedure and purified by recrystallization from methanol.^[7] Acetonitrile used for UV/Vis/NIR and emission spectroscopy (Optima® LC/MS Grade, Fisher Scientific) was used as received. Acetonitrile for reactions (HPLC-Gradient Grade, VWR Chemicals) was used as received. Solvents for column chromatography were obtained from different commercial sources in >95 % purity and used as received.

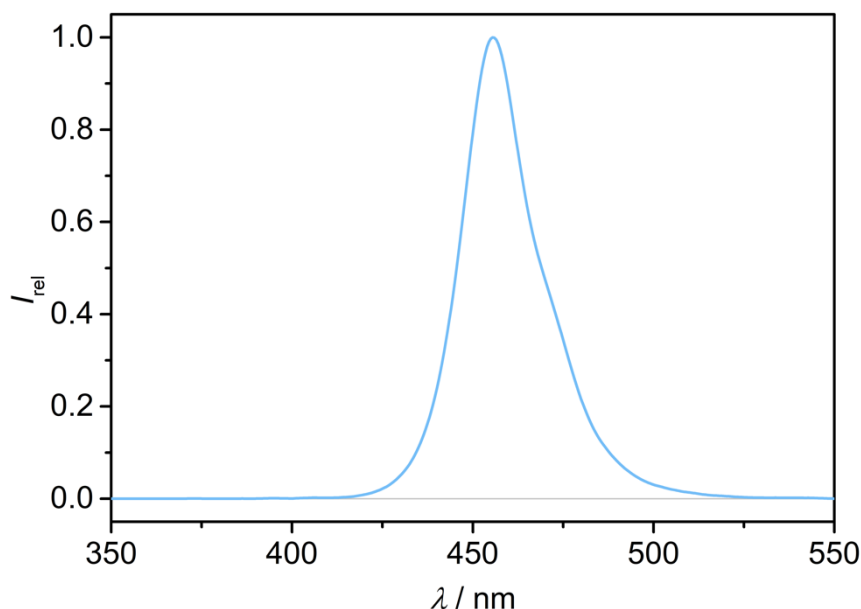
Electrochemical experiments were conducted using a BioLogic SP-50 voltammetric analyzer. Platinum electrodes were used as both working and counter electrodes, while a 0.01 M $\text{Ag}/\text{Ag}[\text{NO}_3]$ electrode served as reference electrode. Cyclic and square wave voltammetry measurements were carried out at scan rates of $50\text{--}200 \text{ mV s}^{-1}$ using 100 M $[\text{tBu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{tBu}_4\text{N}][\text{PF}_6]$ in CH_3CN as supporting electrolyte. Potentials are referenced against the ferrocene/ferrocenium couple.

Luminescence decay curves were recorded with a FLS1000 spectrometer from *Edinburgh Instruments* equipped with the cooled red sensitive photomultiplier detector PMT-980. Measurements were performed in the multi-channel scaling mode employing the μs -xenon flashlamp $\mu\text{F}2$ (pulse width ca. 2 μs) or a variable pulsed laser VPL-450 ($\lambda_{\text{exc}} = 451.3 \text{ nm}$, CW output power: 55.0 mW, pulse width: 100 ns to 1000 μs) as excitation source.

Stern-Volmer analyses were performed in long-neck inert gas 1.0 cm quartz cuvettes with a *Schott* valve. The photocatalyst solutions were purged with argon for about 20 minutes using a cannula. The cuvette was then closed under continued argon flow. The emission lifetime was measured and the obtained value was used as a starting point for the Stern-Volmer analysis. The solution of the quencher was degassed as described above and titrated to the photocatalyst solution using *Eppendorf* pipettes. The resulting solution was purged with argon for about 5 minutes, the cuvette was closed and the emission lifetime of the photocatalyst was measured again. Due to the extremely long lifetime and the high excited state redox potential of $^*[\text{Cr}(\text{tpe})_2]^{3+}$ its luminescence is quenched efficiently even by trace impurities, so that it is very challenging to obtain the natural lifetime τ_0 . Consequently, highly purified samples and a particularly cautious conduction of the experiments is mandatory.

UV/Vis/NIR spectra were recorded before and after the irradiation experiments on a *Jasco V770* spectrometer.

Photolysis experiments were conducted by irradiating deaerated solutions of the photocatalysts with the respective substrates in inert gas cuvettes. An Ultra-High Power collimated LED from *Prizmatix* (UHP-T-460-DI; output power (free): 5.5 W) with a maximum at 456 nm and the centroid at 460 nm was used. The output power was adjusted individually for each experiment using a UHPTLCC-02-USB Controller. The beam of light was focused onto the cuvette with a plano convex lense. At the cuvette the beam diameter was roughly 1 cm. The temperature of the irradiated solution was kept at 20 °C with a Peltier module.



Laser flash photolysis (LFP) measurements were carried out on the LP980KS setup from *Edinburgh Instruments* equipped with an Nd:YAG laser from *Litron* (Nano LG 300-10). The frequency-tripled (355 nm) output served as excitation source to record transient absorption (TA) signals. The laser pulse duration was about 10 ns and the pulse frequency was 10 Hz. Pulse energy determinations were carried out each measuring day using a pyroelectric detector with broadband absorber from *gentec-eo* (QE25LP-S-MB-QED-D0). Pulse energies were not changed in between each series of experiments and control measurements established the laser output stability, which is of particular importance for quantitative measurements and relative actinometry. A beam expander (*Thorlabs*) was used to ensure homogenous excitation in the detection volume (the beam diameter in front of the cuvette window was about 1.2 cm), thus allowing the precise determination of excited state concentrations in the cuvette. Single-wavelength kinetics were recorded using a photomultiplier tube from *Hamamatsu* (R928), while the detection of transient absorption spectra occurred using an *Andor* iCCD camera. LFP experiments were performed at 20 °C utilizing a temperature-controlled cuvette holder, and the TA spectra were integrated over 100 ns. Due to partially irreversible decomposition of the complexes under the measuring conditions, a new solution was used for each measurement, based on a freshly prepared stock solution.

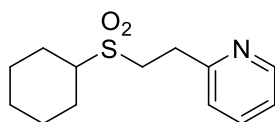
Catalytic experiments were performed at $\lambda_{\text{max}} = 430$ nm using commercially available High Power 3 W LED from *Avonec* (<https://www.avonec.de>). For each irradiation reaction the reaction vessel was placed before two 3W LEDs (distance 1 – 2 cm). A custom-made photoreactor box with an incorporated magnetic stirrer was used with three interchangeable heatsinks with mounted LEDs arranged around the reaction vessels. The temperature inside the box was maintained below 30 °C (internal reaction temperature ≥ 30 °C) with an integrated fan.



Column chromatography was performed with Silica 60 (0.04–0.063 mm, 230–400 mesh) and the specified solvent mixture. Thin layer chromatography was performed on aluminum sheets coated with SiO_2 (TLC silica gel 60 F254). The spots were visualized by ultraviolet light or cerium ammonium molybdate (CAM).

Proton and carbon nuclear magnetic resonance spectra (^1H NMR, ^{13}C NMR) were recorded at 400 or 600 MHz for ^1H NMR and 101 or 151 MHz for ^{13}C NMR, respectively. Chemical shifts are reported as δ values relative to the non-deuterated residual of the respective solvent: CDCl_3 ($\delta = 7.26$ ppm for ^1H and $\delta = 77.16$ ppm for ^{13}C), CD_3CN ($\delta = 1.96$ ppm for ^1H and $\delta = 118.26$ ppm for ^{13}C). Coupling constants (J) are given in Hz and multiplicities of the signals are abbreviated as follows: s = singlet; bs = broad singlet; d = doublet; t = triplet; q = quartet; m = multiplet; dd = doublet of doublets and dt = doublet of triplets.

Synthesis of 2-[2-(cyclohexylsulfonyl)ethyl]pyridine



Representative example:

A 10 mL tube with a stir bar was charged with CyBF_3K (71.3 mg, 0.375 mmol, 1.5 eq.), 2-vinylpyridine (30 μL , 0.25 mmol, 1.0 eq.), DABSO (60.1 mg, 0.25 mmol, 1.0 eq.) and $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (10.4 mg, 0.0125 mmol, 5 mol-%) and CH_3CN (2.5 mL). The tube was sealed with a rubber septum and the reaction mixture degassed by bubbling nitrogen through the mixture for 10 – 15 minutes in an ultrasonic bath. The resulting suspension of a colorless precipitate in a yellow solution was irradiated with blue LED light ($\lambda_{\text{max}} = 430 \text{ nm}$) for 18 h at room temperature. After completion of the reaction, the resulting reaction mixture was directly purified by column chromatography on silica gel [*n*-hexane/EtOAc = 9:1 $\rightarrow$ 3:2 (v/v)] to afford the analytically pure product as colorless oil (21 mg, 33 %).

Analytical data are in accordance with the literature.^[8]

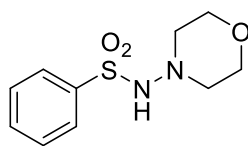
$R_f = 0.14$ (*n*-hexane/EtOAc = 3:2 (v/v)).

^1H NMR (400 MHz, CD_3CN): $\delta = 8.53 - 8.47$ (m, 1H), 7.69 (td, $J = 7.7, 1.9 \text{ Hz}$, 1H), 7.30 (dt, $J = 7.8, 1.1 \text{ Hz}$, 1H), 7.21 (ddd, $J = 7.6, 4.8, 1.1 \text{ Hz}$, 1H), 3.45 – 3.36 (m, 2H), 3.24 – 3.16 (m, 2H), 2.87 (tt, $J = 12.1, 3.5 \text{ Hz}$, 1H), 2.13 – 2.05 (m, 2H), 1.90 – 1.81 (m, 2H), 1.71 – 1.63 (m, 1H), 1.44 (qd, $J = 12.3, 3.1 \text{ Hz}$, 2H), 1.35 – 1.12 (m, 3H) ppm.

^{13}C NMR (101 MHz, CD_3CN): $\delta = 159.0, 150.2, 137.6, 124.2, 122.8, 61.2, 49.1, 30.3, 25.8, 25.7, 25.6$ ppm.

MS (APCI): m/z calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+ = 254.11$, found 254.2.

Synthesis of *N*-4-morpholinylbenzenesulfonamide



Representative example:

A 10 mL tube with a stir bar was charged with Ph_2IPF_6 (106 mg, 0.375 mmol, 1.5 eq.), 4-aminomorpholine (40 μL , 0.25 mmol, 1.0 eq.), DABSO (60.1 mg, 0.25 mmol, 1.0 eq.), $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ (4.5 mg, 0.005 mmol, 2 mol-%) and CH_3CN (2.5 mL). The tube was sealed with a rubber septum and the reaction mixture degassed by bubbling nitrogen through the mixture for 10 – 15 minutes in an ultrasonic bath. The resulting suspension of a colorless precipitate in a yellow solution was irradiated with blue LED light ($\lambda_{\text{max}} = 430 \text{ nm}$) for 18 h at room temperature. After completion of the reaction, the resulting reaction mixture was directly purified by column chromatography on silica gel [*n*-hexane/EtOAc = 9:1 $\rightarrow$ 3:2 (v/v)] to afford the analytically pure product as colorless solid (34 mg, 56 %).

Analytical data are in accordance with the literature.^[9]

$R_f = 0.30$ (*n*-hexane/EtOAc = 3:2 (v/v)).

m.p. = 111 – 113 °C

^1H NMR (400 MHz, CDCl_3): δ = 8.01 – 7.94 (m, 2H), 7.66 – 7.57 (m, 1H), 7.57 – 7.48 (m, 2H), 5.46 (s, 1H), 3.64 – 3.57 (m, 4H), 2.65 – 2.58 (m, 4H) ppm.

^{13}C NMR (101 MHz, CDCl_3): δ = 138.7, 133.3, 129.0, 128.3, 66.8, 56.9 ppm.

MS (APCI): m/z calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+ = 243.07$, found 243.2.

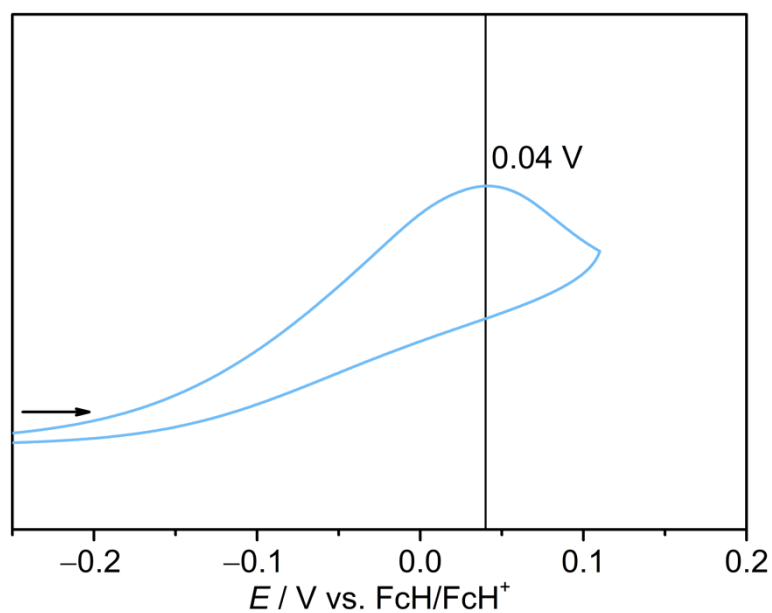


Fig. S1. Cyclic voltammogram of 5 mM 4-aminomorpholine in a 100 mM solution of [n Bu $_4$ N][PF $_6$] in CH $_3$ CN.

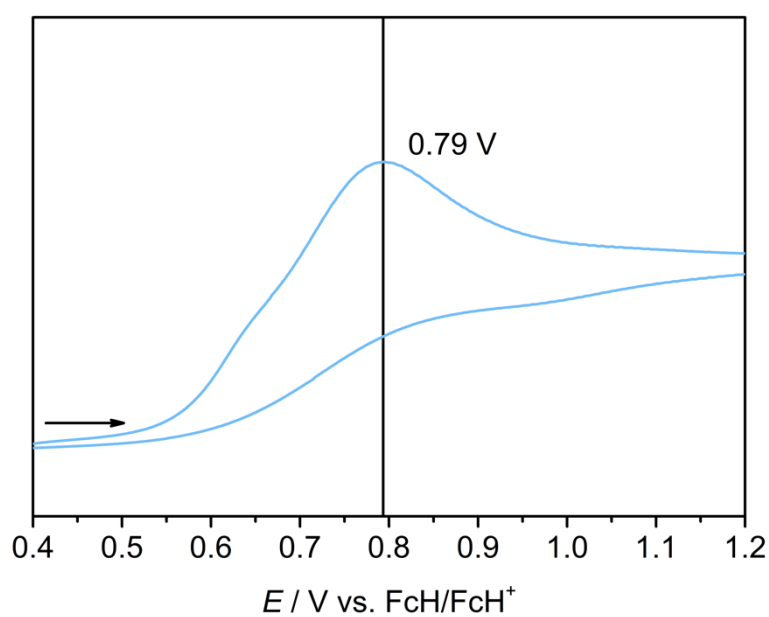


Fig. S2. Cyclic voltammogram of 1 mM potassium cyclohexyltrifluoroborate in a 100 mM solution of [n Bu $_4$ N][PF $_6$] in CH $_3$ CN. The peak potential determined here differs from a previously reported value (1.10 V vs. FcH/FcH $^+$).^[10]

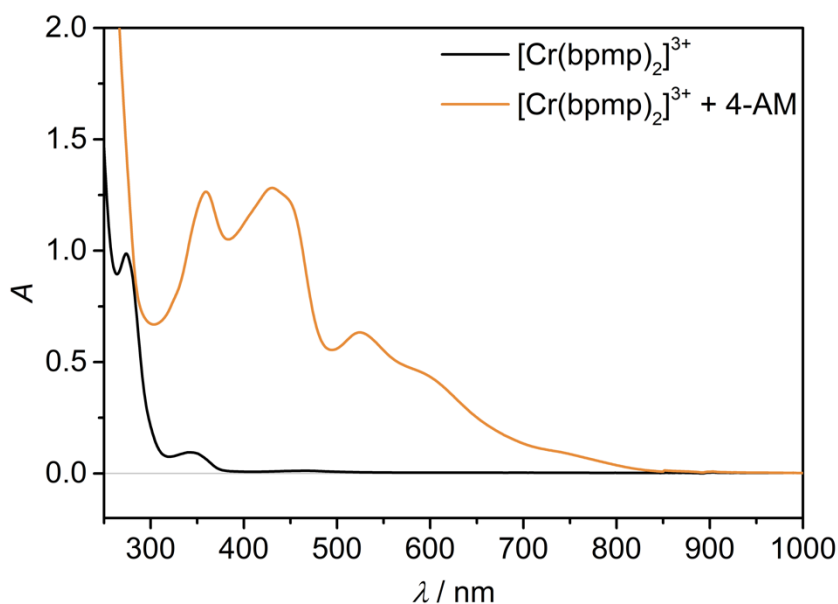


Fig. S3. UV/vis/NIR absorption spectra of 0.1 mM $[\text{Cr}(\text{bpmp})_2][\text{OTf}]_3$ in CH_3CN (black), in a 100 mM solution of 4-aminomorpholine in CH_3CN under argon (orange). The absorption spectrum of the 4-aminomorpholine containing solution indicates the deprotonation of the photocatalyst.^[2]

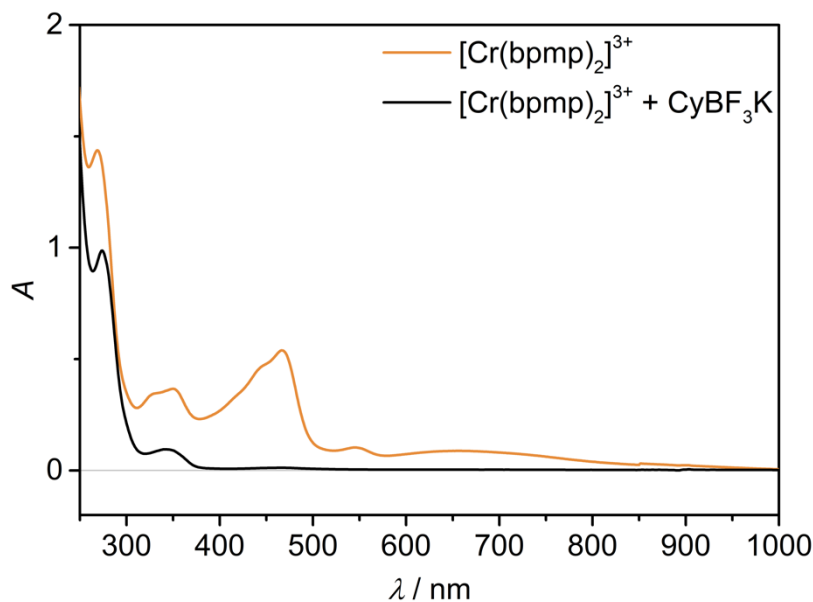


Fig. S4. UV/vis/NIR absorption spectra of 0.1 mM $[\text{Cr}(\text{bpmp})_2][\text{OTf}]_3$ in CH_3CN (black) and in a 2 mM solution of potassium cyclohexyltrifluoroborate in CH_3CN under argon (orange). The absorption spectrum of the potassium cyclohexyltrifluoroborate containing solution indicates the deprotonation of the photocatalyst.^[2]

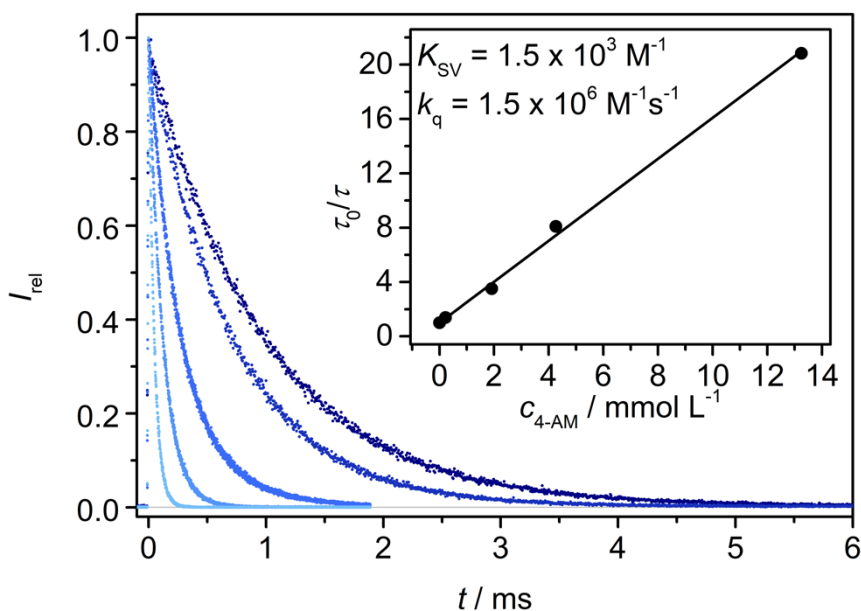


Fig. S5. Reductive Quenching of $[\text{Cr}(\text{ddpd})_2]^{3+}$ by 4-aminomorpholine. Main plot: emission decay traces recorded at 775 nm following excitation (451.3 nm, 10 μs pulse duration) of a 0.1 mM solution of $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ in deaerated acetonitrile at various concentrations of 4-aminomorpholine (0 mM, 0.22 mM, 1.92 mM, 4.26 mM, 13.3 mM). Inset: corresponding Stern-Volmer plot with best-fit function; obtained values for K_{SV} and k_q .

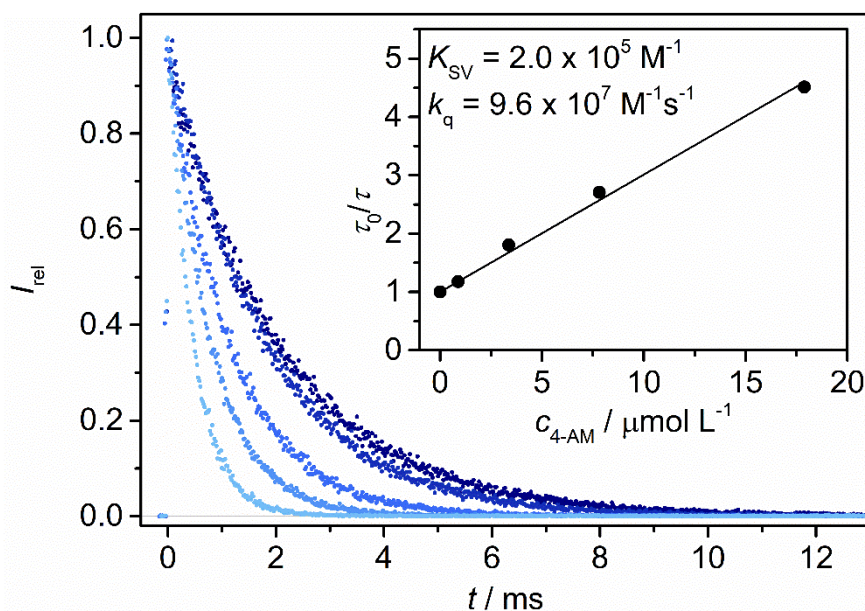


Fig. S6. Reductive Quenching of $[\text{Cr}(\text{tpe})_2]^{3+}$ by 4-aminomorpholine. Main plot: emission decay traces recorded at 742 nm following excitation (435 nm, 2 μs pulse duration) of a 1 mM solution of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ in deaerated acetonitrile at various concentrations of 4-aminomorpholine (0 μM , 0.88 μM , 3.37 μM , 7.81 μM , 17.8 μM). Inset: corresponding Stern-Volmer plot with best-fit function; obtained values for K_{SV} and k_q .

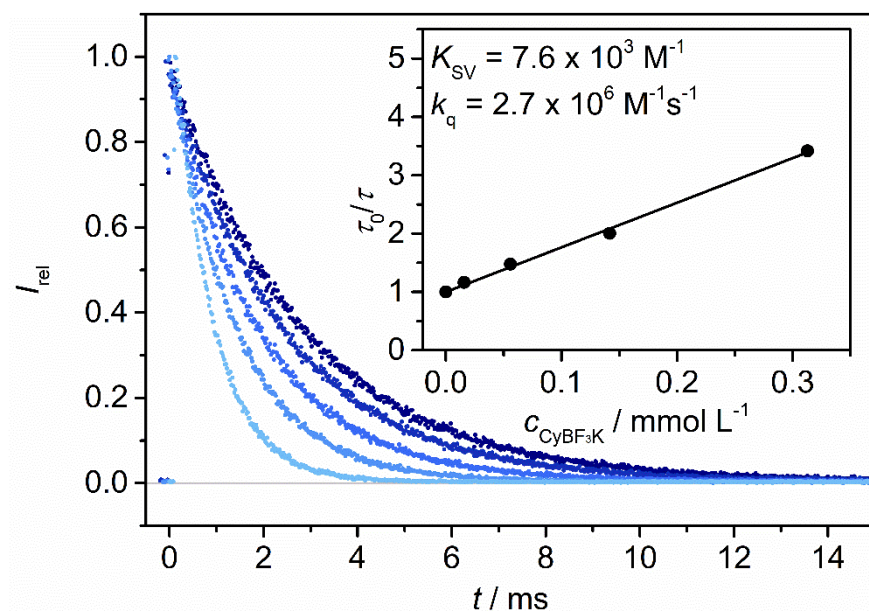


Fig. S7. Reductive Quenching of $^*\text{[Cr(tpe)}_2\text{]}^{3+}$ by potassium cyclohexyltrifluoroborate. Main plot: emission decay traces recorded at 742 nm following excitation (451.3 nm, 10 μs pulse duration) of a 1 mM solution of $[\text{Cr(tpe)}_2][\text{BF}_4]_3$ in deaerated acetonitrile at various concentrations of potassium cyclohexyltrifluoroborate (0 mM, 0.02 mM, 0.06 mM, 0.14 mM, 0.31 mM). Inset: corresponding Stern-Volmer plot with best-fit function; obtained values for K_{SV} and k_{q} .

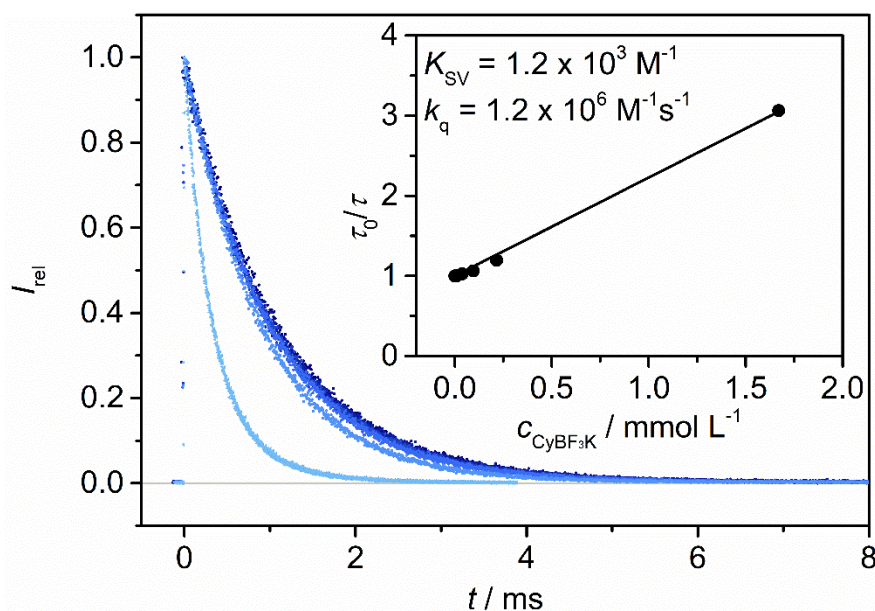


Fig. S8. Reductive Quenching of $^*\text{[Cr(ddpd)}_2\text{]}^{3+}$ by potassium cyclohexyltrifluoroborate. Main plot: emission decay traces recorded at 775 nm following excitation (451.3 nm, 10 μs pulse duration) of a 0.1 mM solution of $[\text{Cr(ddpd)}_2][\text{BF}_4]_3$ in deaerated acetonitrile at various concentrations of potassium cyclohexyltrifluoroborate (0.01 mM, 0.04 mM, 0.09 mM, 0.22 mM, 1.67 mM). Inset: corresponding Stern-Volmer plot with best-fit function; obtained values for K_{SV} and k_{q} .

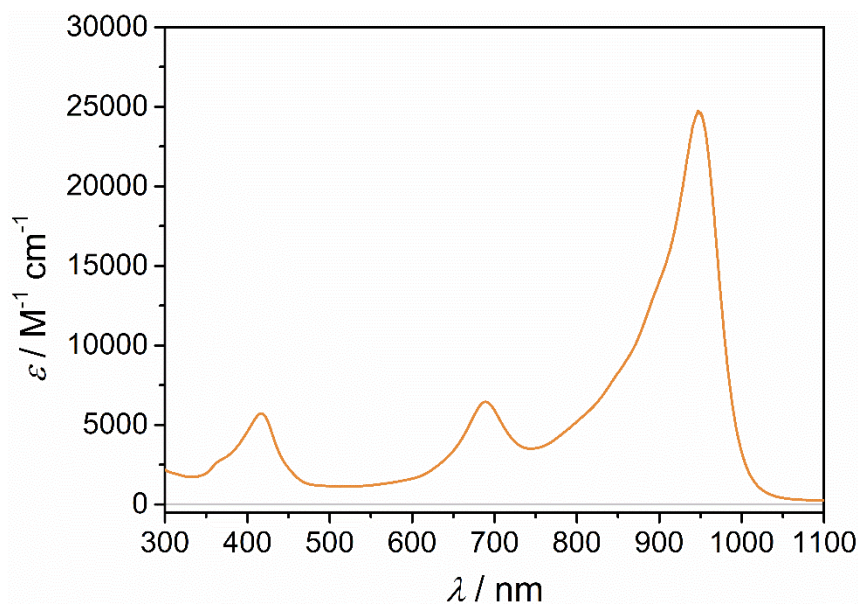


Fig. S9. UV/vis/NIR absorption spectrum of $[\text{Cr}(\text{tpe})_2]^{2+}$ prepared by reduction of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ with cobaltocene under argon; corrected for the absorptions of the resulting cobaltocenium ion in CH_3CN . For absorption spectra of cobaltocene and cobaltocenium hexafluorophosphate in CH_3CN see ref. [11].

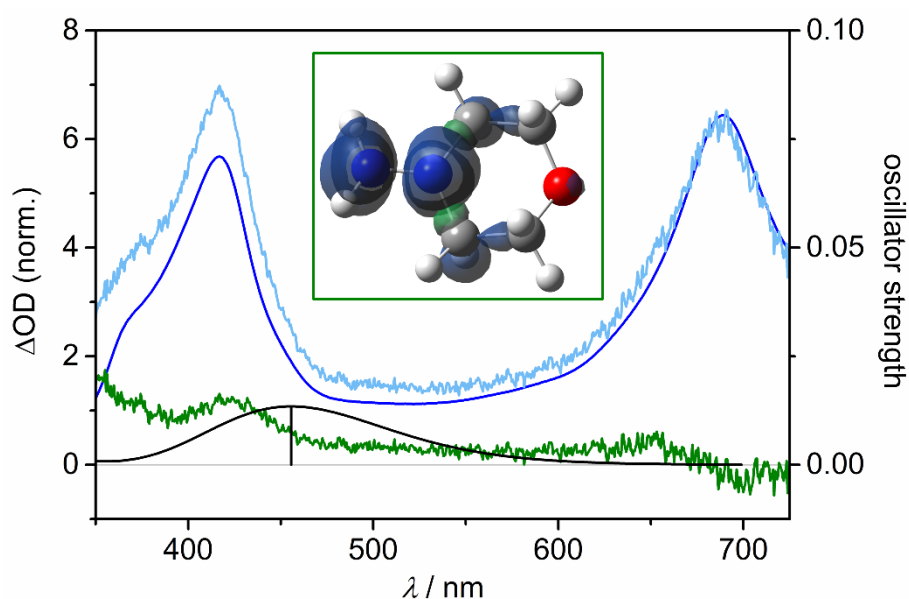


Fig. S10. Double difference spectrum (green) between the normalized transient absorption spectrum taken from Fig. 3b of the main paper (light blue) and the normalized difference spectrum (dark blue, taken from Fig. 4c of the main paper) of $[\text{Cr}(\text{tpe})_2]^{2+}$ to find evidence for the presence of the 4-aminomorpholine radical cation ($4\text{-AM}^{\bullet+}$), which is the quenching co-product. The inset displays the DFT-optimized structure of $4\text{-AM}^{\bullet+}$ and the computed spin densities, which are mainly localized on both nitrogen atoms. Further TD-DFT calculations predict a rather weak (oscillator strength of the corresponding transition, 0.0133) absorption band at ~ 450 nm (black) for $4\text{-AM}^{\bullet+}$, which is close to the maximum of the double difference spectrum (~ 425 nm, see green spectrum). The same calculation method as in a recent publication by one of us has been used (Gaussian 09, B3LYP functional, 6-311+G(d,p) basis set).^[12]

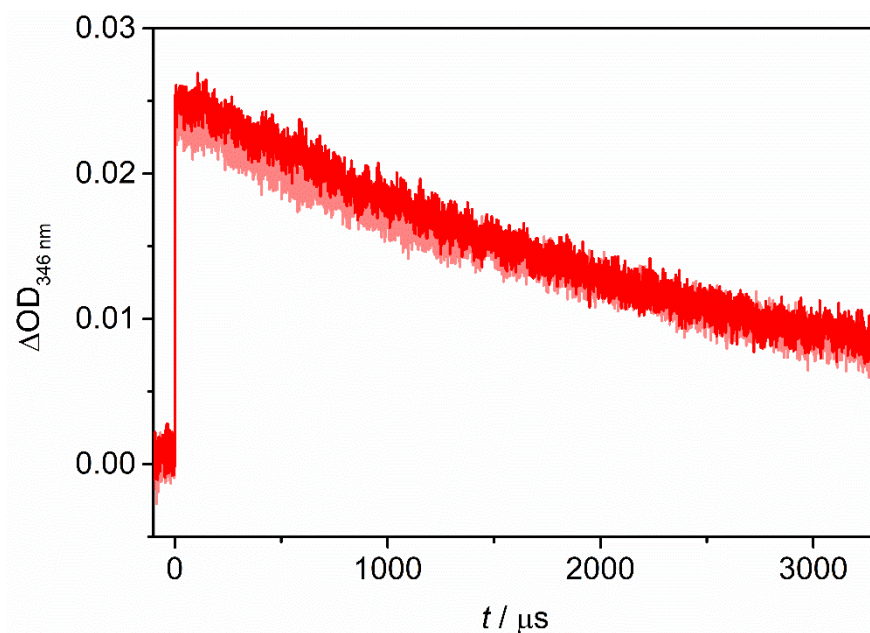


Fig. S11. Transient absorption traces at 346 nm, corresponding to the decay of $^{*}[\text{Cr}(\text{tpe})_2]^{3+}$ in the absence (red) and in the presence (light red) of 1.0 mM diphenyliodonium triflate upon 355 nm laser excitation with 2.3 mJ laser pulses of 10 ns duration. Deaerated solutions of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (350 μM) in CH_3CN were used. No decrease in lifetime was observed and the slight signal decrease is attributed to a weak filter effect caused by the iodonium salt at the excitation wavelength. Further control experiments on the iodonium salt alone did not reveal any new absorption bands in the transient absorption spectra.

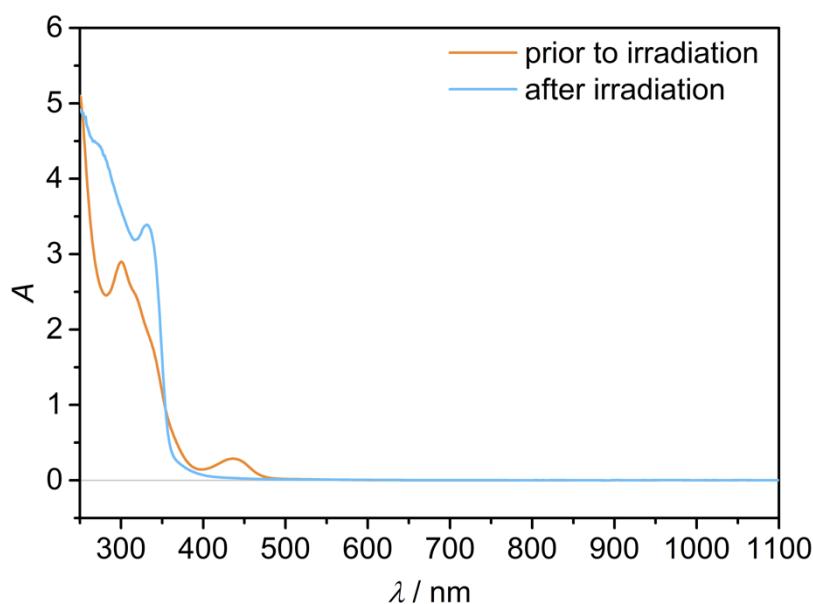


Fig. S12. UV/vis/NIR absorption spectra of 0.1 mM $[\text{Cr}(\text{dddpd})_2][\text{BF}_4]_3$ in a 100 mM solution of 4-aminomorpholine in CH_3CN prior to irradiation (orange) and after 30 s of UHP-LED irradiation ($\lambda_{\text{exc}} = 460 \text{ nm}$) at 20% output power under argon (blue). The absence of the characteristic band of the very sensitive high-spin Cr^{II} complex $[\text{Cr}(\text{dddpd})_2]^{2+}$ at 435 nm indicates decomposition of the photocatalyst.^[13]

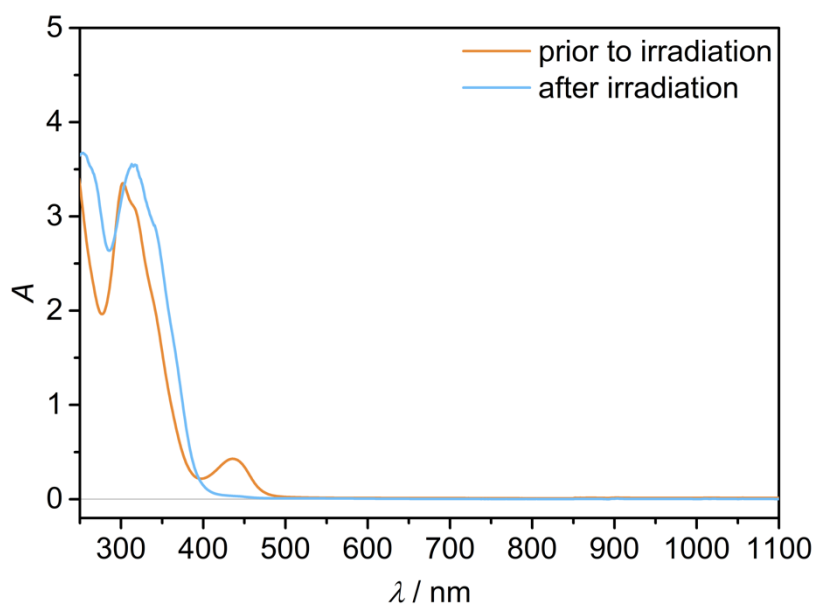


Fig. S13. UV/vis/NIR absorption spectra of 0.1 mM $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ in a 2 mM solution of potassium cyclohexyltrifluoroborate in CH_3CN prior to irradiation (orange) and 270 s of UHP-LED irradiation ($\lambda_{\text{exc}} = 460 \text{ nm}$) at 20% output power under argon (blue). The absence of the characteristic band of the very sensitive high-spin Cr^{II} complex $[\text{Cr}(\text{ddpd})_2]^{2+}$ at 435 nm indicates decomposition of the photocatalyst.^[13]

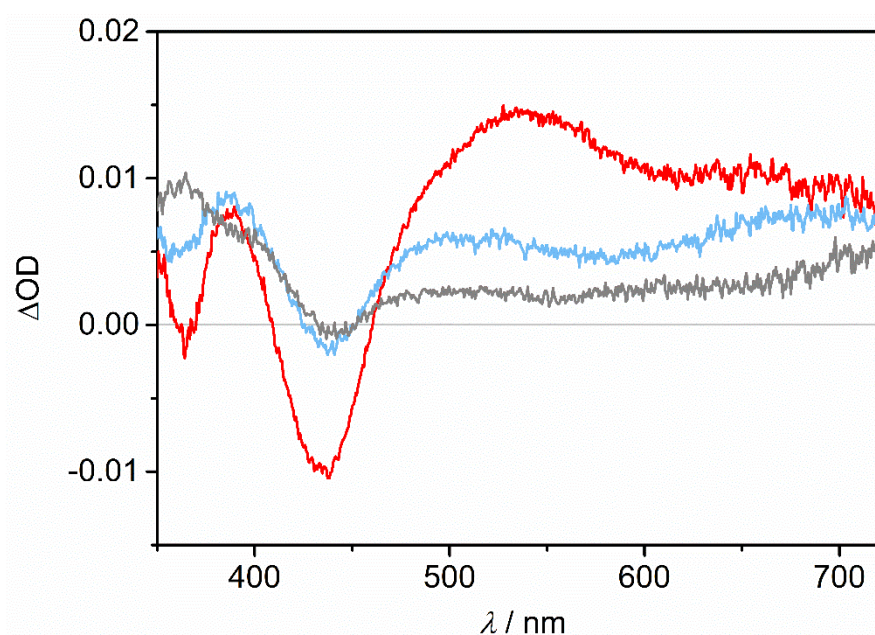


Fig. S14. Transient absorption spectra of a deaerated solution of $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ (22 μM) and 4-aminomorpholine (200 mM) 15 ns (red), 12 μs (blue) and 500 μs (grey) after laser excitation at 355 nm with 12.2 mJ laser pulses of 10 ns duration. The intense band at $\sim 535 \text{ nm}$ in the spectrum recorded right after the laser pulse (red) corresponds to $[\text{Cr}(\text{ddpd})_2]^{3+}$ and it is in line with a recent study employing ultrafast TA.^[14] The expected absorption bands of the reduced complex $[\text{Cr}(\text{ddpd})_2]^{2+}$ are at $\sim 415 \text{ nm}$ and at wavelengths greater than 600 nm,^[13] of which the increasing absorption at 650 nm (in the spectrum after a delay of 12 μs) is easier to detect in the solution used. Corresponding kinetic traces in the absence and in the presence of diphenyliodonium triflate are shown in Fig. S19. The spectrum delayed by 500 μs shows signals that can be partially assigned to degradation products of $[\text{Cr}(\text{ddpd})_2]^{2+}$ (increasing absorption at wavelengths below 400 nm, cf. Fig. S12). Corresponding kinetic traces are shown in Fig. S19.

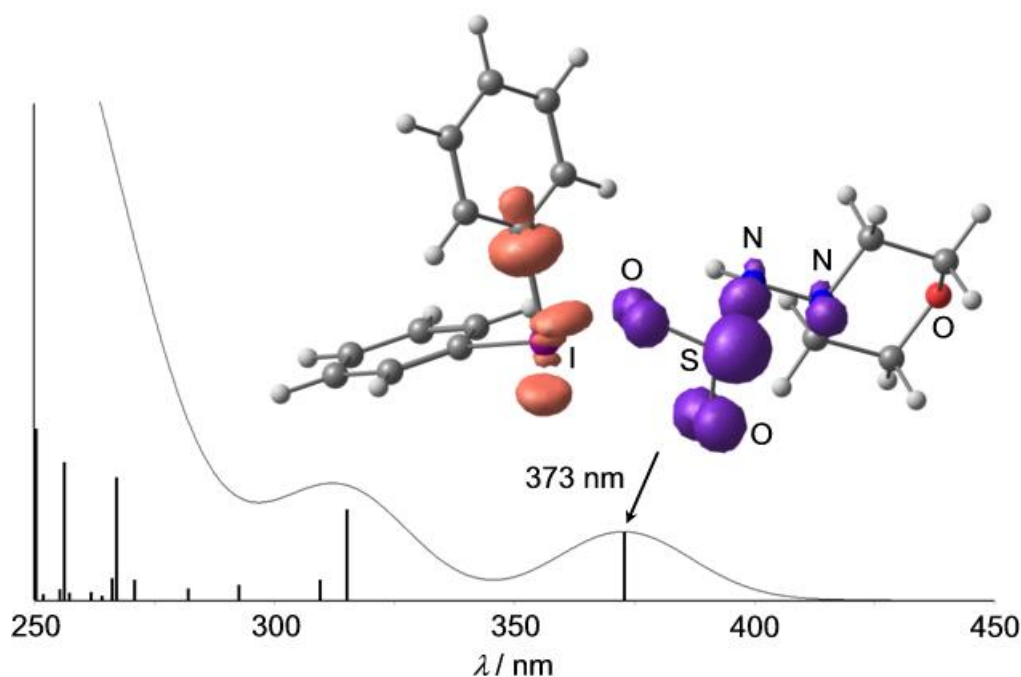


Fig. S15. TD-DFT calculated UV/Vis absorption spectrum and difference electron density of the lowest energy transition (373 nm) of the ion pair $[\text{Ph}_2\text{I}][\text{R}_2\text{N-NH-SO}_2]$ (orange = electron density gain; purple = electron density depletion; isosurface value 0.01). The structure was optimized on the CPCM(CH_3CN)-RJCOSX-B3LYP-D3BJ-ZORA-def2-TZVPP/SARC-ZORA-TZVP(I) level.^[15] The zero order relativistic approximation was used to describe relativistic effects. Grimme's empirical dispersion correction D3(BJ) was employed. A conductor-like screening model modeling acetonitrile was used to incorporate solvent effects. Fifty vertical spin-allowed transitions were calculated. Coordinates are given in Table S2.

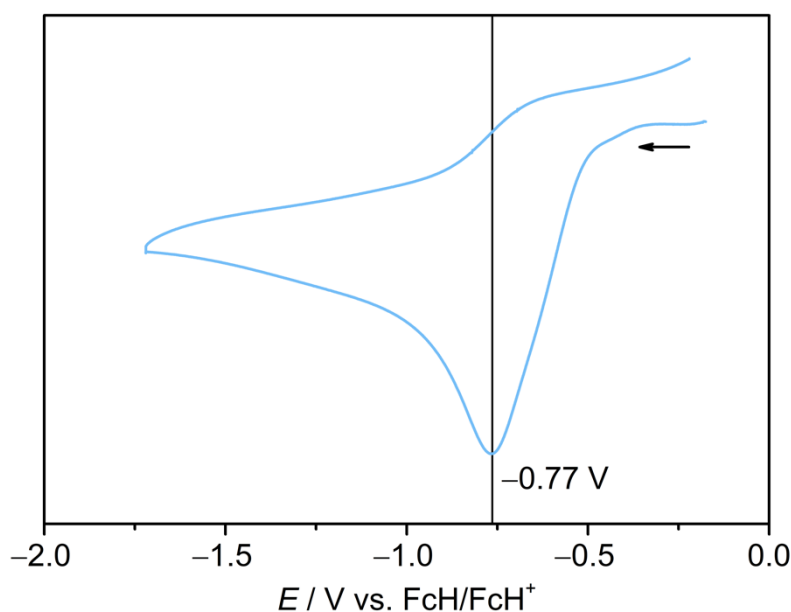


Fig S16. Cyclic voltammogram of 0.2 mM diphenyliodonium triflate (**Ph₂IOTf**) in a 100 mM solution of $[\text{tBu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CH_3CN . As iodonium salts are known to form layers on the working electrode at higher concentration,^[16,17] a dilute solution ($< 1 \text{ mM}$) was used.

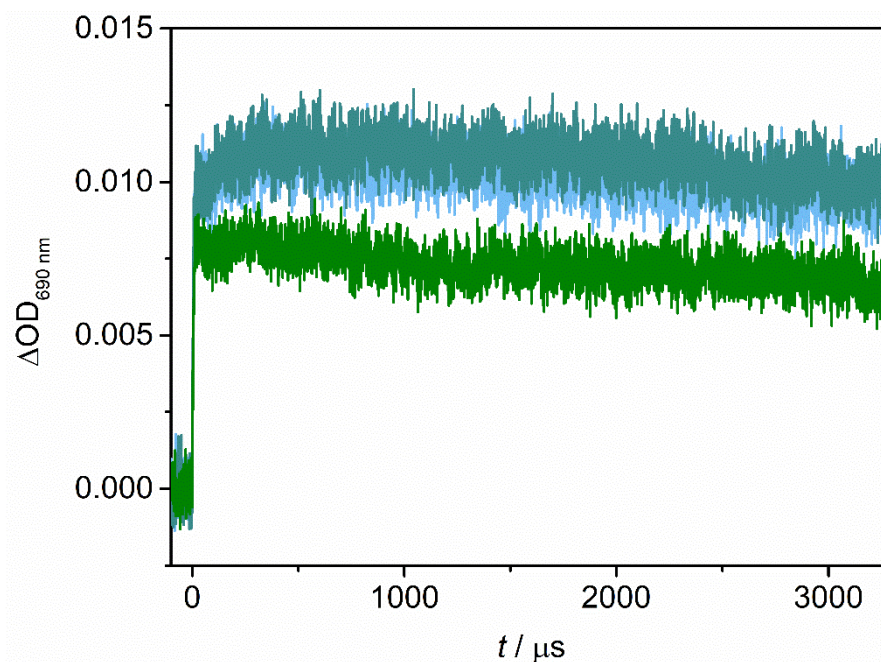


Fig. S17. Transient absorption traces at 690 nm monitoring $[\text{Cr}(\text{tpe})_2]^{2+}$ in the absence (blue) and in the presence of 0.1 mM (turquoise) and 6.7 mM (green) diphenyliodonium triflate. Solutions of 350 μM $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ and 5.2 mM 4-aminomorpholine in deaerated CH_3CN were irradiated at 355 nm with 2.3 mJ laser pulses of 10 ns duration. Owing to a filter effect caused by the iodonium salt at the excitation wavelength, the transient absorption signal of the solution with 6.7 mM iodonium salt is weaker compared to the other two solutions. No significant decrease in $[\text{Cr}(\text{tpe})_2]^{2+}$ lifetime was observed, which is also shown in Fig. S18 after normalization of the 0 mM and 6.7 mM iodonium salt solutions.

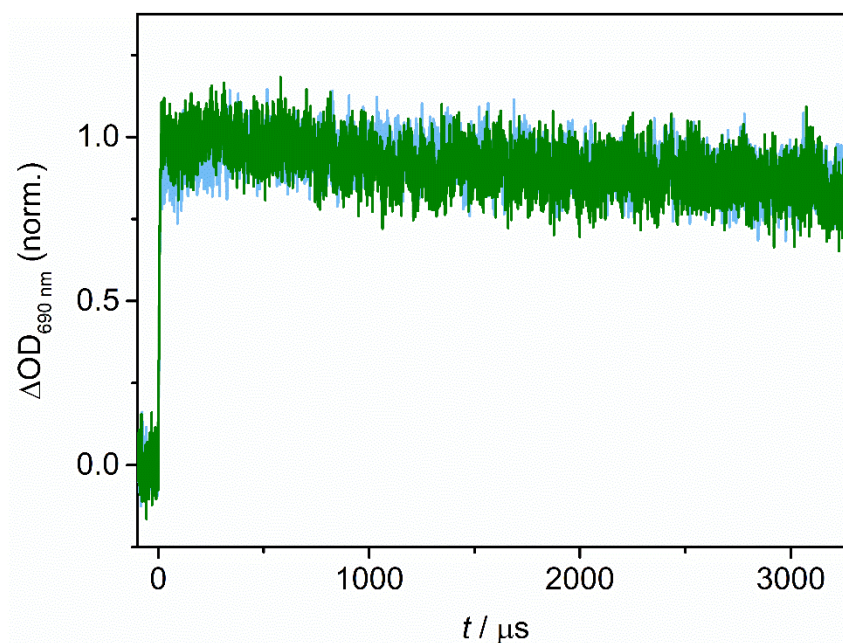


Fig. S18. Normalized transient absorption traces at 690 nm monitoring $[\text{Cr}(\text{tpe})_2]^{2+}$ in the absence (blue) and in the presence of 6.7 mM (green) diphenyliodonium triflate using the raw data sets shown in Fig. S17.

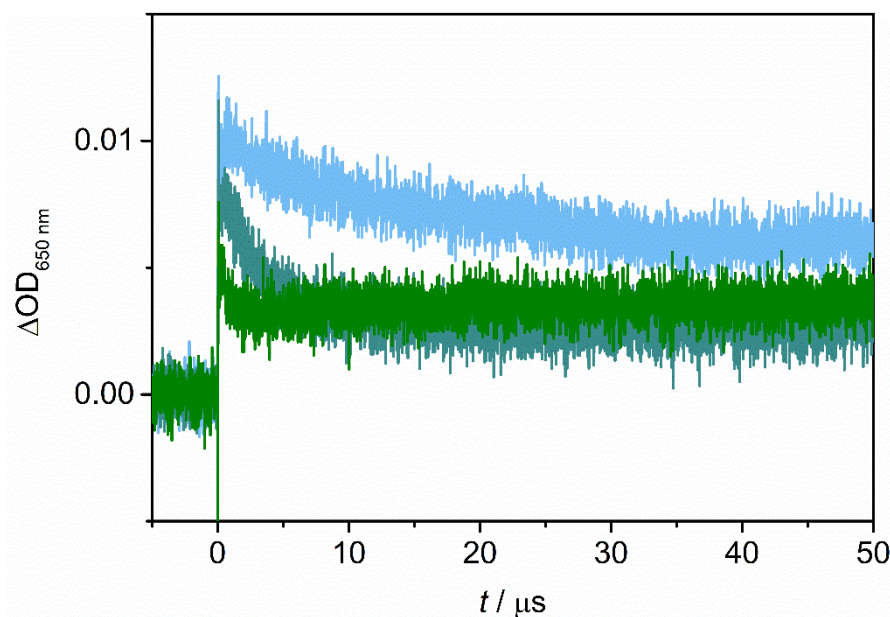


Fig. S19. Transient absorption traces at 650 nm monitoring the formation and decay of $[\text{Cr}(\text{ddpd})_2]^{2+}$ in the absence (blue) and in the presence of 0.1 mM (turquoise) or 1.1 mM (green) diphenyliodonium triflate. Deaerated solutions of 22 μM $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ and 200 mM 4-aminomorpholine in CH_3CN were irradiated at 355 nm with 12.2 mJ laser pulses of 10 ns duration. The remaining offset after the quenching of the $[\text{Cr}(\text{ddpd})_2]^{2+}$ absorption is likely due to decomposition and follow-up products that are not – in contrast to the photocatalysis experiments – trapped by SO_2 . A quantitative analysis of the lifetimes is therefore not reliable. However, these results clearly demonstrate that $[\text{Cr}(\text{ddpd})_2]^{2+}$ reacts much more rapidly with the iodonium salt than $[\text{Cr}(\text{tpe})_2]^{2+}$ does (compare Figure S17 and S18).

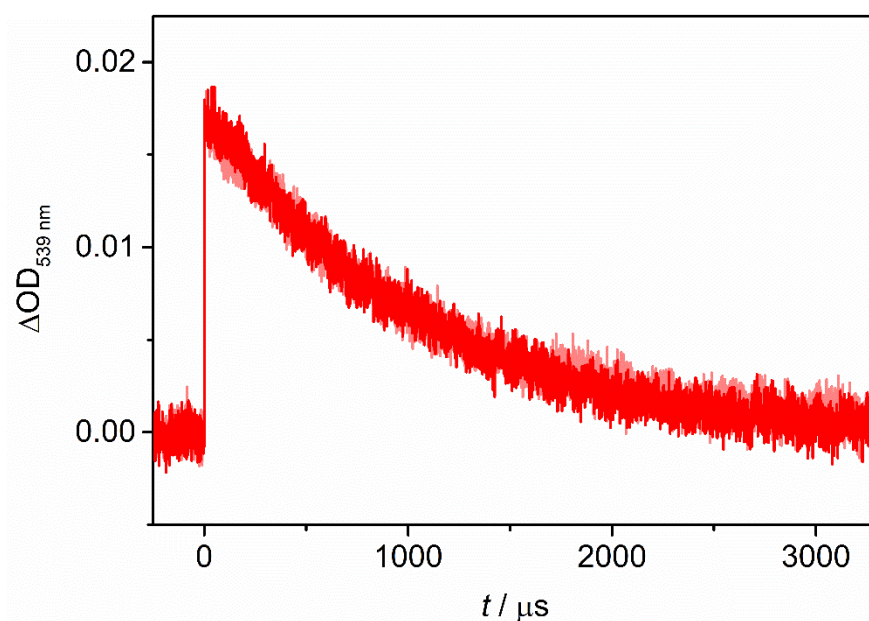
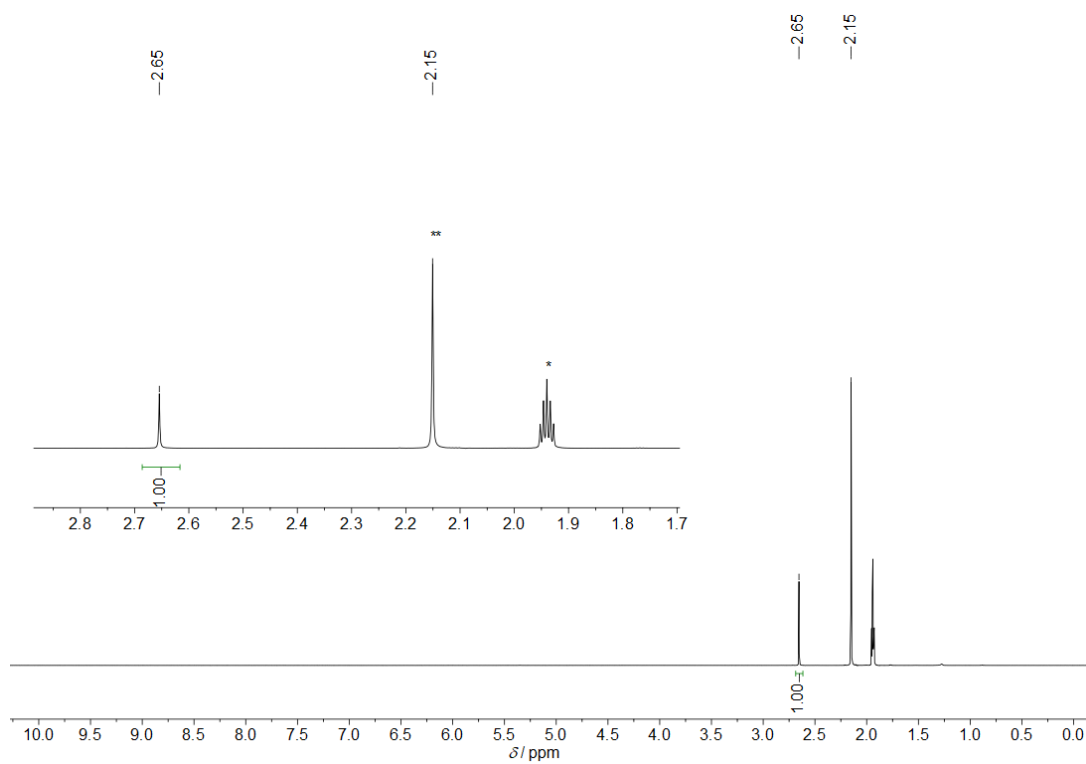
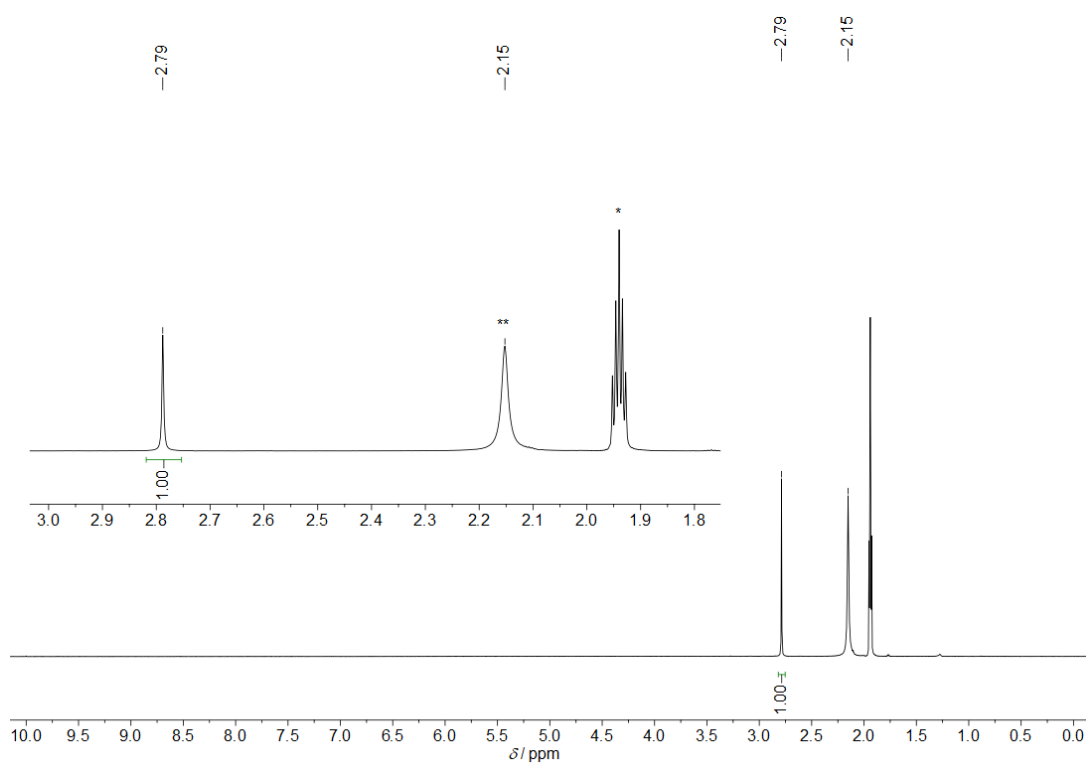


Fig. S20. Transient absorption traces at 539 nm, corresponding to the decay of $^*[\text{Cr}(\text{ddpd})_2]^{3+}$ in the absence (red) and in the presence (light red) of 0.1 mM diphenyliodonium triflate upon 355 nm laser excitation with 12.2 mJ laser pulses of 10 ns duration. Deaerated solutions of $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ (22 μM) in CH_3CN were irradiated. $^*[\text{Cr}(\text{ddpd})_2]^{3+}$ does not react with the iodonium salt under these conditions, in contrast to what has been observed with the reduced complex at the very same quencher concentration (Fig. S19).

a)



b)



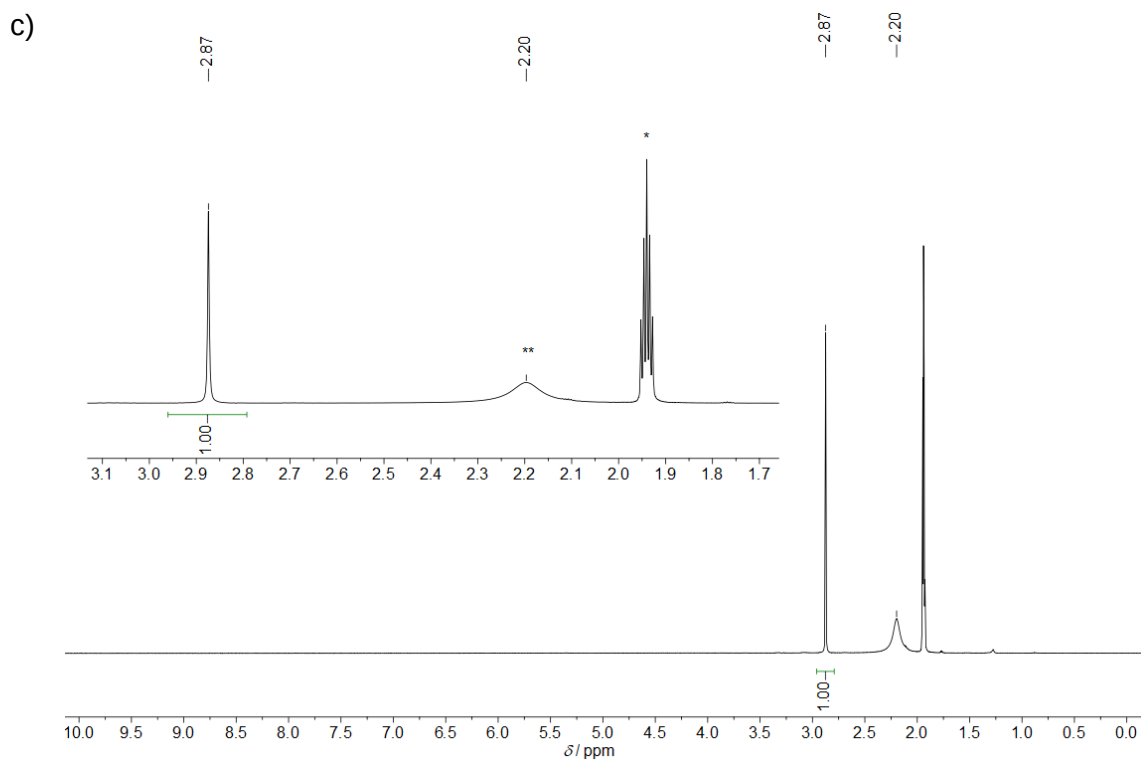


Fig. S21. ^1H NMR spectra of DABCO (top), DABSO (center) and a 1:1 mixture of DABCO/DABSO (bottom) in CD_3CN . * denotes residual solvent resonance, ** denotes resonance of water.

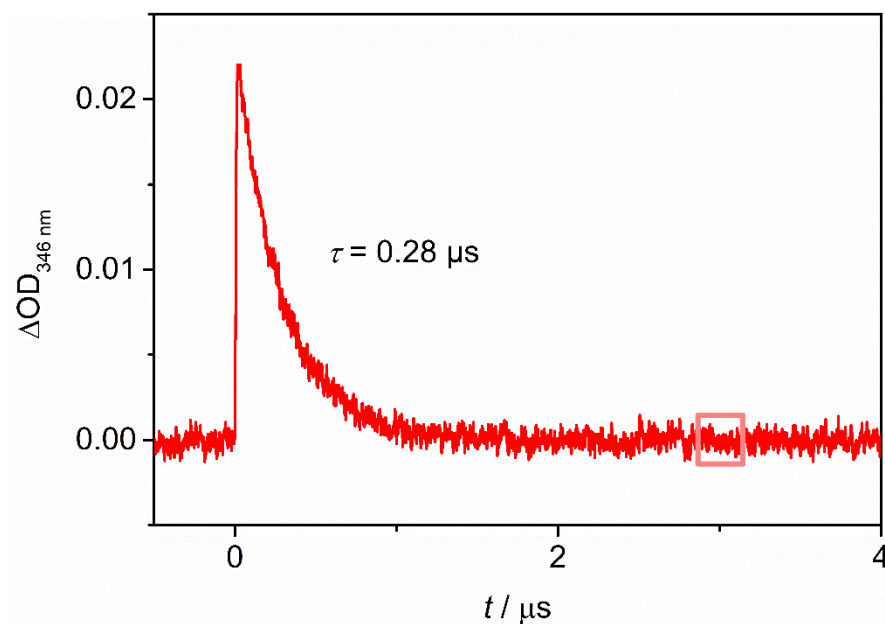


Fig. S22. Transient absorption trace at 346 nm, corresponding to the decay of $^*[\text{Cr}(\text{tpe})_2]^{3+}$ in the presence of 1.45 mM 1,4-diazabicyclo[2.2.2]octane upon 355 nm laser excitation with 2.3 mJ laser pulses of 10 ns duration. A deaerated solution containing 350 μM $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ in CH_3CN was irradiated. The pale red box marks the time of acquisition for the transient spectrum in Fig. S23.

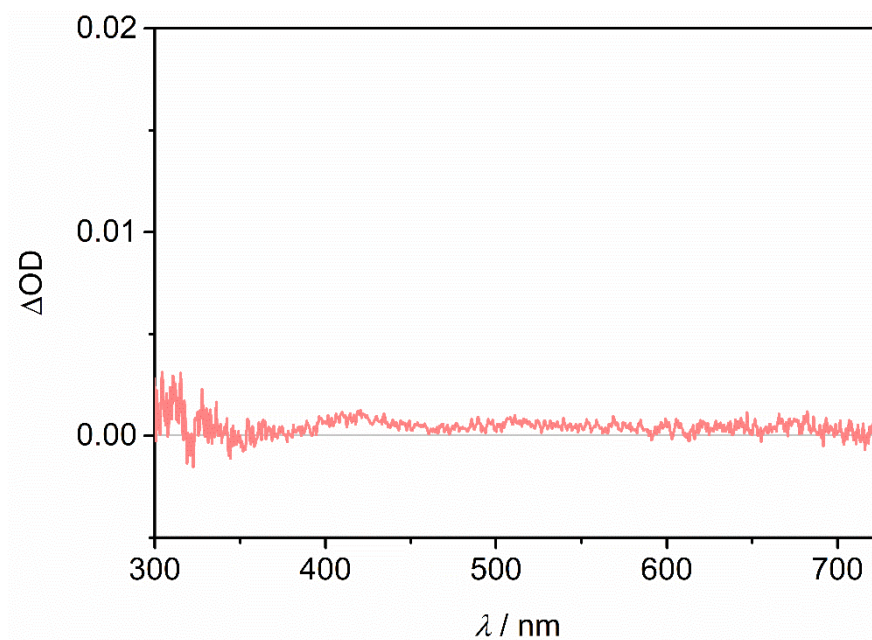


Fig. S23. Transient absorption spectrum of a deaerated solution of $[\text{Cr}(\text{tpe})_2][\text{BF}_4]_3$ (350 μM) and 1,4-diazabicyclo[2.2.2]octane (1.45 mM) 3 μs after laser excitation at 355 nm with 2.3 mJ laser pulses of 10 ns duration. No accumulation of $[\text{Cr}(\text{tpe})_2]^{2+}$ could be observed, most likely due to the low cage escape efficiency when this quencher is used. The corresponding kinetic trace is shown in Fig. S22.

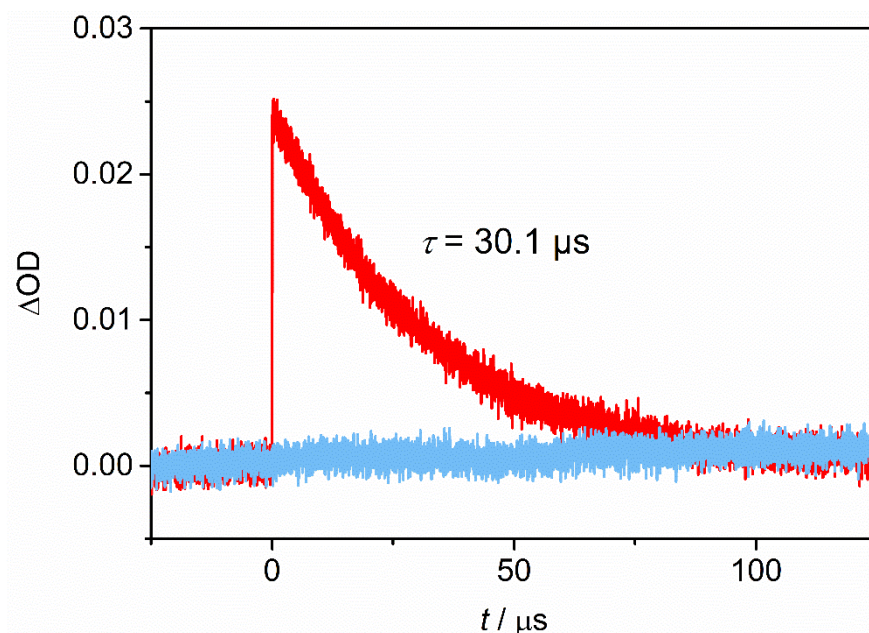


Fig. S24. Transient absorption traces at 346 nm (red), corresponding to the decay of $^*\text{[Cr(tpe)}_2\text{]}^{3+}$ in the presence of 0.27 mM 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct, and at 690 nm (blue), corresponding to the typical detection wavelength used for $\text{[Cr(tpe)}_2\text{]}^{2+}$ after reductive quenching. A 350 μM $\text{[Cr(tpe)}_2\text{][BF}_4\text{]}_3$ solution in deaerated CH_3CN was irradiated at 355 nm with 2.3 mJ laser pulses of 10 ns duration. Transient spectra after different detection delay times are shown in Fig. S25.

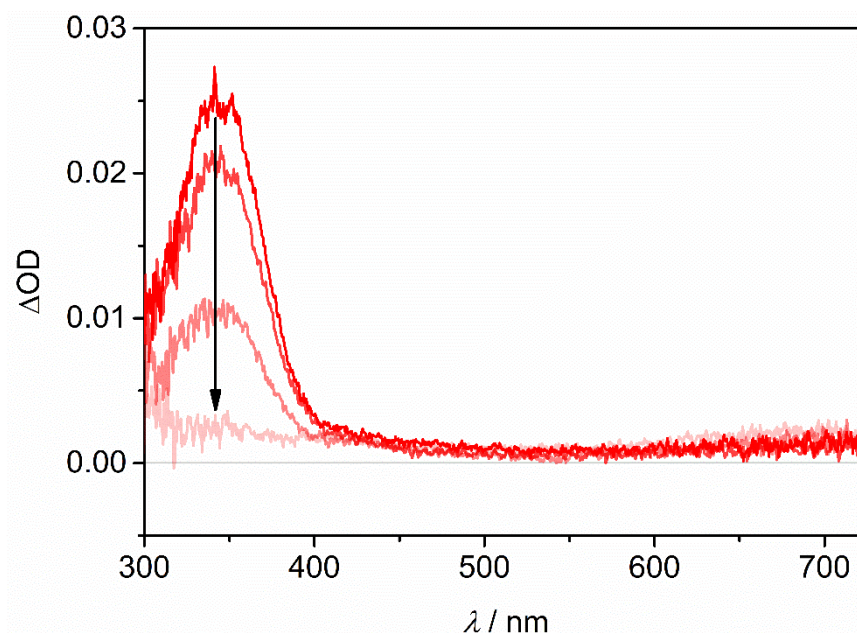


Fig. S25. Transient absorption spectra of a deaerated solution of $\text{[Cr(tpe)}_2\text{][BF}_4\text{]}_3$ (350 μM) and 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (0.27 mM) 10 ns, 10 μs , 30 μs and 100 μs after laser excitation at 355 nm with 2.3 mJ laser pulses of 10 ns duration. No accumulation of $\text{[Cr(tpe)}_2\text{]}^{2+}$ could be observed, most likely due to the low cage escape efficiency when this quencher is used. The corresponding kinetic traces are shown in Fig. S24.

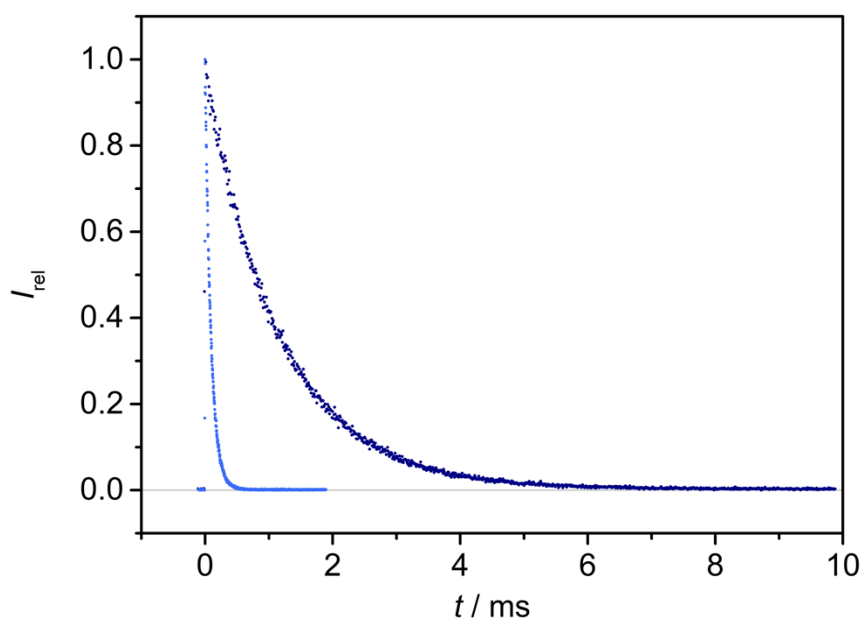


Fig. S26. Reductive Quenching of $^*\text{[Cr(ddpd)}_2\text{]}^{3+}$ by 1,4-diazabicyclo[2.2.2]octane. Emission decay traces recorded at 775 nm following excitation (435 nm, 10 μs pulse duration) of a 0.1 mM solution of $[\text{Cr(ddpd)}_2][\text{BF}_4]_3$ in deaerated acetonitrile without (dark blue) and with 1,4-diazabicyclo[2.2.2]octane (0.12 mM; light blue).

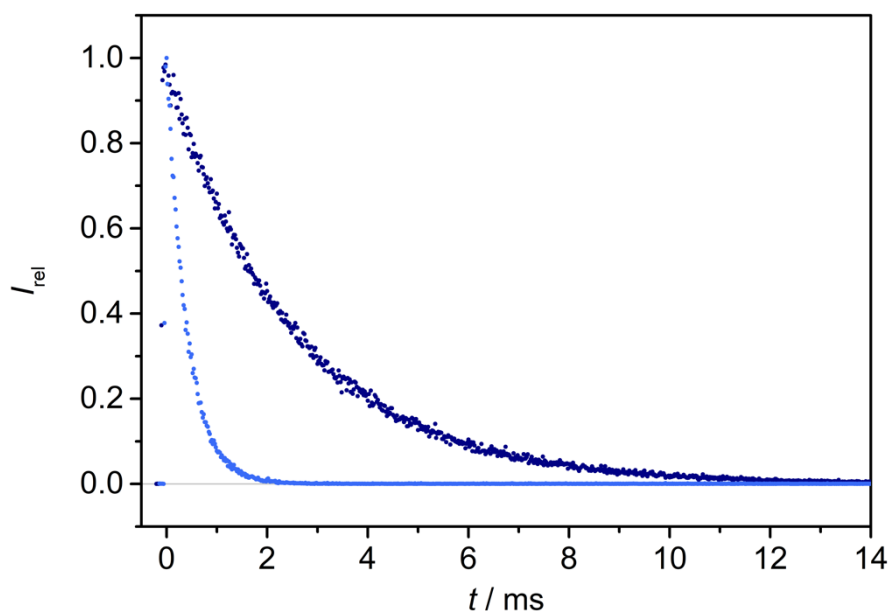


Fig. S27. Reductive Quenching of $^*\text{[Cr(tpe)}_2\text{]}^{3+}$ by 1,4-diazabicyclo[2.2.2]octane. Emission decay traces recorded at 742 nm following excitation (435 nm, 2 μs pulse duration) of a 1 mM solution of $[\text{Cr(tpe)}_2][\text{BF}_4]_3$ in deaerated acetonitrile without (dark blue) and with 1,4-diazabicyclo[2.2.2]octane (0.01 mM; light blue).

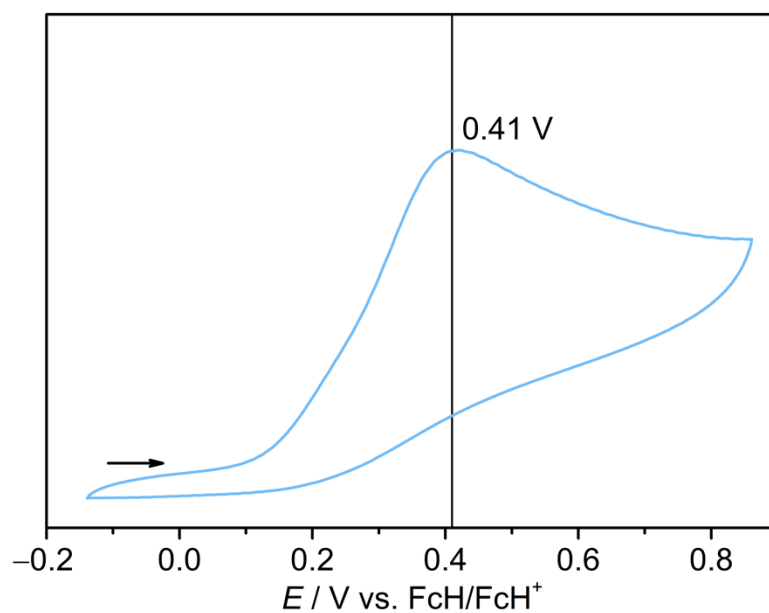


Fig. S28. Cyclic voltammogram of 2 mM 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) in a 100 mM solution of $[n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CH_3CN .

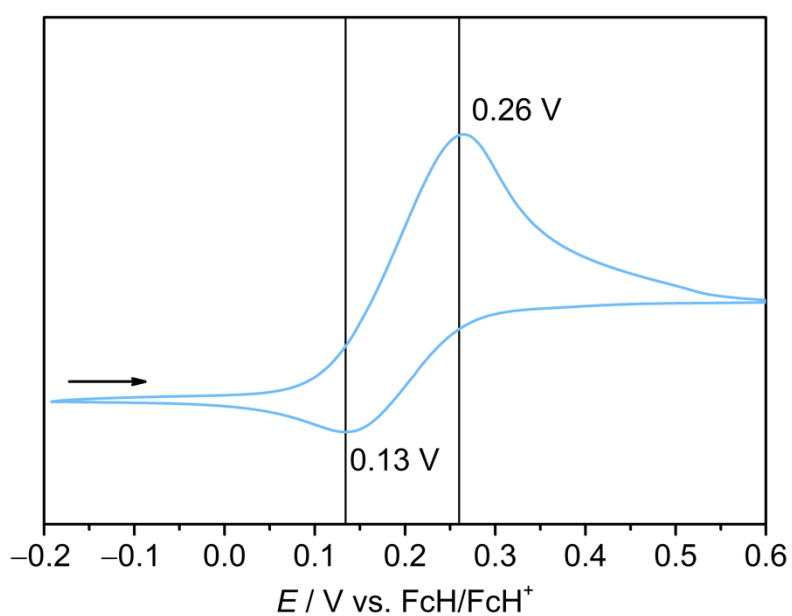


Fig. S29. Cyclic voltammogram of 5 mM 1,4-diazabicyclo[2.2.2]octane in a 100 mM solution of $[n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CH_3CN .

Molar absorption coefficient determination via relative actinometry

To determine the molar absorption coefficient of $^*\text{[Cr(tpe)}_2\text{)]}^{3+}$ relative actinometry was performed. For that purpose, a comparison is made between the transient absorption at a certain wavelength λ_{ref} upon excitation of the reference compound, for which the absorption coefficient ε_{ref} is known, and the absorption change produced under comparable conditions of the sample with unknown absorption coefficient ε_s at a specific wavelength λ_s . With ΔOD as the observed change in optical density and Φ as the (known) quantum yield of intersystem crossing for the production of long-lived excited states, the molar absorption coefficient of the sample is given by equation (1).^[18]

$$\varepsilon_s(\lambda_s) = \frac{\Delta\text{OD}_s \Phi_{\text{ref}}}{\Delta\text{OD}_{\text{ref}} \Phi_s} \varepsilon_{\text{ref}}(\lambda_{\text{ref}}). \quad (1)$$

The concentrations of both solutions (reference and sample) are adjusted so that the same number of excitation photons is absorbed (see Fig. 4a of the main paper).

To quantify the difference molar absorption coefficient at the TA maximum of $^*\text{[Cr(tpe)}_2\text{)]}^{3+}$ in deaerated CH_3CN (346 nm), we used the known and established value of $^3\text{[Ru(bpy)}_3\text{)]}^{2+}$ at its ground state bleach ($\Delta\varepsilon_{455\text{nm}} = -10100 \text{ M}^{-1}\text{cm}^{-1}$) in Ar-saturated aqueous solution.^[19] As the refractive indices of water and acetonitrile differ by less than 1%,^[20] further corrections of the TA data sets are not necessary. The kinetic traces of the transient absorption at 346 nm and 455 nm were recorded after excitation with 2.3 mJ and 13.7 mJ laser pulses of 10 ns duration (Fig. 4b, main paper). The intersystem crossing quantum yield of $[\text{Ru(bpy)}_3]^{2+}$ is well established (100%) and based on recent transient absorption studies with a structurally related chromium(III) complex^[21] we also assume quantitative formation of $^*\text{[Cr(tpe)}_2\text{)]}^{3+}$. Using the maximum change in optical density right after the laser pulse, the difference molar absorption coefficient of $^*\text{[Cr(tpe)}_2\text{)]}^{3+}$ at 346 nm could be determined as $\Delta\varepsilon_{346\text{nm}} = 10600 \text{ M}^{-1}\text{cm}^{-1}$. This is the average value from the two independent measurements with pulse energies of 2.3 mJ and of 13.7 mJ. Saturation or biphotonic decomposition effects can be excluded at these low laser pulse intensities and the two individual results differ by less than 10% from the mean value. During these measurements all conditions remained constant and only the sample was changed to ensure identical excitation and detection conditions.

Raw data sets for cage escape yield determinations

The difference molar absorption coefficient of $^*\text{[Cr(tpe)}_2\text{)]}^{3+}$ at 346 nm $\Delta\varepsilon_{346\text{nm}} = 10600 \text{ M}^{-1}\text{cm}^{-1}$ (see above) and that of $[\text{Cr(tpe)}_2]^{2+}$ at 690 nm $\Delta\varepsilon_{690\text{nm}} = 6440 \text{ M}^{-1}\text{cm}^{-1}$ from Fig. S9 were used for relative concentration determinations of the photoexcited precursor and the reduced complex as quenching product. Identical concentrations and excitation conditions allow us to quantitatively compare the TA signals at both wavelengths. Due to the high stability of the reduced complex, a decrease of the absorption band of $[\text{Cr(tpe)}_2]^{2+}$ at 690 nm in the selected time window is unlikely. The ratio of the corresponding concentrations of $^*\text{[Cr(tpe)}_2\text{)]}^{3+}$ and $[\text{Cr(tpe)}_2]^{2+}$ (the latter has been corrected using the quenching efficiency η_q to avoid an overestimation of the amount of reduced complex that can be generated), gives the cage escape yields η_{ce} for a given system (Table S1). The quenching efficiencies were obtained from lifetime determinations under the conditions of the cage escape yield measurements.

Tab. S1. Raw data sets for cage escape yield determinations of $^*[\text{Cr}(\text{tpe})_2]^{3+}$ with different reductive quenchers Q, concentration c , change in optical density ΔOD at specific wavelengths, quenching efficiency η_q , and cage escape efficiency η_{ce} . See text for details.

Quencher Q (and Fig. with corr. raw data given in brackets)	$c(\text{Q})$ [mM]	$\Delta\text{OD}(^*\text{Cr}^{3+})$ @346nm	η_q	$\Delta\text{OD}(\text{Cr}^{2+})$ @690nm	$c(^*\text{Cr}^{3+})$ [μM]	$c(\text{Cr}^{2+})^{[b]}$ [μM]	η_{ce}
4-aminomorpholine (spectra in Fig. 3b, main paper)	2.1	0.0415	>99%	0.0183	3.92	2.84	73%
CyBF ₃ K (spectra in Fig. 3a, main paper)	2.0	0.0225	91%	0.0034	2.12	0.58	27%
DABCO (Fig. S22 ($^*\text{Cr}^{3+}$) and Fig. S23 (Cr^{2+}))	1.45	0.0221	>99%	<0.0010 ^[a]	2.08	<0.16	<8%
DABSO (Fig. S24 ($^*\text{Cr}^{3+}$) and Fig. S25 (Cr^{2+}))	0.27	0.0245	98.5%	<0.0010 ^[a]	2.31	<0.16	<7%

^[a] Due to a low signal-to-noise ratio, only an upper limit of the formation of the photoproduct could be determined for DABCO and DABSO. ^[b] Corrected using η_q .

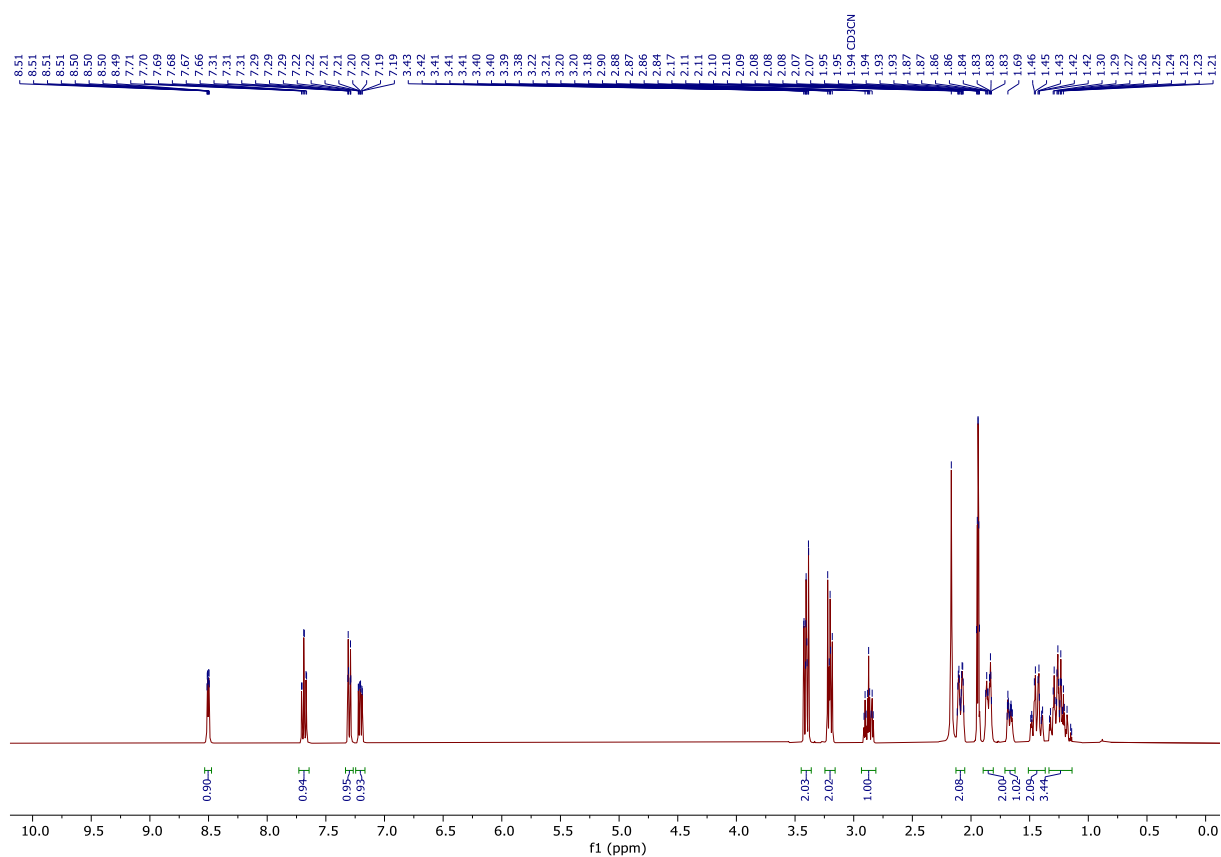


Fig. S30. ¹H (400 MHz) NMR spectra of 2-[2-(cyclohexylsulfonyl)ethyl]pyridine in CD₃CN.

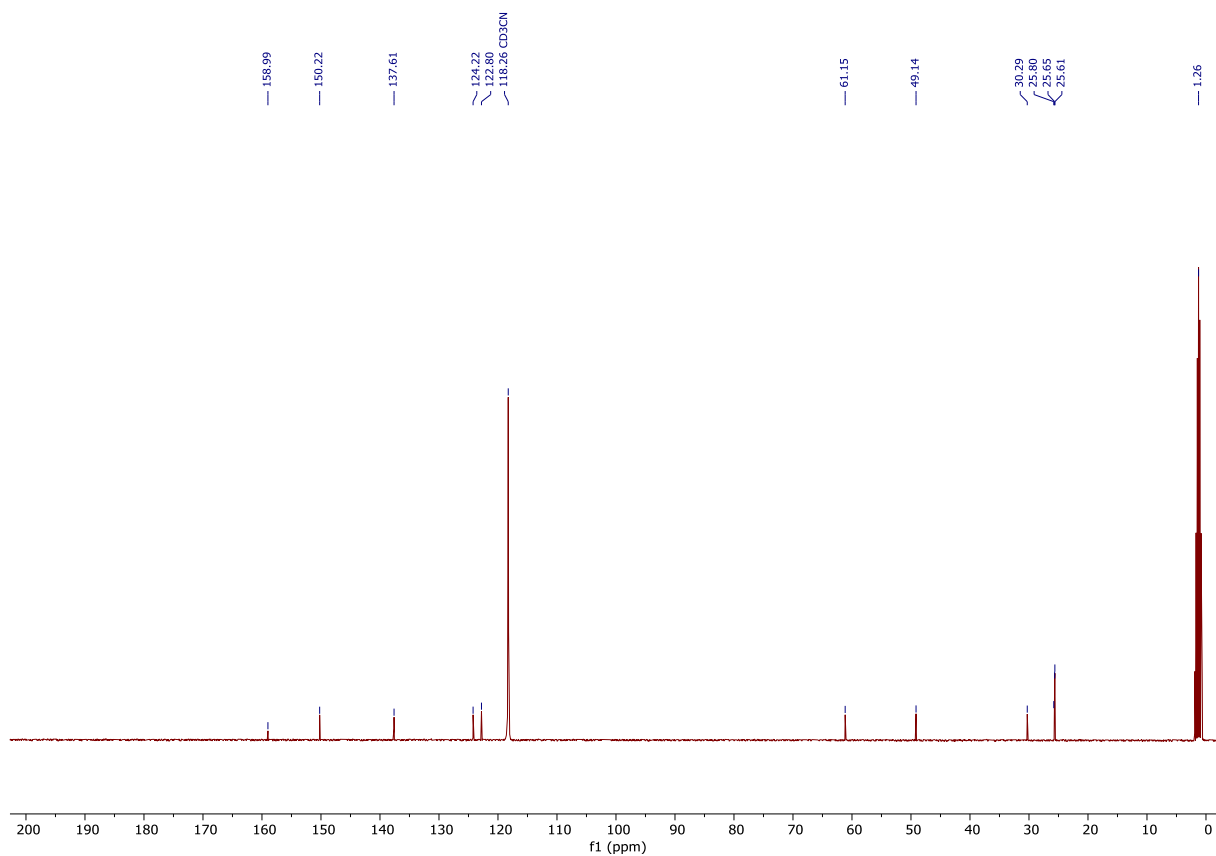


Fig. S31. ¹³C{¹H} (101 MHz) NMR spectra of 2-[2-(cyclohexylsulfonyl)ethyl]pyridine in CD₃CN.

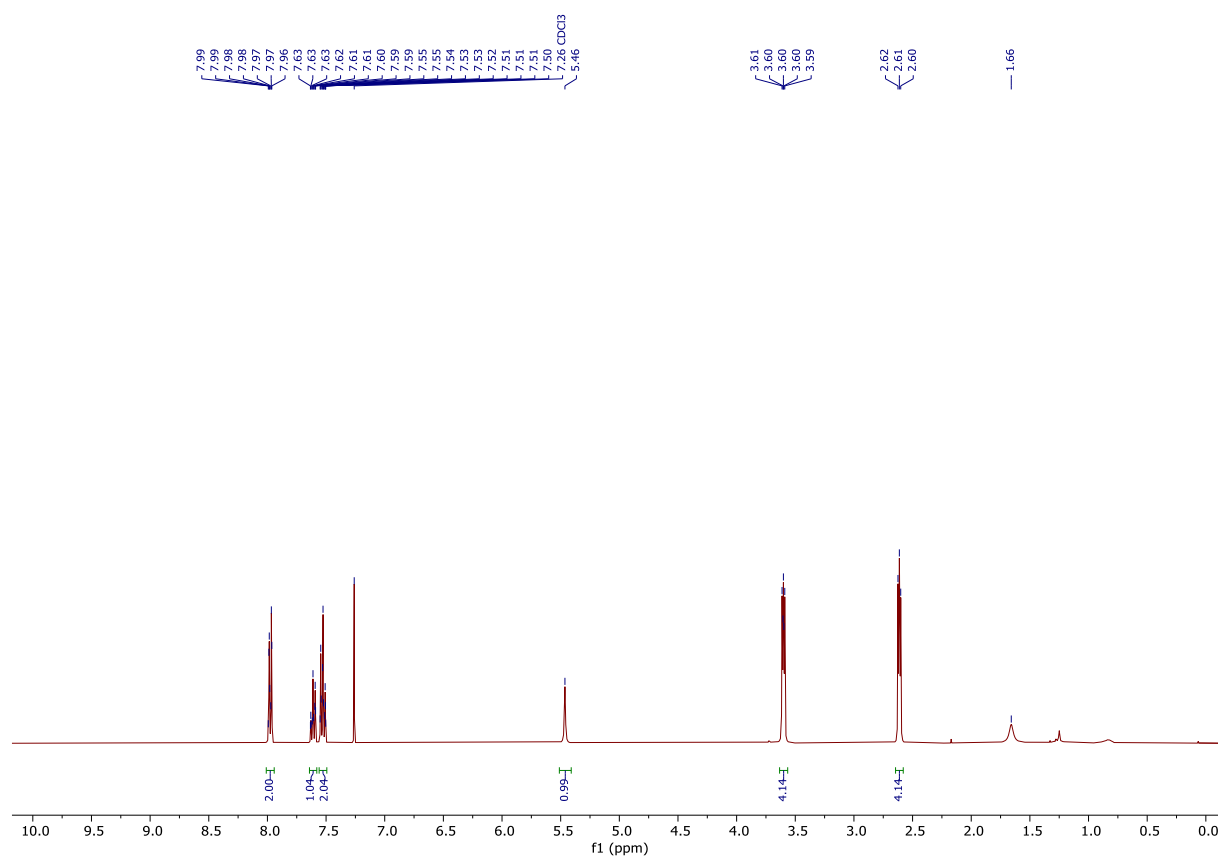


Fig. S32. ^1H (400 MHz) NMR spectra of *N*-4-morpholinylbenzenesulfonamide in CDCl_3 .

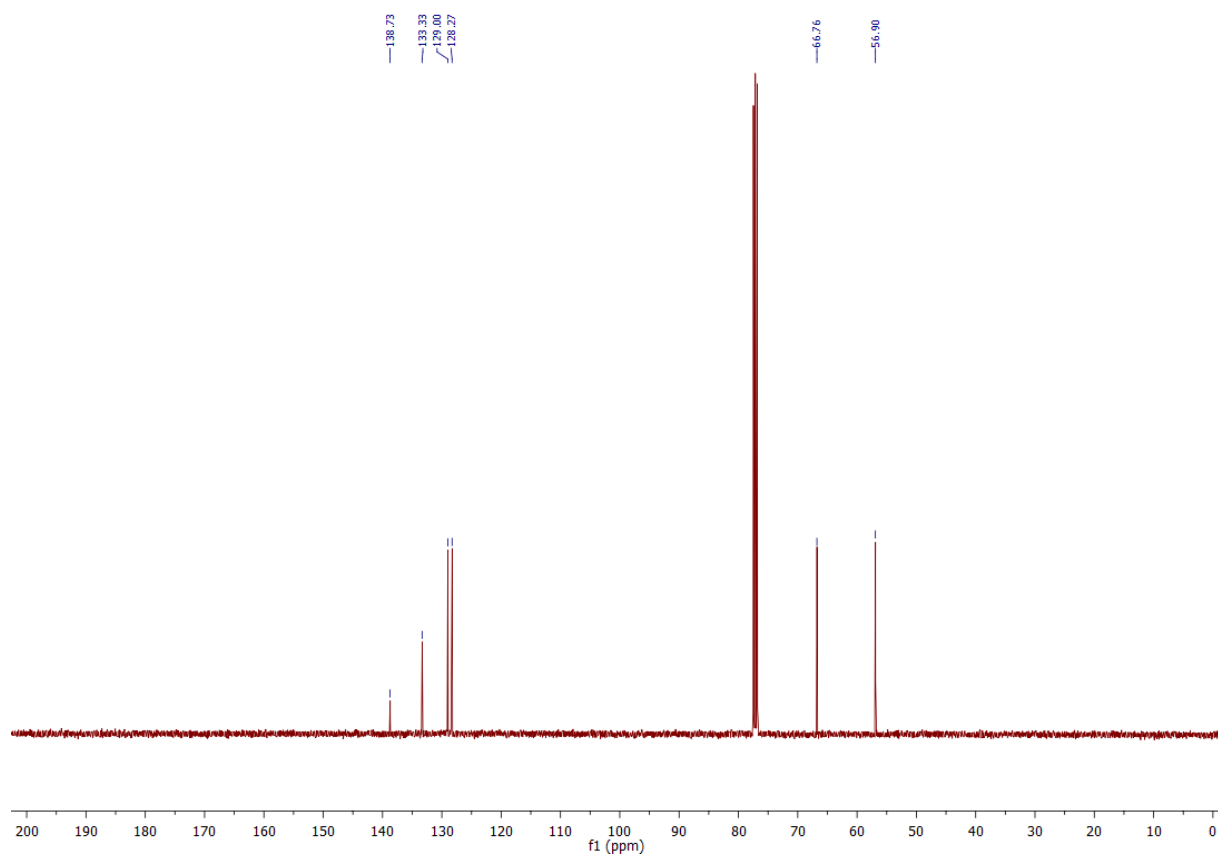


Fig. S33. $^{13}\text{C}\{^1\text{H}\}$ (101 MHz) NMR spectra of *N*-4-morpholinylbenzenesulfonamide in CDCl_3 .

Table S2. Cartesian coordinates of the geometry optimized ion pair [Ph₂I][4-AM-H].

6	-8.082303000	-3.597028000	-19.268763000
6	-8.890094000	-4.708083000	-19.470488000
6	-7.732725000	-2.736978000	-20.301193000
6	-9.367760000	-4.957620000	-20.753750000
6	-8.220061000	-3.000007000	-21.577734000
6	-9.033863000	-4.106338000	-21.802308000
1	-9.148694000	-5.364739000	-18.651660000
1	-7.099355000	-1.879357000	-20.122372000
1	-10.000062000	-5.817632000	-20.929337000
1	-7.959934000	-2.339680000	-22.394149000
1	-9.407558000	-4.306125000	-22.797582000
53	-7.346615000	-3.200934000	-17.294367000
6	-8.972197000	-1.912523000	-16.821174000
6	-8.801895000	-0.549504000	-16.999645000
6	-10.154566000	-2.480290000	-16.376454000
6	-9.881040000	0.282498000	-16.716957000
6	-11.221183000	-1.628726000	-16.101751000
6	-11.084397000	-0.254905000	-16.271223000
1	-7.864491000	-0.140316000	-17.346936000
1	-10.253182000	-3.548278000	-16.248648000
1	-9.774481000	1.350787000	-16.848349000
1	-12.156302000	-2.046395000	-15.753964000
1	-11.918075000	0.399372000	-16.055013000
6	-3.324539000	-0.326299000	-16.375258000
6	-1.916395000	0.240901000	-16.347796000
8	-1.910041000	1.607167000	-15.939753000
6	-2.508253000	1.749553000	-14.652628000
6	-3.935317000	1.229805000	-14.646394000
7	-3.946097000	-0.173948000	-15.057658000
1	-3.295677000	-1.384571000	-16.624977000
1	-3.920885000	0.197420000	-17.140216000
1	-1.474186000	0.207503000	-17.342315000
1	-1.294654000	-0.348442000	-15.663090000
1	-2.489644000	2.811230000	-14.411434000
1	-1.911903000	1.206266000	-13.909514000
1	-4.352591000	1.303107000	-13.642594000
1	-4.552226000	1.841395000	-15.322326000
7	-5.265493000	-0.685095000	-15.012640000
1	-5.742357000	-0.609849000	-15.915941000
16	-5.332361000	-2.337398000	-14.447007000
8	-4.479026000	-3.160262000	-15.361494000
8	-6.799978000	-2.599762000	-14.756652000

References

- [1] S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572–11576; *Angew. Chem.* **2015**, *127*, 11735–11739
- [2] F. Reichenauer, C. Wang, C. Förster, P. Boden, N. Ugur, R. Báez-Cruz, J. Kalmbach, L. M. Carrella, E. Rentschler, C. Ramanan, G. Niedner-Schatteburg, M. Gerhards, M. Seitz, U. Resch-Genger, K. Heinze, *J. Am. Chem. Soc.* **2021**, *143*, 11843–11855.
- [3] S. Treiling, C. Wang, C. Förster, F. Reichenauer, J. Kalmbach, P. Boden, J. P. Harris, L. M. Carrella, E. Rentschler, U. Resch-Genger, C. Reber, M. Seitz, M. Gerhards, K. Heinze, *Angew. Chem. Int. Ed.* **2019**, *58*, 18075–11576; *Angew. Chem.* **2019**, *131*, 18243–11739.
- [4] B. Nguyen, E. J. Emmett, M. C. Willis, *J. Am. Chem. Soc.* **2010**, *132*, 16372–16373.
- [5] L. Martial, L. Bischoff in *Organic Syntheses*, John Wiley & Sons, Inc, Hoboken, NJ, USA, **2013**, pp. 301–305.
- [6] L. Malet-Sanz, J. Madrzak, S. V. Ley, I. R. Baxendale, *Org. Biomol. Chem.* **2010**, *8*, 5324–5332.
- [7] R. J. LeSuer, C. Buttolph, W. E. Geiger, *Anal. Chem.* **2004**, *76*, 6395–6041.
- [8] T. Liu, Y. Li, L. Lai, J. Cheng, J. Sun, J. Wu, *Org. Lett.* **2018**, *20*, 3605–3608.
- [9] N.-W. Liu, S. Liang, G. Manolikakes, *Adv. Synth. Catal.* **2017**, *359*, 1308–1319.
- [10] Y. Yasu, T. Koike, M. Akita, *Adv. Synth. Catal.* **2012**, *354*, 3414–3420.
- [11] M. Dorn, D. Hunger, C. Förster, R. Naumann, J. van Slageren, K. Heinze, *Chem. Eur. J.* **2022**, in press. DOI: 10.1002/chem.202202898.
- [12] T. J. B. Zähringer, J. A. Moghtader, M.-S. Bertrams, B. Roy, M. Uji, N. Yanai, C. Kerzig, *Angew. Chem. Int. Ed.*, in press (DOI: 10.1002/anie.202215340).
- [13] P. M. Becker, C. Förster, L. M. Carrella, P. Boden, D. Hunger, J. van Slageren, M. Gerhards, E. Rentschler, K. Heinze, *Chem. Eur. J.* **2020**, *26*, 7199–7204.
- [14] W. R. Kitzmann, C. Ramanan, R. Naumann, K. Heinze, *Dalton Trans.* **2022**, *51*, 6519–6525.
- [15] F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.
- [16] S. M. Dirk, S. Pylypenko, S. W. Howell, J. E. Fulghum, D. R. Wheeler, *Langmuir* **2005**, *21*, 10899–10901.
- [17] K. H. Vase, A. H. Holm, K. Norrman, S. U. Pedersen, K. Daasbjerg, *Langmuir* **2007**, *23*, 3786–3793.
- [18] I. Carmichael, G. L. Hug, *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.
- [19] a) S. Neumann, C. Kerzig, O. S. Wenger, *Chem. Sci.* **2019**, *10*, 5624–5633; b) P. Müller, K. Brettel, *Photochem. Photobiol. Sci.* **2012**, *11*, 632–636; c) T. H. Bürgin, F. Glaser, O. S. Wenger, *J. Am. Chem. Soc.* **2022**, *144*, 14181–14194; d) M. Goez, C. Kerzig, R. Naumann, *Angew. Chem. Int. Ed.* **2014**, *53*, 9914–9916.
- [20] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Handbook of photochemistry*, CRC/Taylor & Francis, Boca Raton, 3rd ed., **2006**.
- [21] C. Wang, F. Reichenauer, W. R. Kitzmann, C. Kerzig, K. Heinze, U. Resch-Genger, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202238.

6.3 Supporting Information: Gram-Scale Photocatalysis with a Stable and Recyclable Chromium(III) Photocatalyst in Acetonitrile and in Water

Supporting Information

Gram-Scale Photocatalysis with a Stable and Recyclable Chromium(III) Photocatalyst in Acetonitrile and in Water

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Supporting Information

Sustainable Gram-Scale Photocatalysis with a Stable and Recyclable Chromium(III) Photocatalyst in Acetonitrile and in Water

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Experimental Details

General. The photocatalyst $[\text{Cr}(\text{tpe})_2]^{3+}$ was synthesized according to the method detailed below. 2-Ethylpyridine (>98%, TCI), lithium bis(trimethylsilyl)amide (95%, Thermo Fisher Scientific), 2-fluoropyridine (99%, abcr), chromium(III) chloride hexahydrate (>99.5%, Alfa Aesar), zinc ($\geq 99.8\%$ granular, 20–30 mesh, Sigma-Aldrich), $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ for synthesis (>98%, TCI), $[n\text{-Bu}_4\text{N}][\text{NO}_3]$ (98%, Thermo Fisher Scientific), oleic acid ($\geq 99.0\%$, TCI), 4-methoxyphenol (99%, Sigma-Aldrich), dimethylthiocarbomoyl chloride (99%, Thermo Fisher Scientific), sodium hydride (>95%, dry, Sigma-Aldrich), *trans*-anethol (99%, Sigma-Aldrich), 2-phenylisobutyric acid (>98%, TCI), sodium hydroxide (Thermo Fisher Scientific), Selectfluor® ($\geq 95\%$, Sigma-Aldrich), caffeine (*ReagentPlus*®, Sigma-Aldrich), sodium trifluoromethanesulfinate ($\geq 95.0\%$, Sigma-Aldrich), ammonium peroxodisulfate (98%, Thermo Fisher Scientific), THF, dioxane, methanol, diethylether, DMF, acetonitrile for photoreactions (VWR Chemicals, HPLC grade), acetonitrile for spectroscopy (Supelco, hypergrade), water for photoreactions and spectroscopy (Fisher Chemical, Optima® LC/MS), ethylenecarbonate (>99%, Thermo Fisher Scientific), CD_3CN , D_2O and CDCl_3 (Deutero®) were commercially available and used as received. 2,3-Dimethyl-1,3-butadiene (98%, stabilized with 100 ppm 2,6-di-*tert*-butyl-4-methylphenol, Sigma-Aldrich) was distilled before use. $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ for electrochemical experiments ($\geq 99\%$ for electrochemical analysis, Sigma-Aldrich) was dried at 80 °C at reduced pressure (10^{-3} mbar) for three days and then stored under argon.

Electrochemical experiments were carried out on a *BioLogic SP-200* voltammetric analyzer. In water, a glassy carbon electrode was used as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (3 M KCl in water) as the reference electrode. 100 mM KCl as supporting electrolyte and 1 mM of the sample were used. In acetonitrile, the same working- and counter electrodes were used and 10 mM Ag/AgNO₃ (100 mM $[n\text{-Bu}_4\text{N}][\text{ClO}_4]$ in acetonitrile) was used as the reference electrode. 100 mM $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte and 1 mM of the sample were used. Cyclic voltammetry experiments were carried out at scan rates of 50–100 mV s⁻¹. Potentials were referenced relative to the ferrocenium/ferrocene couple. Potentials were then converted to the saturated calomel electrode (SCE) according to Pavlishchuk and Addison.^[1]

UV/vis absorption spectra were recorded on a *Jasco V770* spectrometer using 1.0 cm quartz cells. When needed, 1.00 cm quartz cells with a Schott valve were used to maintain an inert atmosphere. For very dilute solutions, an *Agilent Cary 5000 UV-Vis-NIR spectrophotometer* was used.

Emission spectra and luminescence decay curves were recorded with a *FLS1000 spectrometer* from *Edinburgh Instruments* equipped with the cooled red and NIR sensitive photomultiplier detectors PMT-980 and N-G09 PMT-1700, together covering the entire spectral range between 200 nm and 1700 nm. A xenon arc lamp Xe2 (450 W) was used for excitation in steady-state measurements. Time-resolved luminescence experiments were performed in the multi-channel scaling mode employing a variable pulsed laser VPL-450 ($\lambda_{\text{exc}} = 451.3$ nm, CW output power: 55.0 mW, pulse width: 100 ns to 1000 ms) as excitation source.

Solubility of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in water and acetonitrile and $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in acetonitrile were estimated by stirring an excess amount of the finely powdered complex salt in the respective solvent for 2 h. Due to the generally slow dissolution of the $[\text{PF}_6]^-$ in cold acetonitrile (and the poor solubility of the $[\text{PF}_6]^-$ salt in water and the $[\text{NO}_3]^-$ salt in acetonitrile) the suspensions were heated to 80 °C for 5 minutes. The mixtures were cooled to room temperature and left to stand overnight. The suspensions were filtered and the concentration of the dissolved complex was determined *via* UV/vis absorption spectroscopy. The solubility of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in water was estimated by dissolving small portions of the salt until and undissolved residue remained.

This method was chosen, since the dissolution of the $[\text{NO}_3]^-$ salt is very fast in water at room temperature.

Stern-Volmer analyses were performed in long-neck inert gas 1.00 cm quartz cuvettes with a *Schott* valve. The photocatalyst solutions were irradiated for photochemical self-cleaning for 5 minutes and purged with argon for about 15 minutes using a cannula. The cuvette was then closed under continued argon flow. The emission lifetime was measured, and the obtained value was used as a starting point for the Stern-Volmer analysis. The solution of the quencher was degassed as described above and titrated to the photocatalyst solution using *Eppendorf* pipettes. The resulting solution was purged with argon for about 5 minutes, the cuvette was closed and the emission lifetime of the photocatalyst was measured again. Due to the extremely long excited state lifetime in the millisecond range and the high excited state redox potential of $^*\text{[Cr(tpe)}_2\text{]}^{3+}$ its luminescence is quenched efficiently even by trace impurities. Therefore, it is very challenging to reproducibly obtain the natural lifetime τ_0 . Consequently, highly purified samples and a particularly cautious conduction of the experiments is mandatory, otherwise erroneous τ_0 lower than ms are obtained.

For the Stern-Volmer analysis with sodium 2-phenylisobutyrate, the increasing ionic strength of the solution was accounted for, using the Brønsted-Bjerrum equation (eq. S1):^[2–4]

$$\log k = \log k_0 + 1.018Z_A Z_B \sqrt{\mu} \quad (\text{S1})$$

where k is the rate constant of the quenching, k_0 is the rate constant in a medium of zero ionic strength, $Z_A = +3$ is the charge of $^*\text{[Cr(tpe)}_2\text{]}^{3+}$, $Z_B = -1$ is the charge of 2-phenylisobutyrate and μ is the ionic strength of the solution.

IR spectra were recorded with a *Bruker Alpha II FTIR spectrometer* with an ATR unit containing a diamond crystal. The intensities are qualitatively indicated with weak (w), medium (m) and strong (s).

Intensity data for crystal structure determination of $[\text{Cr(tpe)}_2][\text{NO}_3]_3$ were collected with a *STOE IPDS-2T* diffractometer from STOE & CIE GmbH with an Oxford cooling using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The diffraction frames were integrated using the STOE X-Area^[5] software package and were corrected for absorption with MULABS^[6] of the PLATON software package.^[7] The structures were solved with SHELXT^[8] and refined by the full-matrix method based on F^2 using SHELXL^[9] of the SHELX^[10] software package and the ShelXle^[11] graphical interface. 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-2387074..

Crystallographic data of $[\text{Cr(tpe)}_2][\text{NO}_3]_3$: $\text{C}_{38}\text{H}_{46}\text{Cr}_3\text{N}_9\text{O}_{13}$ (888.84); triclinic; $P\bar{1}$, $a = 11.046(2) \text{ \AA}$, $b = 11.427(2) \text{ \AA}$, $c = 18.618(4) \text{ \AA}$, $\alpha = 72.82(3)^\circ$, $\beta = 89.91(3)^\circ$, $\gamma = 64.09(3)^\circ$; $V = 1997.1(9) \text{ \AA}^3$, $Z = 2$; density (calculated) = 1.478 g/cm^3 ; $T = 120(2) \text{ K}$; $\mu = 0.365 \text{ mm}^{-1}$; $F(000) = 930$; crystal size $0.700 \times 0.620 \times 0.520 \text{ mm}^3$; $\theta = 2.565$ to 27.915 deg. ; $-14 \leq h \leq 14$, $-15 \leq k \leq 14$, $-24 \leq l \leq 24$; rfln collected = 20467; rfln unique = 9469 [$R(\text{int}) = 0.0428$]; completeness to $\theta = 25.242 \text{ deg.} = 99.7 \%$; semi empirical absorption correction from equivalents; max. and min. transmission 1.1875 and 0.8340; Data 9469; restraints 346; parameters 687; goodness-of-fit on $F^2 = 1.060$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0442$, $wR_2 = 0.1146$; R indices (all data) $R_1 = 0.0506$, $wR_2 = 0.1203$; largest diff. peak and hole 0.588 and $-0.541 \text{ e \AA}^{-3}$.

NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 400.13 MHz (^1H) or 376.50 MHz (^{19}F). Proton resonances are reported in ppm versus the solvent signal as an internal standard ($\delta(\text{CD}_3\text{CN}) = 1.94$; $\delta(\text{CDCl}_3) = 7.26$; $\delta(\text{D}_2\text{O}) = 4.79$).^[12] Fluorine resonances are reported in ppm versus CFCl_3 ($\delta(\text{CFCl}_3) = 0$) as the external standard. (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (h) = heptet, (m) = multiplet, (br) = broad singlet.

Photolysis experiments were conducted by irradiating dilute solutions ($A \approx 0.01$) of the photocatalysts in long-neck inert gas 1.00 cm quartz cuvettes with a *Schott* valve. An Ultra-High Power collimated LED from *Prizmatix* (UHP-T-460-DI; output power (free): 6.5 W) with a maximum at 456 nm and the centroid at 460 nm was used (Figure S1). The beam of light was focused onto the cuvette with a plano convex lens. At the cuvette the beam diameter was roughly 0.5 cm. The temperature of the irradiated solution was kept at 20 °C with a Peltier module. As discussed for the Stern-Volmer analyses, due high reactivity of $^*\text{[Cr(tpe)}_2\text{]}^{3+}$, even trace impurities, and potentially their oxidation products, will react with the long-lived excited complex $^*\text{[Cr(tpe)}_2\text{]}^{3+}$. Very pure samples are required to ensure the reproducibility of the challenging photolysis experiments.

Cuvette-scale photocatalytic experiments were conducted by irradiating the reaction mixtures in 1.00 cm quartz cuvettes (aerated conditions) or in long-neck inert gas 1.00 cm quartz cuvettes with a *Schott* valve (deaerated conditions). An Ultra-High Power collimated LED from *Prizmatix* (UHP-T-460-DI; output power (free): 6.5 W) with a maximum at 456 nm and the centroid at 460 nm was used (Figure S1). The output power was adjusted individually for each experiment using a UHPTLCC-02-USB controller. The beam of light was focused onto the cuvette with a plano convex lens. At the cuvette the beam diameter was roughly 0.5 cm. The temperature of the irradiated solution was kept at 20 °C with a Peltier module.

Laboratory-scale photocatalytic experiments were performed in a 100 mL round-bottom flask, using the same light source as above, placed at ca. 20 cm distance to the flask. At the flask, the dimensions of the beam were roughly 4x4 cm. The reaction vessel was air-cooled with a fan (Figure S2).

For photocatalytic experiments reaching high turnover numbers a continuous wave laser ($\lambda_{\text{exc}} = 450$ nm; 1 W; *Roithner Lasertechnik GmbH*, RLTMDL-450-1W-3) was used as the light source. A long cuvette with 10 cm path length was used as the reaction vessel. The path length was doubled to 2 x 10 cm by placing a mirror behind the cuvette.

Reaction Quantum Yields were estimated by employing $[\text{Ru}(\text{bpy})_3]^{2+}$ as a chemical actinometer.

For the cuvette scale, a dilute solution of $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ in deaerated MeCN (3 mL) was irradiated in a quartz cuvette with a *Schott* valve, as described for the photolysis experiments. The complex concentration was monitored using the phosphorescence band centered at 620 nm (Figure S26), which was measured with an *FLS1000 spectrometer* from *Edinburgh Instruments*.

For the laboratory scale, a solution of $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ in deaerated MeCN (80 mL), which was isoabsorptive to a 2 mM solution of $[\text{Cr(tpe)}_2]^{3+}$ at 456 nm (emission maximum of the UHP-LED; Figure S24) was irradiated as described for the laboratory-scale photocatalytic experiments. After distinct periods of irradiation, aliquots (1 mL) were taken from the solution and diluted with MeCN (2 mL). These diluted solutions were used to monitor the complex concentration (Figure S25) as described above.

In both cases, the decay of the emission intensities was fitted with a monoexponential fit function (eq. S2).

$$f(t) = A \exp(-t/\tau) \quad (\text{S2})$$

The derivative of this fit function at $t = 0$ (eq. S3) corresponds to the initial decomposition rate N'_{degr} (mol s^{-1}), given by eq. S4. With the literature-known photodegradation quantum yield of $[\text{Ru}(\text{bpy})_3]^{2+}$ in MeCN ($\Phi_{\text{deg}} = 0.022\%$),^[13] the photon absorption rate N'_{abs} (mol s^{-1}) was determined.

$$f'(0) = -A/\tau = N'_{\text{degr}} \quad (\text{S3})$$

$$N'_{\text{abs}} = N'_{\text{degr}}/\Phi_{\text{deg}} \quad (\text{S4})$$

The product formation rate N'_{Prod} (mol s^{-1}) was determined from the NMR spectroscopic reaction controls, recorded after distinct times of irradiation (Figures S20–23). The reaction quantum yields Φ_{R} were determined from eq. S5.

$$\Phi_{\text{R}} = N'_{\text{abs}}/N'_{\text{Prod}} \quad (\text{S5})$$

Photocatalysis using sunlight was performed in a 100 mL round-bottom flask, which was placed in direct sunlight for 8 h (9 am to 5 pm; Aug 28, 2024).

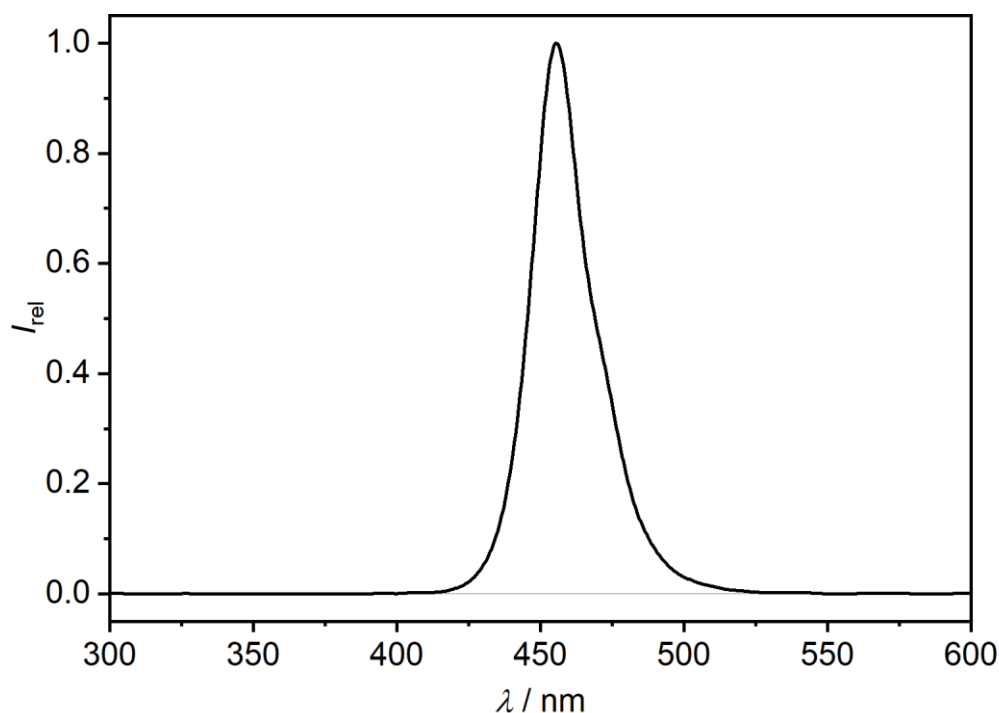


Figure S1. Emission spectrum of the employed LED (UHP-T-460-DI).

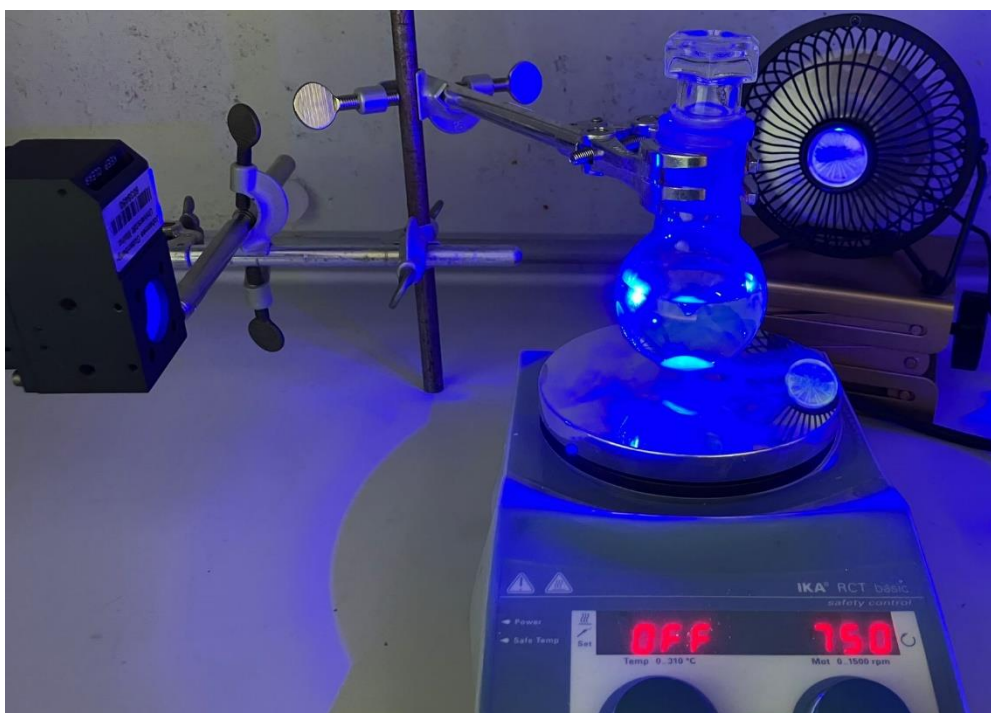


Figure S2. Photograph of the laboratory-scale irradiation setup using a 100 mL round-bottom flask and a 460 nm UHP-LED. The intensity was diminished to 5% to reduce overexposure on the photograph.

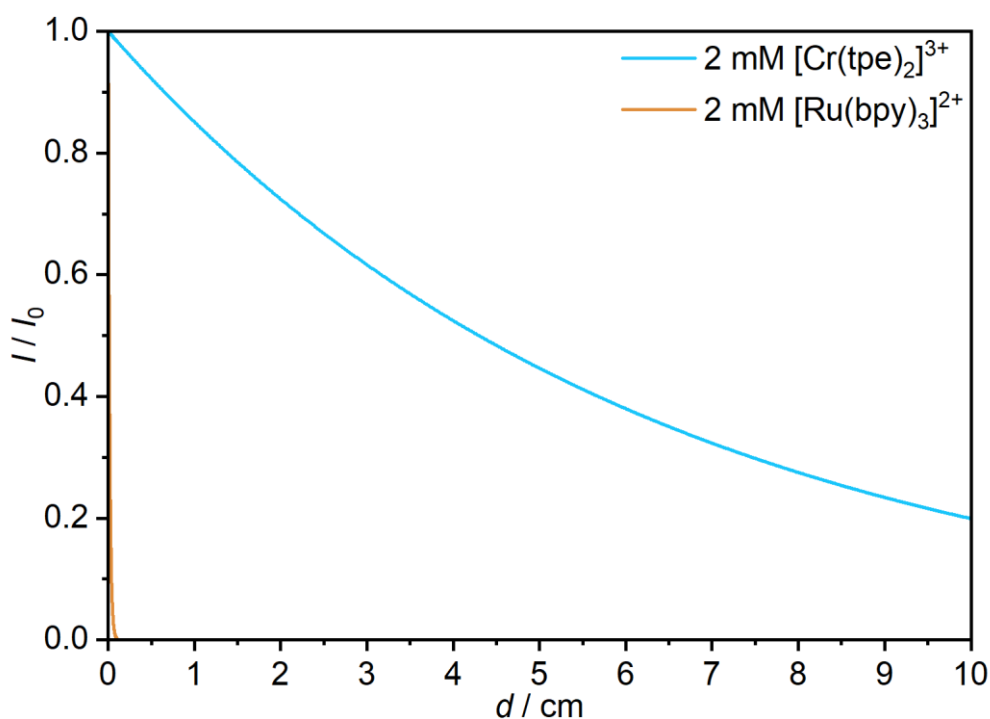


Figure S3. Plot of the light transmission vs. the optical path length for the respective absorption maxima in the visible region for $[\text{Cr}(\text{tpe})_2]^{3+}$ ($\epsilon_{431} = 35 \text{ M}^{-1} \text{ cm}^{-1}$)^[14] and $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\epsilon_{452} = 13000 \text{ M}^{-1} \text{ cm}^{-1}$)^[15] using the Beer-Lambert law.

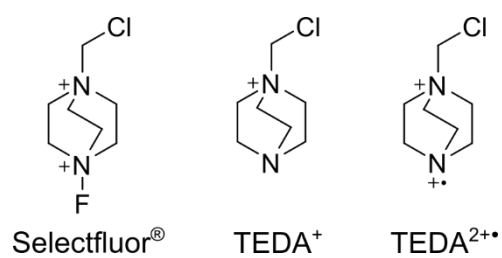
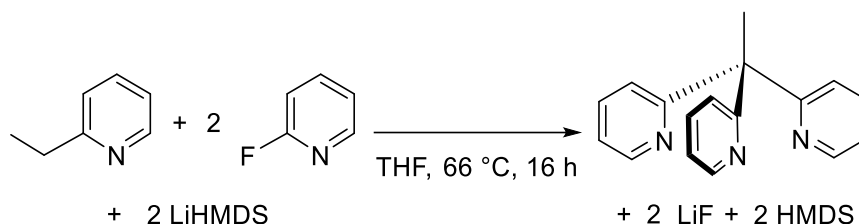


Figure S4. Structures of the cations of Selectfluor[®] and its derivatives TEDA⁺ and TEDA²⁺ (TEDA: *N*-(chloromethyl)triethylenediamine).

Syntheses of [Cr(tpe)₂]³⁺ and Substrates

Synthesis of tpe



The following procedure is carried out under an inert atmosphere until the quenching step. Glassware should be oven-dried and flushed with inert gas.

In a 500 mL three-neck round-bottom flask, lithium bis(trimethylsilyl)amide (LiHMDS; 50.0 g, 299 mmol, 2.05 eq.) is dissolved in 300 mL of dry THF. To this solution, 2-ethylpyridine (15.6 g, 146 mmol, 1.00 eq.) is added via syringe and the mixture is heated under reflux for 1 h. The resulting yellow solution is cooled to room temperature. Subsequently, 2-fluoropyridine (29.0 g, 299 mmol, 2.05 eq.) is added via syringe, yielding a red solution. This solution is heated under reflux for 16 h,^{a)} cooled to room temperature and poured into 150 mL of water containing 150 g of ice. The resulting mixture is stirred for 30 min and changes to a pale-yellow color. THF is removed by rotary evaporation. The remaining aqueous phase is filtered under reduced pressure to remove precipitated LiF and then extracted four times with 100 mL of ethyl acetate. The combined organic extracts are dried over anhydrous sodium sulfate, filtered, and the solvent is removed by rotary evaporation. The obtained product is dried under reduced pressure (10⁻³ mbar) and obtained as a beige solid^{b)} (27.5 g, 105 mmol, 72%).^{c)} This crude product is sufficiently pure for use in the following synthetic steps. If further purification is desired, the product can be recrystallized from acetone (0.8 mL/g), yielding beige crystals (25.3 g, 96.8 mmol, 66%).

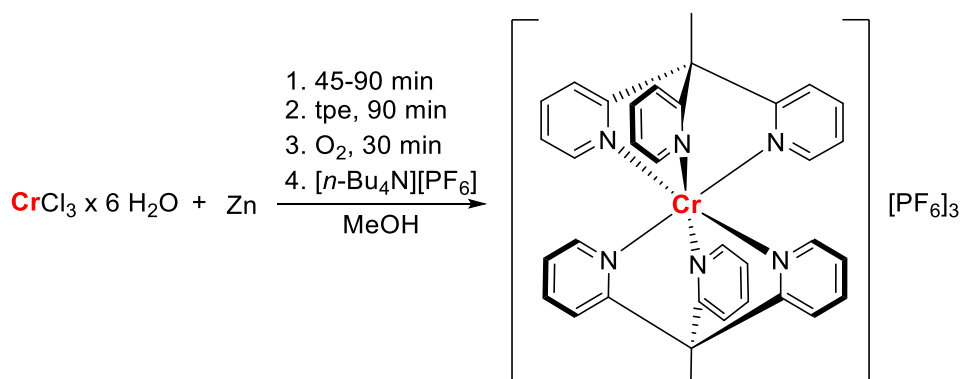
¹H NMR (400 MHz, CD₃CN): δ /ppm = 8.48 (ddd, 3H), 7.62 (ddd, 3H), 7.17 (ddd, 3H), 7.08 (dt, 3H), 2.23 (s, 3H).

^{a)} The reaction time can be shortened, resulting in slightly lower yield. Refluxing the mixture for 2 h yields 60–65% of crude product on a smaller scale (2 g 2-ethylpyridine).

^{b)} The product usually crystallizes during rotary evaporation. Occasionally, it is obtained as a yellow oil, which crystallizes upon standing at room temperature or under reduced pressure.

^{c)} For the synthesis on the scale described above, we used commercially obtained LiHMDS, which showed a light-brown coloration and was slightly damp. Optimization experiments on a smaller scale (2 g 2-ethylpyridine) were conducted with LiHMDS prepared in our laboratory (colorless, free-flowing powder) and gave yields of ca. 85%. It is conceivable, that the quality of the base may influence the yield.

Synthesis of $[\text{Cr}(\text{tpe})_2]^{3+}$



Activation of zinc: To obtain activated zinc for the reduction of chromium(III) to chromium(II) ions, zinc (granular, 20–30 mesh) is suspended under vigorous stirring in 50 mL glacial acetic acid and refluxed for 30 minutes. The suspension is allowed to cool for 5 minutes. The zinc is isolated *via* vacuum filtration on a glass fritted funnel. The metal is washed with water (8x40 mL) and with methanol (3x20 mL).^{d)} The zinc is dried on the glass fritted funnel for three minutes and is immediately used.

^{d)} It is critical to remove any traces of acid to prevent protonation of the tpe ligand during the following steps. To this end it is advisable to wash the activated zinc by filling the glass fritted funnel with water, stirring the solid thoroughly with a spatula and then applying a vacuum to remove the water.

Synthesis of $[\text{Cr}(\text{tpe})_2][\text{X}]_3$ on a laboratory scale:

$\text{CrCl}_3 \times 6 \text{H}_2\text{O}$ (4.00 g, 15.01 mmol, 1.0 eq.) is dissolved into 250 mL of methanol in a Schlenk flask, and the resulting green solution is degassed for 15 minutes. Activated zinc (9.82 g, 150 mmol, 10.0 eq.; weight determined before the activation) is added and the suspension is stirred vigorously for 45 to 90 minutes. During this time the supernatant changes color from green to light blue, indicating the formation of chromium(II).^{e)} In a separate Schlenk flask, tpe (11.76 g, 45.0 mmol, 3.0 eq.) is dissolved in 80 mL of methanol and degassed for 15 minutes. The chromium(II) solution is added to the ligand solution dropwise while stirring. The mixture turns dark green immediately and is stirred for about 90 minutes after the addition is complete.^{f)} The Schlenk flask is opened to air and the solution is stirred under air until the oxidation to chromium(III) is completed, resulting in a color change from dark green to a dark yellow-brown. This oxidation process can be accelerated by bubbling air through the solution. If an undissolved residue is present after the oxidation, the suspension is filtered. The filtrate is added dropwise under stirring to a solution of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ (29.08 g, 75.1 mmol, 5.0 eq.) in methanol (200 mL) yielding $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ as a pale yellow solid. After the addition, the suspension is left to stand for one hour, to complete the precipitation. The solid is filtered, washed with methanol (4x50 mL) and diethylether (2x50 mL) and dried in air. The yield of this crude product is typically around 75–82%. Much of the excess ligand can be reobtained by evaporating the solvent of the filtrate and extracting the solid residue (tpe ligand and $[n\text{-Bu}_4\text{N}][\text{PF}_6]$) with ether (4x30 mL). This recovers ca. 1.90 g of tpe in high purity.

^{e)} The time required for complete reduction varies based on e.g. the flask size and stirring speed. The end point of the reduction is easily recognized by the characteristic light blue color of the chromium(II) solution. In some of the runs we conducted, a slight green tinge remained, however, this didn't seem to impact the yield noticeably. Generally, it is advisable to maintain

a slight overpressure of inert gas on the flask during the reduction step, to avoid potential reoxidation.

⁹⁾ On a smaller scale, this step is easily performed using an argon-flushed syringe. On a larger scale it is recommended to employ cannula transfer. We strongly advise against the use of rubber septa at any point during the syntheses. Instead, parafilm should be used, as we noted that the emission of $[\text{Cr}(\text{tpe})_2]^{3+}$ is quenched when working with rubber septa (likely by escaped plasticizers).

Purification and access to different salts of $[\text{Cr}(\text{tpe})_2]^{3+}$:

To obtain spectroscopically pure $[\text{Cr}(\text{tpe})_2]^{3+}$, it is advised to use spectroscopy grade solvents for the following procedures. This is not necessary for photocatalytic applications.

a) $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$

To access the water soluble $[\text{NO}_3]^-$ salt of the complex, the crude $[\text{PF}_6]^-$ salt is dissolved into hot (around 70°C) acetonitrile (ca. 110 mL/g). The solution is cooled to ca. 40°C and then filtered through a syringe filter. A solution of $[n\text{-Bu}_4\text{N}][\text{NO}_3]$ in MeCN (ca. 0.5 g/mL; 5 eq.) is added, leading to the slow precipitation of yellow $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$, leaving the supernatant liquid almost colorless. The solid is isolated via vacuum filtration and washed with spectroscopy grade acetonitrile (3x20 mL). The product is then dissolved in methanol in the dark⁹⁾ (ca. 50 mL/g), filtered through a syringe filter and crystallized by ether diffusion into the solution. The resulting yellow crystals are isolated by filtration and washed with a small amount of spectroscopy grade acetonitrile.

IR (ATR): $\tilde{\nu} / \text{cm}^{-1} = 3376$ (m, very broad), 3135 (m, CH), 3086 (m, CH), 3035 (m, CH), 1651 (w), 1603 (s), 1470 (s), 1439 (m), 1336 (vs, NO), 1302 (vs), 1217 (m), 1169 (m), 1153 (w), 1108 (m), 1080 (w), 1063 (m), 1036 (s), 852 (m), 828 (m), 773 (m), 759 (m), 719 (m), 658 (m), 639 (s), 563 (m), 507 (m), 447 (s).

b) $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$

To obtain crystals of the $[\text{PF}_6]^-$ salt of the complex, the crude product is dissolved into hot (around 70°C) acetonitrile (ca. 110 mL/g). The solution is cooled to ca. 40°C and filtered through a syringe filter and crystallized by ether diffusion.

If spectroscopically pure $[\text{PF}_6]^-$ salt is required, it is necessary to first obtain the $[\text{NO}_3]^-$ salt and wash it thoroughly with acetonitrile. The powder of the $[\text{NO}_3]^-$ salt can then be dissolved in methanol in the dark, precipitated as the $[\text{PF}_6]^-$ salt with $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ and crystallized as described above.

⁹⁾ We have noticed that a slow photooxidation seems to occur when the complex is dissolved in methanol. To avoid the formation of impurities via this photooxidation, we recommend excluding light during this step.

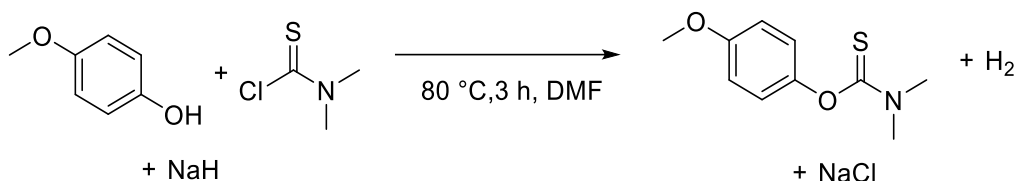
IR (ATR): $\tilde{\nu} / \text{cm}^{-1} = 3140$ (w, CH), 2253 (w, CN), 1604 (m), 1470 (m), 1440 (m), 1390 (w), 1307 (w), 1250 (w), 1219 (w), 1173 (w), 1112 (w), 1060 (m), 1037 (m), 827 (vs, PF), 775 (s), 660 (w), 640 (m), 555 (s, PF), 447 (m).

Table S1. Solubility of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ and $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in water and acetonitrile.

	solubility of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$	solubility of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$
Acetonitrile	ca. 10 g L ⁻¹	ca. 0.8 g L ⁻¹
Water	ca. 1 g L ⁻¹	> 100 g L ⁻¹

The dissolution of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ is generally rather slow and is accelerated by using finely powdered complex salt and/or heating the mixture. While $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ is slightly soluble in acetonitrile, its dissolution is slow and only noticeably observed when heating. At room temperature it is unproblematic to wash $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ with acetonitrile to remove impurities.

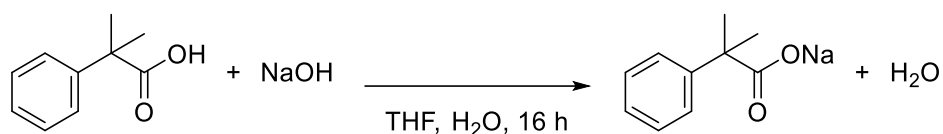
Synthesis of O-(4-methoxyphenyl)-dimethylcarbamothioate



The substrate O-(4-methoxyphenyl)-dimethylcarbamothioate for the photoinduced *Newman-Kwart* rearrangement was synthesized according to a literature procedure in 94% yield.^[16] The thus obtained crude product was purified via recrystallization from ethanol. The colorless crystals were washed twice with 10 mL of ethanol at 0 °C (65% yield). For the photocatalytic experiments the product recrystallized thrice from isopropyl alcohol. NMR data agree with the literature report.^[16]

¹H NMR (400 MHz, CDCl₃): δ /ppm = 7.00–6.96 (m, 2H), 6.92–6.88 (m, 2H), 3.81 (s, 3H), 3.45 (s, 3H), 3.33 (s, 3H).

Synthesis of sodium 2-phenylisobutyrate



2-Phenylisobutyric acid (1.00 g, 6.09 mmol, 1.0 eq.) was dissolved in 3 mL of THF. A solution of sodium hydroxide (0.24 g, 6.00 mmol, 1.0 eq.) in 3 mL of water was added and the mixture was stirred for 1 h at room temperature. THF was removed by rotary evaporation and the aqueous phase was extracted twice with 5 mL of diethyl ether, to remove residual acid. The water was removed by rotary evaporation and the product was obtained as a colorless solid (1.03 g, 5.53 mmol, 91% yield).

¹H NMR (400 MHz, D₂O): δ /ppm = 7.00–6.96 (m, 2H), 6.92–6.88 (m, 2H), 3.81 (s, 3H), 3.45 (s, 3H), 3.33 (s, 3H).

Cost Estimate of $[\text{Cr}(\text{tpe})_2]^{3+}$ and Comparison to Other Common Photocatalysts

We estimated the material cost for the synthesis of $[\text{Cr}(\text{tpe})_2]^{3+}$ by adding up the cost of the reagents used in the ligand and complex syntheses. The price of tpe was calculated assuming a yield of 85%; 82% yield for $[\text{Cr}(\text{tpe})_2]^{3+}$. For the salt metatheses quantitative yields were assumed. The number of equivalents of reagents used was factored in, consistent with the synthetic procedures described above. Most of the zinc (ca. 90%) and about 40% of the excess tpe used can be recycled. However, recycling was not included in the calculation. The price of the solvents and waste was omitted due to their minor costs on the reported scale. The prices of the reagents were obtained from the respective commercial supplier's websites and converted from € to \$, with an exchange rate of 1 € = 1.11 \$ (checked on Sept. 06, 2024).

Table S2. Prices of the reagents used for the synthesis of the ligand tpe and estimated cost.

Reagent	Price per g / \$	Price per mol / \$	Source	Checked
2-Ethylpyridine (97%)	1.35	145	Merck	Sept. 05, 2024
2-Fluoropyridine (99%)	0.84	81.90	abcr	Sept. 05, 2024
LiHMDS (95%)	2.00	128	ThermoFisher	Sept. 05, 2024
tpe	2.58	677	-	-

Table S3. Prices of the reagents used for the synthesis of the different salts of $[\text{Cr}(\text{tpe})_2]^{3+}$.

Reagent	Price per g / \$	Price per mol / \$	Source	Checked
Zinc (>99.8%)	0.18	12.30	Merck	Sept. 05, 2024
Chromium(III)chloride Hexahydrate (99.5%)	0.47	124	ThermoFisher	Sept. 05, 2024
tpe	2.58	677	-	-
$[\text{n-Bu}_4\text{N}][\text{PF}_6]$ (98%)	1.89	735	Merck	Sept. 05, 2024
$[\text{n-Bu}_4\text{N}][\text{NO}_3]$ (98%)	3.14	862	ThermoFisher	Sept. 05, 2024
$[\text{Cr}(\text{tpe})_2]\text{Cl}_3$	4.07	2780	-	-
$[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$	6.39	6460	-	-
$[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$	14.77	11200	-	-

To estimate the material cost of the previously described synthesis of the title complex, the literature yield of 62%, as well as the equivalents of reagents given in the publication were used.^[14]

Table S4. Prices of the reagents used for the synthesis of $[\text{Cr}(\text{tpe})_2]^{3+}$ using the previously described procedure.

Reagent	Price per g / \$	Price per mol / \$	Source	Checked
Chromium(II)chloride (>98.0%)	11.59	1420	TCI	Sept. 11, 2024
tpe	2.58	677	-	-
$[\text{Cr}(\text{tpe})_2]\text{Cl}_3$	6.72	4590	-	-

Table S5. Price comparison between **[Cr(tpe)₂][PF₆]₃** and various commercially available photocatalysts. This merely serves to compare orders of magnitude, since e.g. labor or distribution cost have not been assessed for the title compound.

Photocatalyst	Price per g / \$	Price per mol / \$	Supplier	Checked
[Cr(tpe) ₂][PF ₆] ₃	7.19	6460	-	-
[Ru(bpy) ₃][PF ₆] ₂ (95%)	186	160000	ThermoFisher	Sept. 05, 2024
[Ru(bpz) ₃][PF ₆] ₂ (95%)	2010	1700000	Merck	Sept. 06, 2024
Ir(ppy) ₃ (>98%)	1060	696000	tci	Sept. 05, 2024
[Ir(dF(CF ₃)ppy) ₂ (dtbpy)][PF ₆]	1070	1200000	Merck	Sept. 06, 2024
9-Mesityl-10-methylacridinium tetrafluoroborate	160	63800	Merck	Sept. 06, 2024
1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4-CzIPN; 99%)	2720	2100000	abcr	Sept. 06, 2024
2,4,6-Triphenylpyrylium tetrafluoroborate (97%)	5.33	2110	ThermoFisher	Sept. 06, 2024

Optical Properties of $[\text{Cr}(\text{tpe})_2]^{3+}$

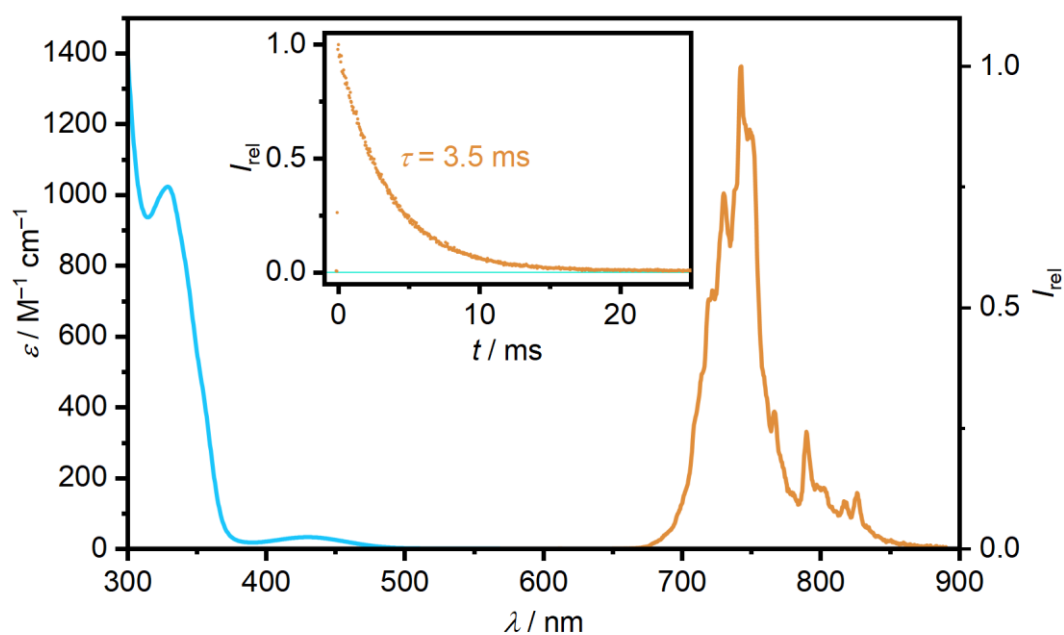


Figure S5. UV/vis absorption spectrum (blue) and emission spectrum (orange) of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile. Inset, emission decay trace recorded at 742 nm.

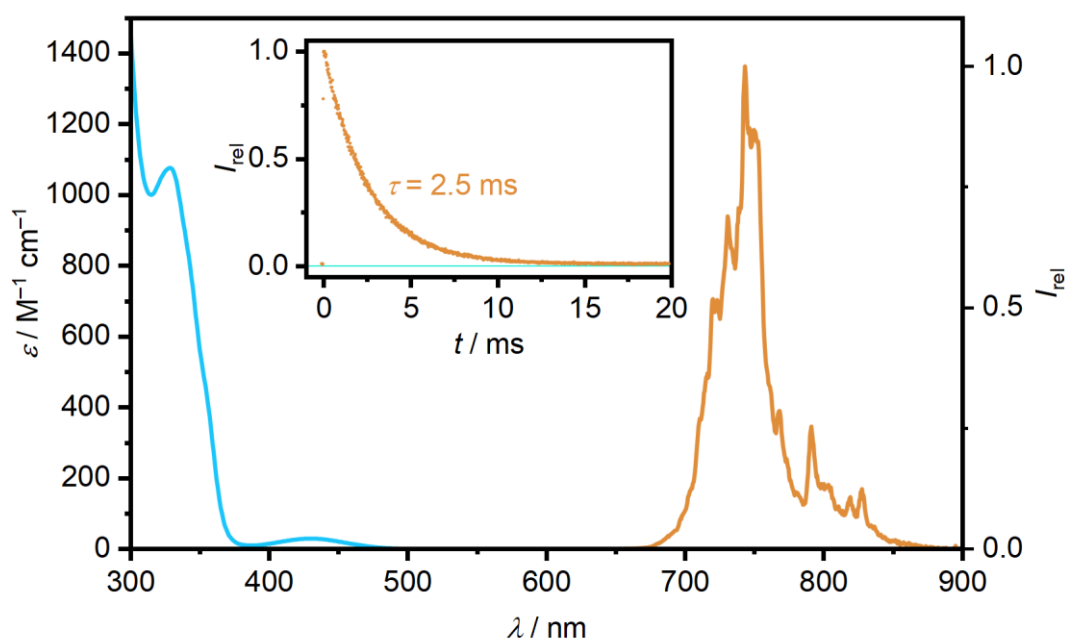


Figure S6. UV/vis absorption spectrum (blue) and emission spectrum (orange) of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in water. Inset, emission decay trace recorded at 742 nm.

Photostability of $[\text{Cr}(\text{tpe})_2]^{3+}$

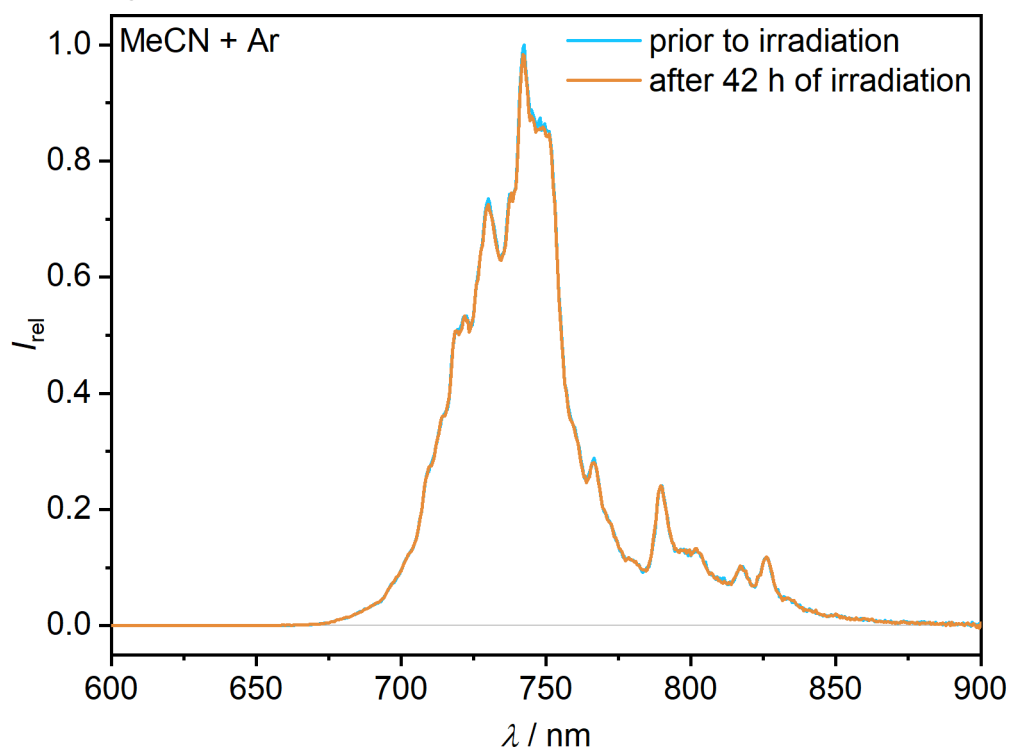


Figure S7. Emission spectra of solutions of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile under deaerated conditions before and after irradiation at 460 nm using a 6.5 W UHP-LED for 42 h. Spectra are normalized to the emission maximum prior to irradiation.

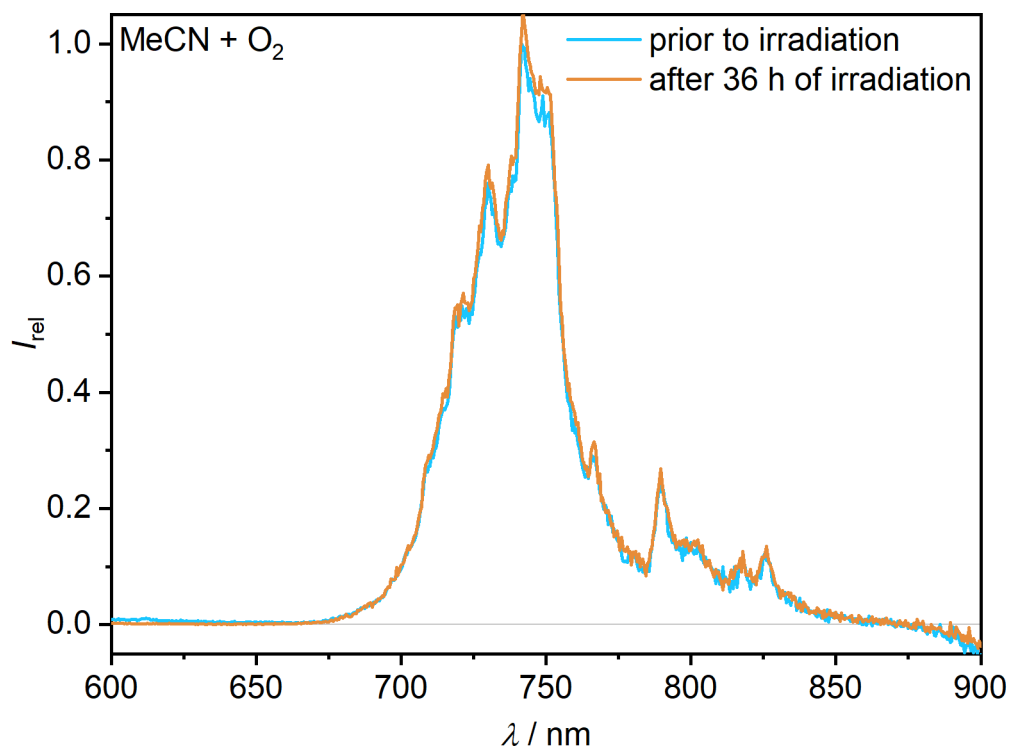


Figure S8. Emission spectra of solutions of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile under aerated conditions before and after irradiation at 460 nm using a 6.5 W UHP-LED for 36 h. Spectra are normalized to the emission maximum prior to irradiation.

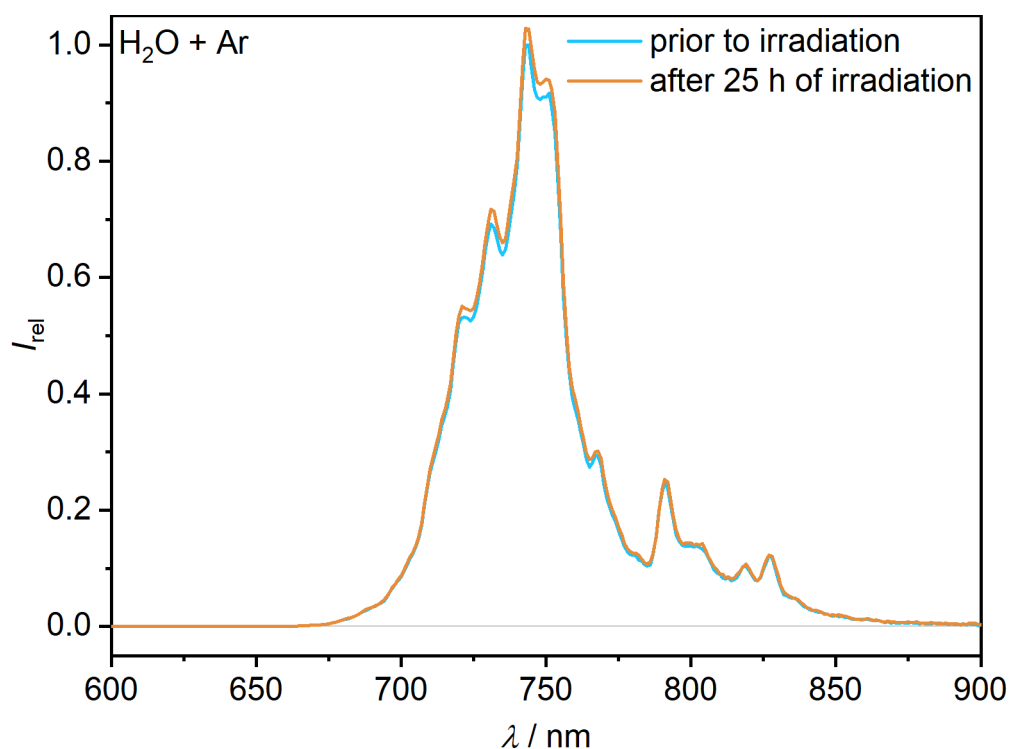


Figure S9. Emission spectra of solutions of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in water under aerated conditions before and after irradiation at 460 nm using a 6.5 W UHP-LED for 25 h. Spectra are normalized to the emission maximum prior to irradiation.

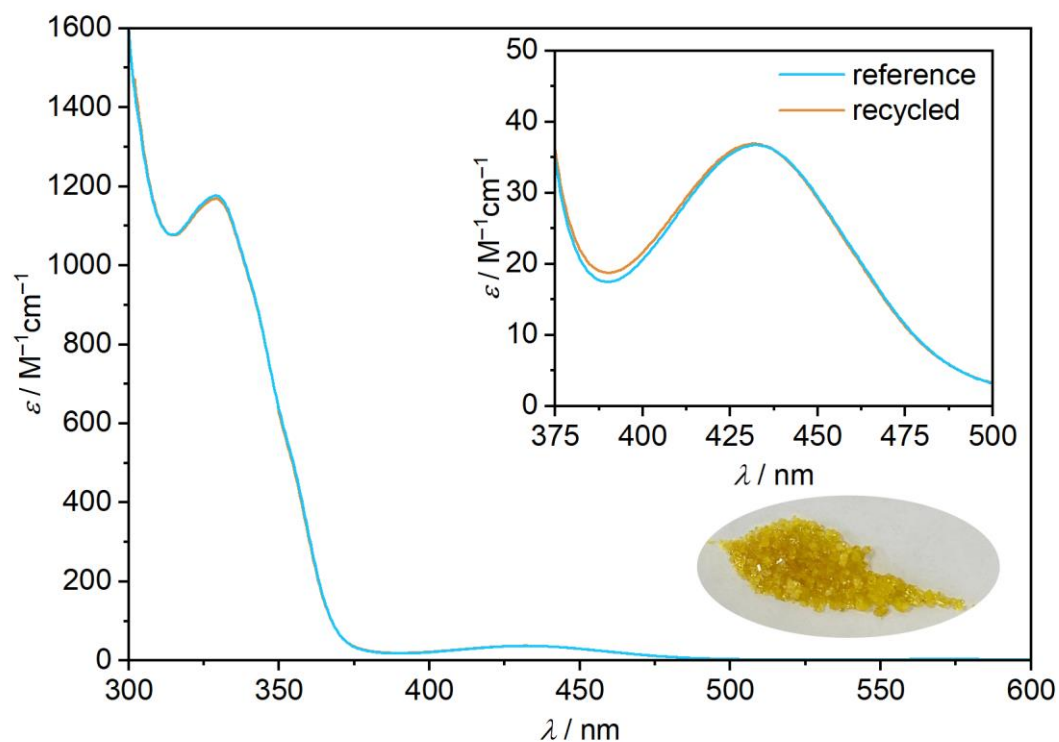


Figure S10. UV/vis absorption spectra of a $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ reference sample (blue) and of a sample recycled after the photocatalytic Newman-Kwart rearrangement (orange) in acetonitrile. The photograph shows the recovered and crystallized catalyst.

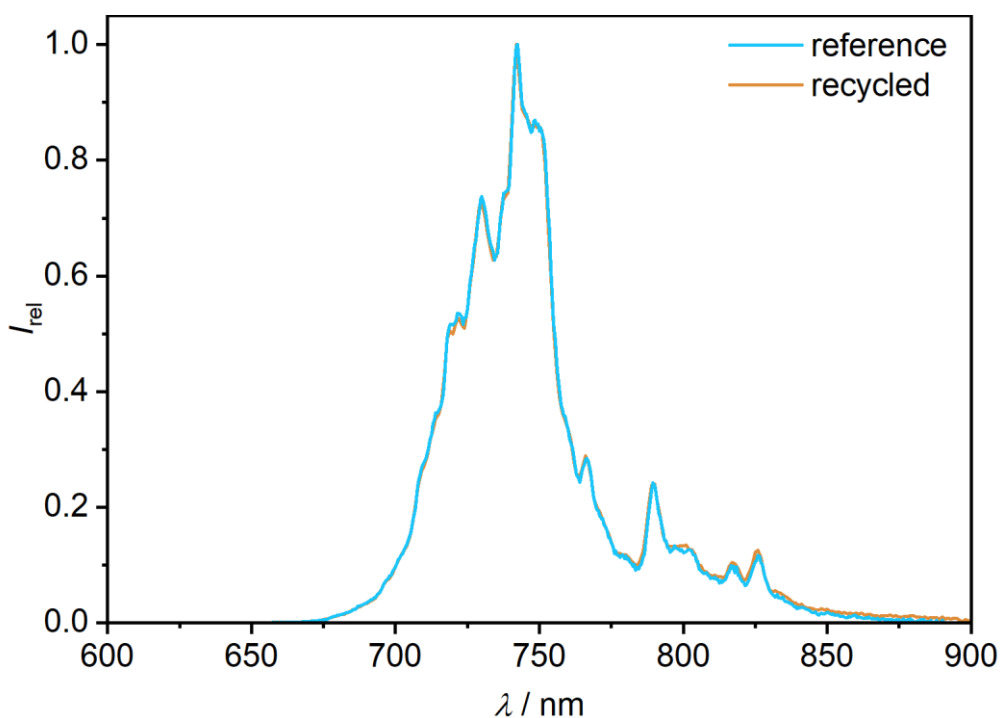


Figure S11. Normalized emission spectra of a $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ reference sample (blue) and of a sample recycled after the photocatalytic Newman-Kwart rearrangement (orange) in acetonitrile.

Cyclic Voltammetry of $[\text{Cr}(\text{tpe})_2]^{3+}$

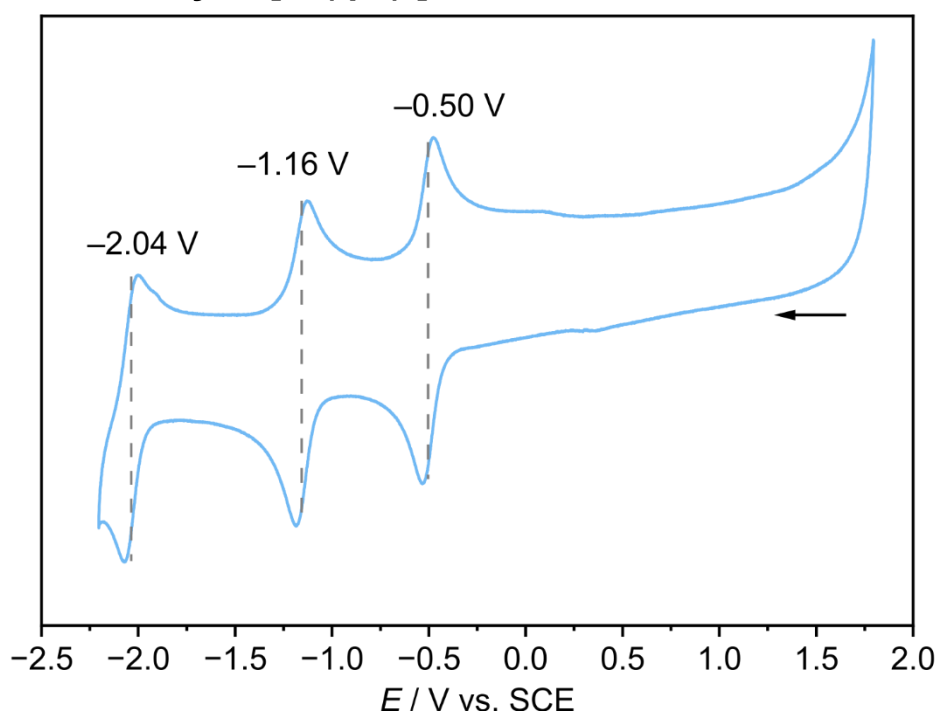


Figure S12. Cyclic voltammogram of 1 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in a 100 mM solution of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ in acetonitrile.

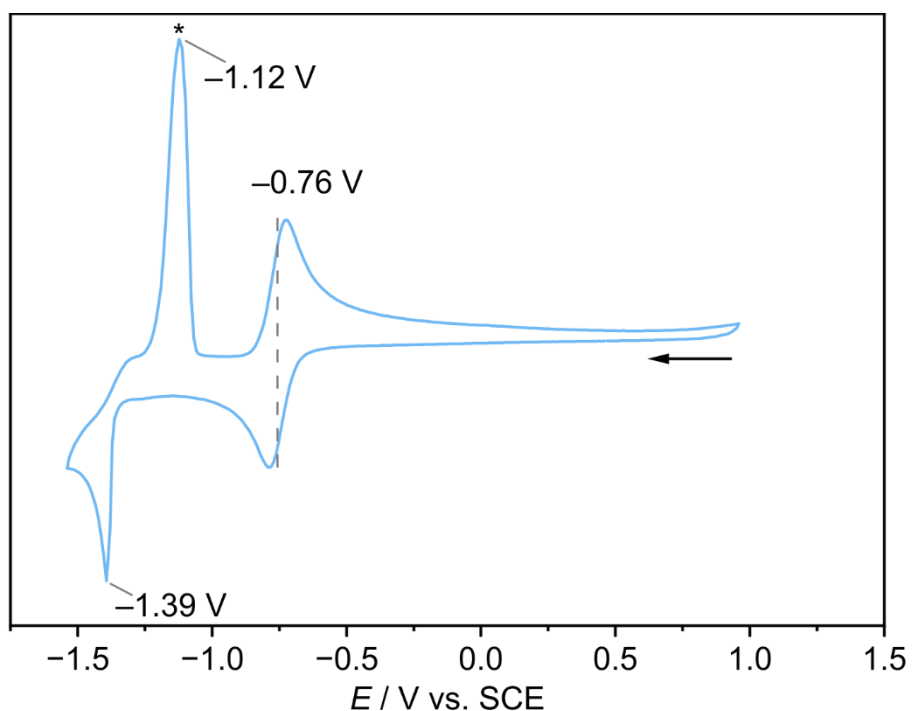


Figure S13. Cyclic voltammogram of 1 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in a 100 mM solution of KCl in water. * This oxidative stripping peak only occurs after the irreversible reduction at -1.39 V.

Structural Data of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$

Table S6. Bond lengths [Å] and angles [deg] of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3 \times 4 \text{ MeOH}$ from XRD measurements. Two independent cations in the asymmetric unit. Both independent cations possess crystallographic inversion symmetry.

Length/Å	$[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ $\times 4 \text{ MeOH}$
Cr1-N1	2.041(2)
Cr1-N2	2.044(2)
Cr1-N3	2.043(2)
Cr2-N4	2.044(2)
Cr2-N5	2.036(2)
Cr2-N6	2.043(2)
Angles/deg	
N1-Cr1-N2	86.52(7)
N1-Cr1-N3	86.69(6)
N2-Cr1-N3	86.76(6)
N5-Cr2-N4	86.85(7)
N6-Cr2-N4	87.01(6)
N6-Cr2-N5	86.56(6)
N1-Cr1-N1 ⁺	180.0

N2-Cr1-N2'	180.0
N3 -Cr1-N3'	180.0
N4-Cr2-N4'	180.0
N5-Cr2-N5'	180.0
N6-Cr2-N6'	180.0

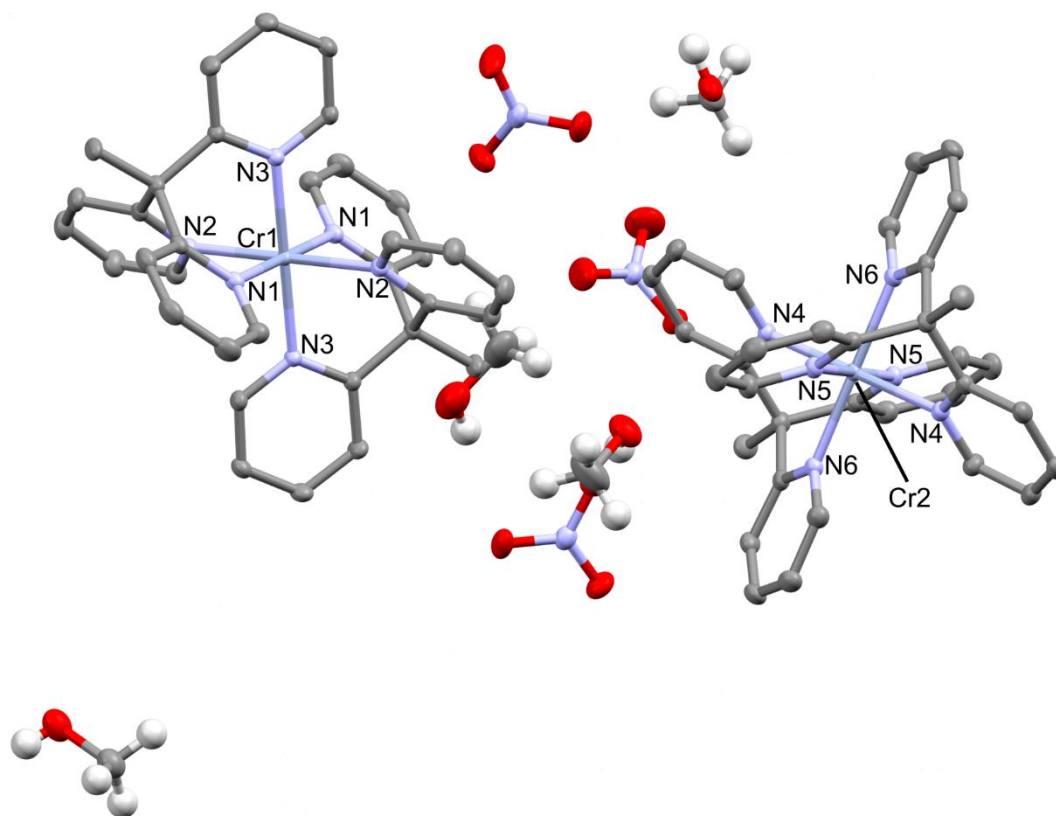


Figure S14. Molecular structures of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3 \times 4 \text{ MeOH}$ with two independent cations. Thermal ellipsoids set to 50% probability. The numbering of atoms corresponds to that used in Table S5. Hydrogen atoms of the complex cations omitted for clarity.

IR Spectra of $[\text{Cr}(\text{tpe})_2]^{3+}$

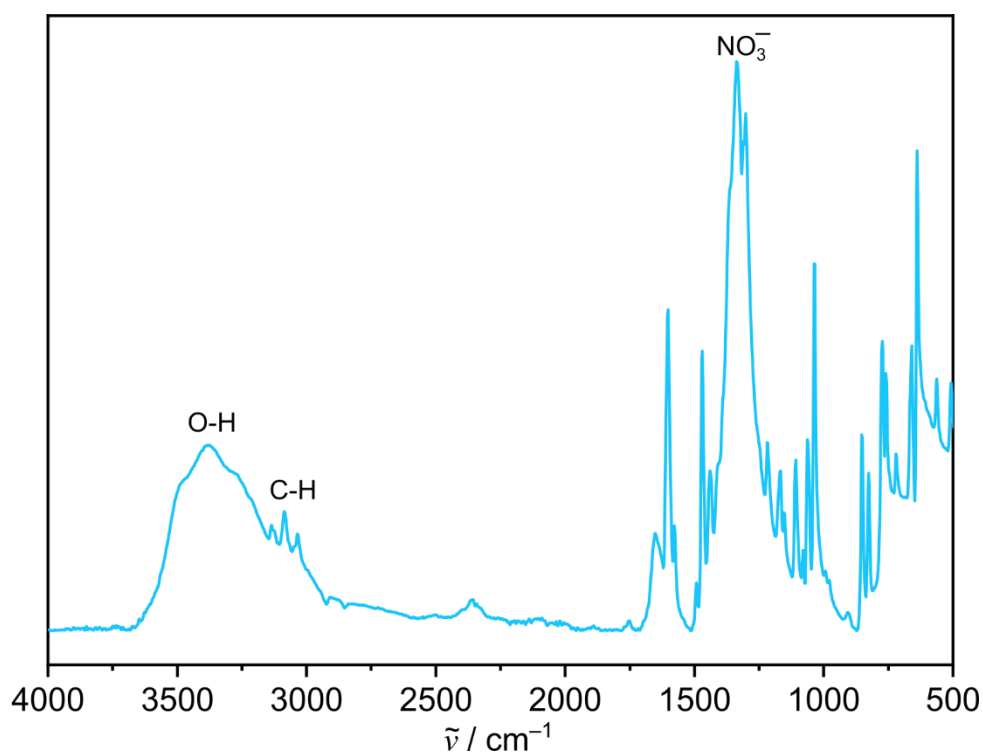


Figure S15. ATR-IR spectrum of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3 \times 4 \text{ MeOH}$. Some of the characteristic bands have been assigned.^[17]

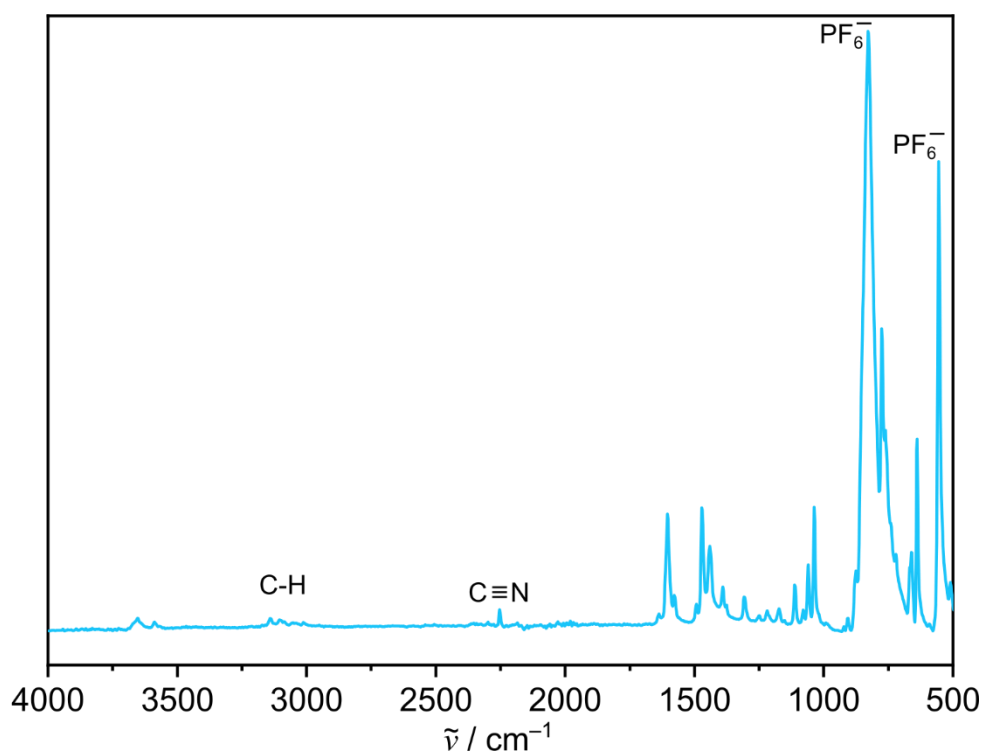


Figure S16. ATR-IR spectrum of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3 \times \text{MeCN}$. Some of the characteristic bands have been assigned.^[14,17]

Stern-Volmer Analyses of $[\text{Cr}(\text{tpe})_2]^{3+}$ with Substrates

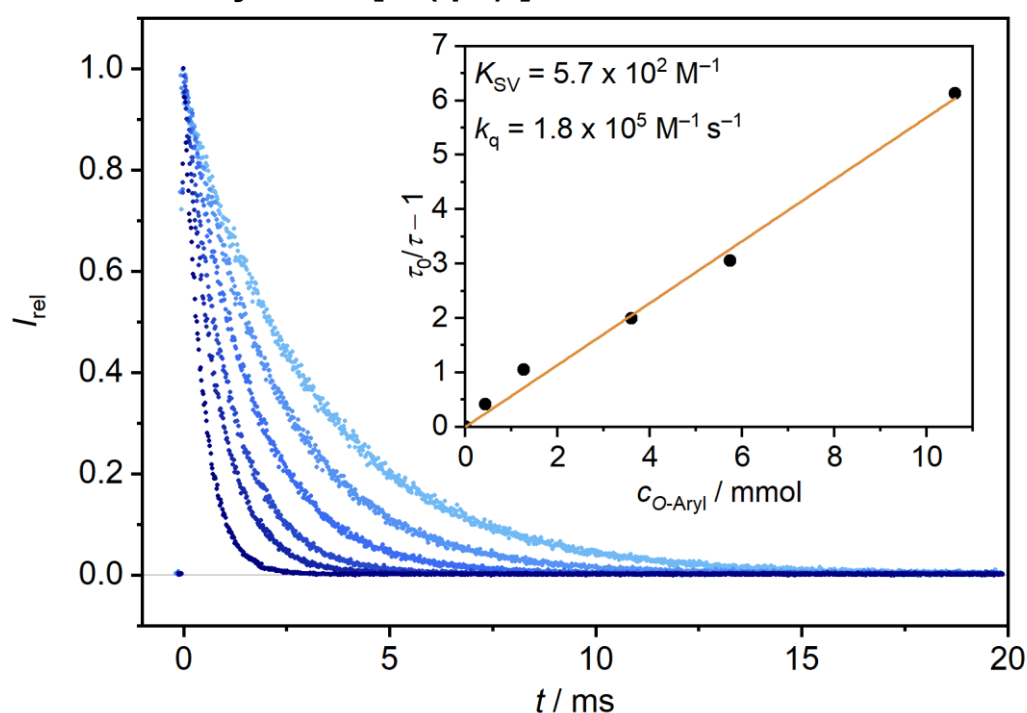


Figure S17. Reductive quenching of $[\text{Cr}(\text{tpe})_2]^{3+}$ by O-(4-methoxyphenyl) dimethylcarbamothioate (indexed as: O-Aryl). Main plot, emission decay traces recorded at 742 nm following excitation (451.3 nm, 10 μs pulse duration) of a $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ (1 mM) solution in deaerated acetonitrile with variable amounts of quencher (0 mM, 0.4 mM, 1.2 mM, 3.6 mM, 5.8 mM, 11 mM). Inset, corresponding Stern-Volmer plot with linear regression; obtained values for K_{SV} and k_{q} .

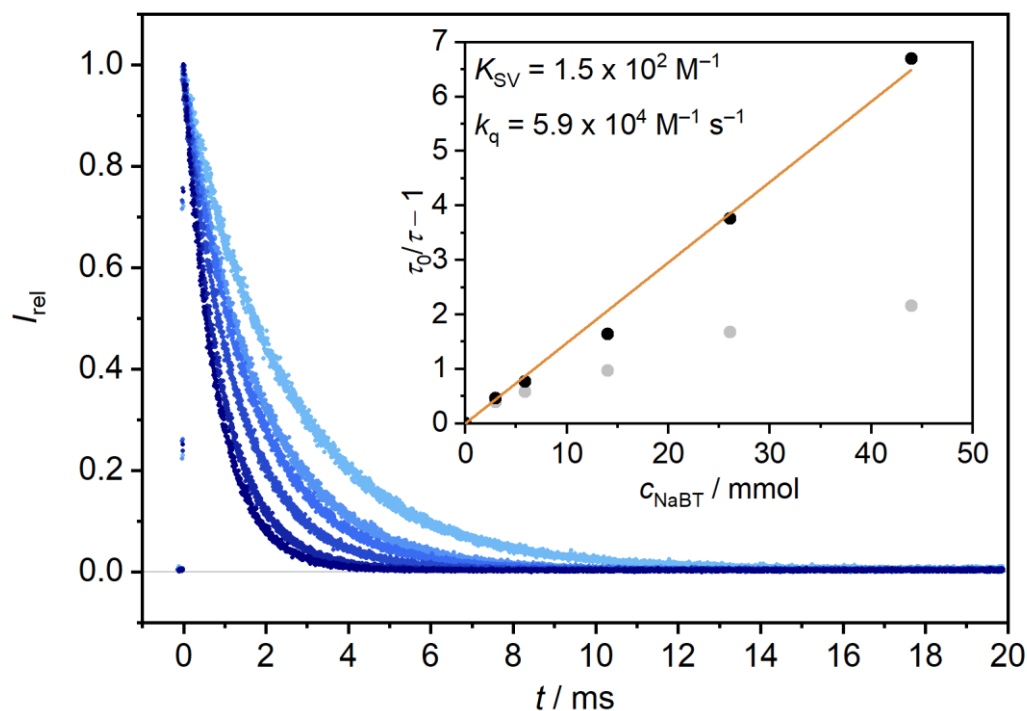


Figure S18. Reductive quenching of $[\text{Cr}(\text{tpe})_2]^{3+}$ by sodium 2-phenylisobutyrate (indexed as: NaBT). Main plot, emission decay traces recorded at 742 nm following excitation (451.3 nm,

10 μ s pulse duration) of a $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ (1 mM) solution in deaerated water with variable amounts of quencher (0 mM, 3.0 mM, 5.9 mM, 14 mM, 26 mM, 44 mM). Inset, corresponding Stern-Volmer plot with linear regression overlaid on the data (orange). Data points corrected regarding ionic strength according to the Brønsted-Bjerrum equation (black); obtained values for K_{SV} and k_{q} . Uncorrected data points depicted in light grey.

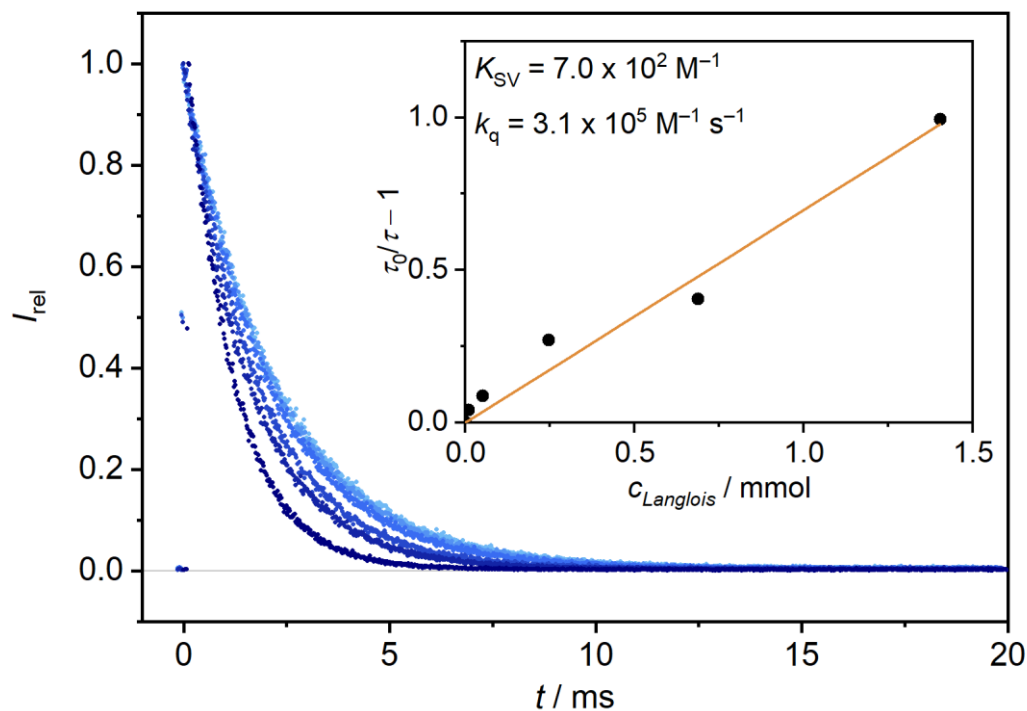
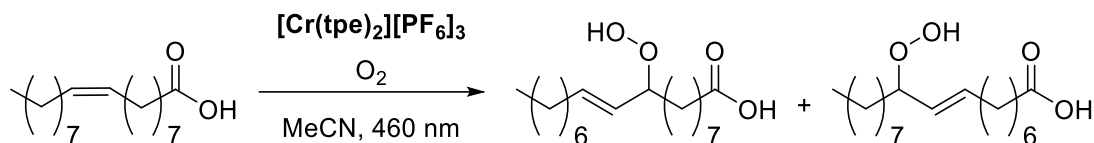


Figure S19. Reductive quenching of $[\text{Cr}(\text{tpe})_2]^{3+}$ by sodium trifluoromethanesulfinate (indexed as: Langlois). Main plot, emission decay traces recorded at 742 nm following excitation (451.3 nm, 10 μ s pulse duration) of a $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ (1 mM) solution in deaerated water with variable amounts of sodium trifluoromethanesulfinate (0 mM, 0.01 mM, 0.05 mM, 0.25 mM, 0.69 mM, 1.40 mM). Inset, corresponding Stern-Volmer plot with linear regression overlaid on the data. A correction for the ionic strength was omitted, due to the low concentration of the substrate.

Photocatalytic Experiments with $[\text{Cr}(\text{tpe})_2]^{3+}$

Photo-oxygenation of oleic acid (Schenck-Ene-reaction)

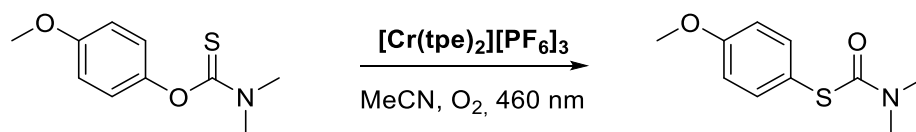


Laboratory scale procedure: In a 100 mL round-bottom flask $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ (162 mg, 0.16 mmol) was dissolved in 75 mL of acetonitrile. The solution was irradiated for 5 minutes for the purpose of photochemical self-cleaning. A solution of oleic acid (1.21 g, 4.28 mmol) in 5 mL of acetonitrile was added and the reaction mixture was irradiated for 4 h under vigorous stirring (1250 rpm) open to air, to ensure a constant supply of oxygen in solution. The loss of solvent that occurred over the course of the reaction was factored in when determining the substrate conversion, using ethylene carbonate as a standard. Neither the substrate nor the products are volatile, allowing for an easy quantification of the conversion. For safety reasons, we did not isolate the hydroperoxides but measured the conversion by ^1H NMR spectroscopy.

^1H NMR (400 MHz, CD_3CN): δ /ppm = 5.70–5.63 (m, 1H), 5.37–5.31 (m, 1H), 4.14 (q, $^3J = 7.3$, 6.8 Hz, 1H), 1.56–1.53 (m, 3H), 1.38–1.27 (m, 20H), 0.90–0.86 (m, 3H).

Due to the presence of protio-MeCN, some proton resonances of the product in the aliphatic region are concealed by the solvent resonance.^[18] The characteristic isolated resonances at 5.70 to 5.63 ppm and 4.14 ppm served to quantify the conversion. To account for solvent loss from evaporation, the volume of the remaining solution was determined after the irradiation was completed. Adding $[n\text{-Bu}_4\text{N}][\text{NO}_3]$ (486 mg, 1.59 mmol) in 1 mL of acetonitrile leads to crystallization of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ overnight. The photocatalyst was recovered by filtration, washed once with 5 mL of acetonitrile and twice with 10 mL of diethyl ether yielding small yellow crystals (62 mg, 0.08 mmol, 51%).

Newman-Kwart rearrangement



Laboratory scale procedure: In a 100 mL round-bottom flask $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ (163 mg, 0.16 mmol) was dissolved in 75 mL of acetonitrile. The solution was irradiated for 5 minutes for the purpose of photochemical self-cleaning. Subsequently, O-(4-methoxyphenyl)-dimethylcarbamothioate (1.69 g, 7.99 mmol) was added. The solution was irradiated for 60 minutes under air and stirring. The solvent was removed by rotary evaporation, and a slightly yellow solid was obtained. The product was isolated by extracting the residue three times with 50 mL of diethyl ether. The ether was removed under reduced pressure, yielding the product as an off-white solid (1.55 g, 7.34 mmol, 92% yield).

^1H NMR (400 MHz, CDCl_3): δ /ppm = 7.39 (d, $^3J = 8.9$ Hz, 2H), 6.91 (d, $^3J = 8.8$ Hz, 2H), 3.81 (s, 3H), 3.04 (br, 6H).

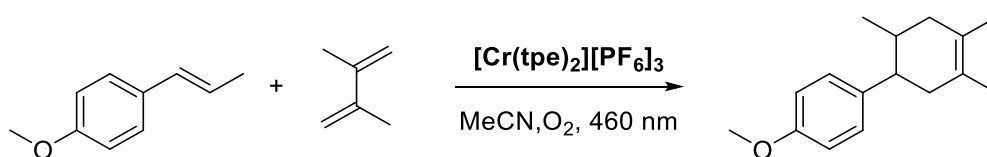
The ^1H NMR data agree with previously reported data.^[16]

The catalyst was recovered by dissolving the yellow solid in 25 mL of hot acetonitrile, cooling the solution to room temperature and crystallizing the complex via ether diffusion (147 mg, 0.15 mmol; 90% of the starting material).

Photocatalysis using sunlight: In a 100 mL round-bottom flask $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ (163 mg, 0.16 mmol) was dissolved in 75 mL of acetonitrile. Subsequently, *O*-(4-methoxyphenyl)-dimethylcarbamothioate (338 mg, 1.59 mmol) was added. The solution was placed in direct sunlight for 8 h under air without stirring. Reaction control via ^1H NMR spectroscopy showed full conversion of the substrate.

^1H NMR (400 MHz, CD_3CN): δ /ppm = 7.35 (d, 3J = 8.8 Hz, 2H), 6.94 (d, 3J = 8.8 Hz, 2H), 3.81 (s, 3H), 2.99 (br, 6H).

Radical Cation [4+2]-Cycloaddition



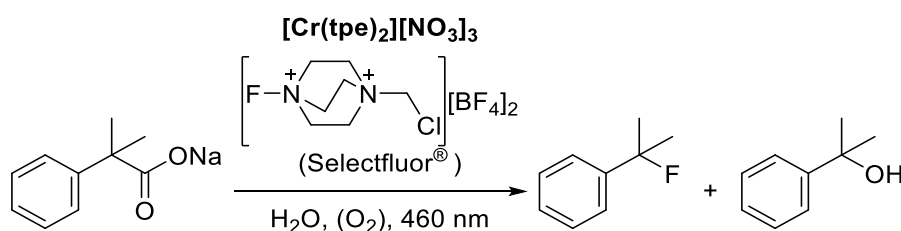
Laboratory scale procedure: In a 100 mL round-bottom flask $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ (163 mg, 0.16 mmol) was dissolved in 75 mL of acetonitrile. The solution was irradiated for 5 minutes for the purpose of photochemical self-cleaning. Subsequently, *trans*-anethol (1.19 g, 8.03 mmol) and freshly distilled 2,3-dimethyl-1,3-butadiene (3.29 g, 40.0 mmol) were added. The solution was irradiated as described above for 25 minutes. The solvent was removed by rotary evaporation, leaving a yellow solid ($[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$) and a slightly yellow oil (cycloaddition product). The product was isolated by extracting the residue three times with 50 mL of diethyl ether. The ether was removed under reduced pressure, yielding the crude product as a slightly yellow oil. The crude product was purified by filtration through a silica plug (cyclohexane). The solvent was removed under reduced pressure, giving the cycloaddition product as a colorless oil (1.52 g, 6.61 mmol; 82% yield).

^1H NMR (400 MHz, CDCl_3): δ /ppm = 7.09 (d, 3J = 8.6 Hz, 2H), 6.85 (d, 3J = 8.6 Hz, 2H), 3.80 (s, 3H), 2.34 (td, 3J = 10.5, 5.8 Hz, 1H), 2.17–2.07 (m, 3H), 1.92–1.79 (m, 2H), 1.65–1.62 (m, 6H), 0.70 (d, 3J = 6.1 Hz, 3H).

The ^1H NMR data agree with previously reported data.^[19]

The catalyst was recovered by dissolving the yellow solid in 25 mL of hot acetonitrile, cooling the mixture to room temperature and crystallizing it via ether diffusion (150 mg, 0.15 mmol; 92% of the starting material).

Decarboxylation of 2-phenylisobutyrate



In a typical procedure 2-phenylisobutyrate (37.2 mg; 200 μmol), Selectfluor[®] (208 mg; 600 μmol) and $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ (3.0 mg; 4.0 μmol) were dissolved in 2 mL of water. If the reaction was carried out under deaerated conditions, the solution was transferred to an inert gas cuvette and purged for 20 minutes with argon. The mixture was irradiated for 2 h. Upon irradiation, gas evolution occurred and a colorless oil separated from the aqueous phase. The mixture was extracted with 1 mL of CDCl_3 . The organic extract was dried over anhydrous sodium sulfate. The extract contained a mixture of 2-fluoro-2-phenylpropane (ca. 80% under aerated conditions; ca. 85% under deaerated conditions) and 2-phenyl-2-propanol (ca. 20% under aerated conditions; ca. 15% under deaerated conditions), which was determined by analysis via ^1H and ^{19}F NMR spectroscopy. The total yield was not determined.

^1H NMR (400 MHz, CDCl_3): δ /ppm = 7.42–7.34 (m, 3H), 7.31–7.24 (m, 2H), 1.70 (d, $^3J_{\text{HF}}$ = 21.9 Hz, 1H). The resonances listed here are those corresponding to 2-fluoro-2-phenylpropane. The resonances of the alcohol are given separately below. The multiplets from 7.42–7.34 ppm and 7.31–7.24 ppm overlap with the resonances of 2-phenyl-2-propanol, leading to deviations in the corresponding integrals. The ratio of the two products was determined by comparing the integrals of the resonances of their corresponding methyl groups. The multiplet from 7.31–7.24 ppm overlaps with the chloroform solvent resonance.

^{19}F NMR (377 MHz, CDCl_3): δ /ppm = –138.59 (h, $^3J_{\text{FH}}$ = 21.9 Hz).

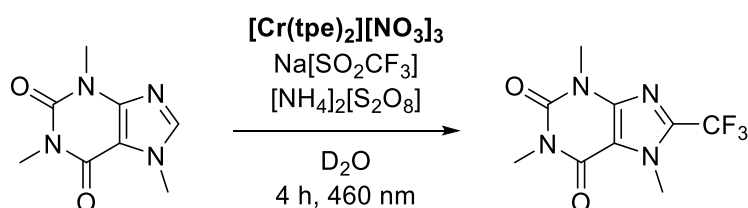
The spectroscopic data of 2-fluoro-2-phenylpropane agree with previously reported data.^[20]

To obtain a ^1H NMR spectrum of the alcohol, the reaction mixture was extracted with pentane after the irradiation and the organic extract was dried over anhydrous sodium sulfate. The extract was decanted and evaporated for about 3 h. The fluorinated product was sufficiently volatile to evaporate, yielding the alcohol 2-phenyl-2-propanol.

^1H NMR (400 MHz, CDCl_3): δ /ppm = 7.51–7.48 (m, 2H), 7.37–7.32 (m, 2H), 7.27–7.23 (m, 1H), 1.59 (s, 6H). The multiplet from 7.27–7.23 ppm overlaps with the chloroform solvent resonance.

The spectroscopic data of 2-phenyl-2-propanol agree with previously reported data.^[21]

Trifluoromethylation of caffeine



In a typical procedure caffeine (5.6 mg, 30 μmol), ammoniumperoxodisulfate (6.8 mg, 30 μmol), sodium trifluoromethanesulfinate (14.3 mg; 92 μmol) and $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ (2.3 mg, 3.0 μmol) were dissolved in 3 mL of D_2O . The solution was transferred to an inert gas cuvette and purged for 15 minutes with argon. The mixture was irradiated for 4 h. The mixture was extracted three times with 5 mL of dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate, decanted and the solvent was removed under reduced pressure. The product 1,3,7-trimethyl-8-(trifluoromethyl)-7H-purine-2,6-dione and unreacted caffeine were obtained as colorless solids (7.2 mg). The yield of the desired product was determined to be around 78% via ^1H NMR spectroscopy.

^1H NMR (400 MHz, CDCl_3): δ /ppm = 4.16–4.15 (m, 3H), 3.59 (s, 3H), 3.42 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3): δ /ppm = -63.55 (s).

The spectroscopic data agree with previously reported data.^[22]

The reaction controls via ^1H NMR spectroscopy in D_2O (Figures S62 and S64) show an overall loss of material (caffeine and trifluoromethylated product) of ca. 10% as well as a slightly lower product formation of ca. 72% (vs. 78% in the isolated mixture) after 4 h of irradiation. We attribute these observations to the limited solubility of the trifluoromethylated product in water. For the conversion vs. time plot, the ratio of product to substrate was used to approximate the conversion and reaction quantum yield Φ_{R} .

Conversion vs. Time Plots and Actinometry

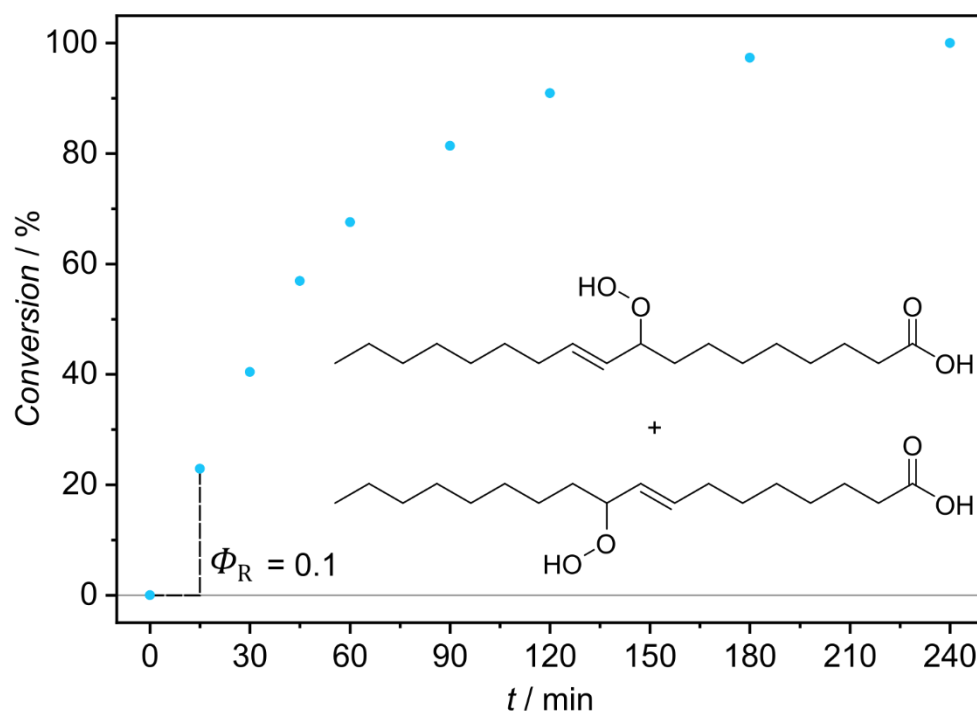


Figure S20. Conversion vs. time plot of the laboratory-scale reaction using 50 mM oleic acid and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile. The reaction quantum yield Φ_R was determined in the range of 0–30 min of irradiation (dashed black lines).

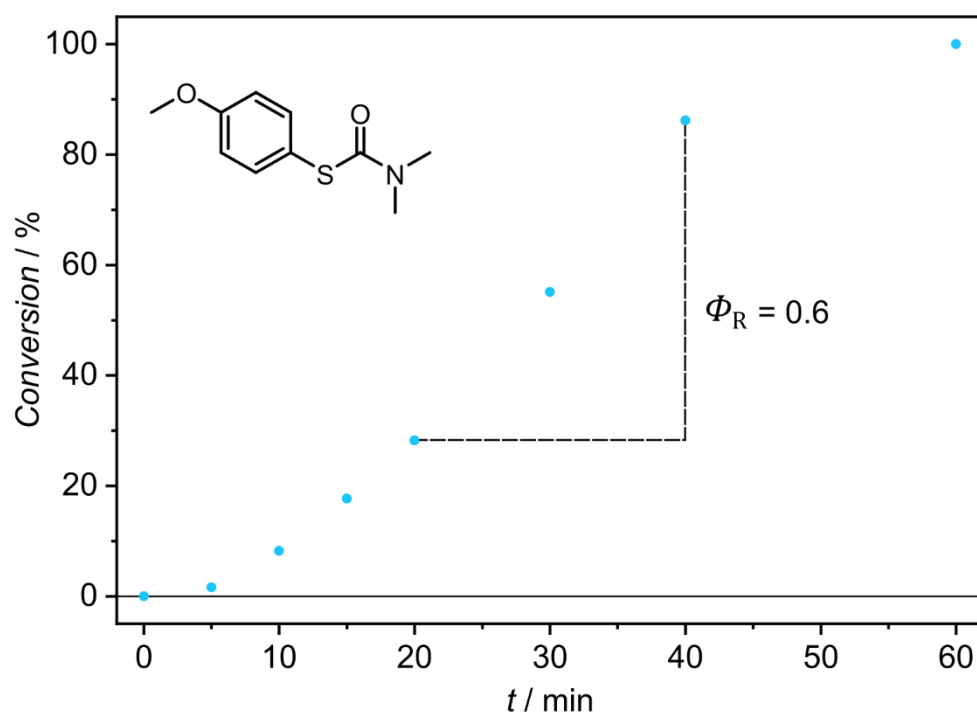


Figure S21. Conversion vs. time plot of the laboratory-scale reaction using 100 mM O-(4-methoxyphenyl)-dimethylcarbamothioate and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile. The reaction quantum yield Φ_R was determined in the range of 20–40 min of irradiation to account for the initiation phase in this reaction (dashed black lines).

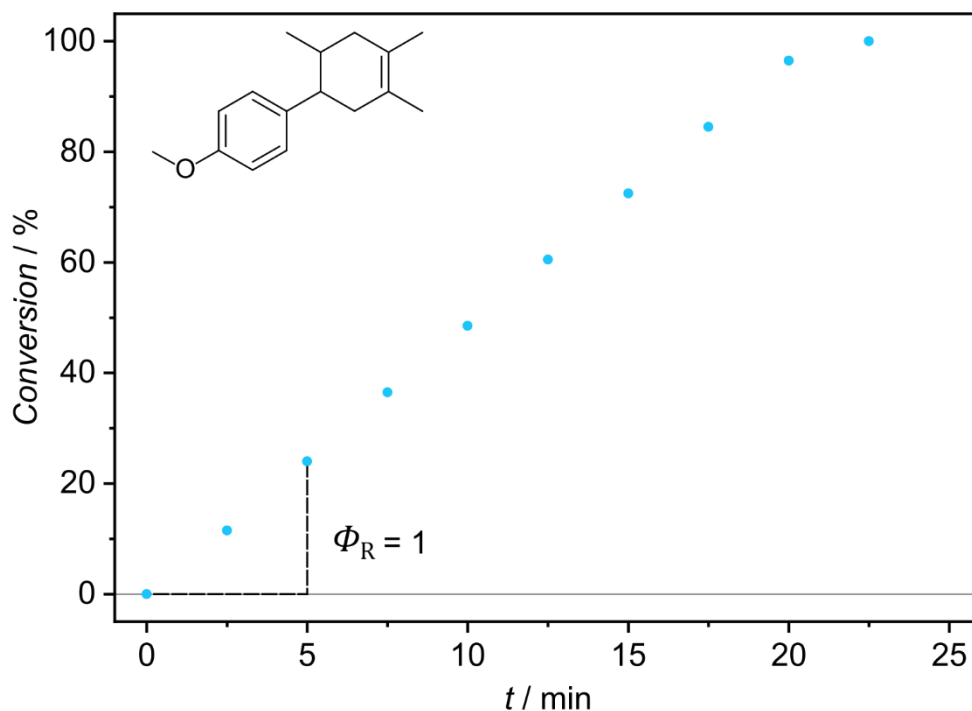


Figure S22. Conversion vs. time plot of the laboratory-scale reaction using 100 mM *trans*-anethole, 500 mM 2,3-dimethyl-1,3-butadiene and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile. The reaction quantum yield Φ_R was determined in the range of 0–5 min of irradiation (dashed black lines).

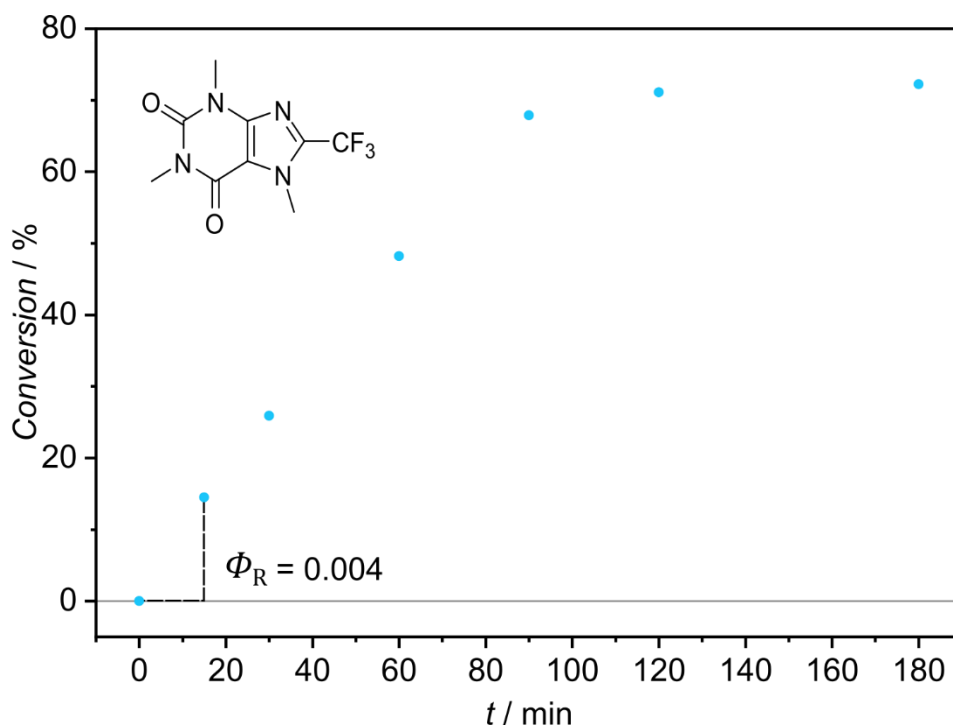


Figure S23. Conversion vs. time plot of the cuvette-scale reaction using 10 mM caffeine (blue), 10 mM ammonium peroxodisulfate, 30 mM Langlois reagent and 2 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in deaerated D_2O . The reaction quantum yield Φ_R was determined in the range of 0–15 min of irradiation (dashed black lines).

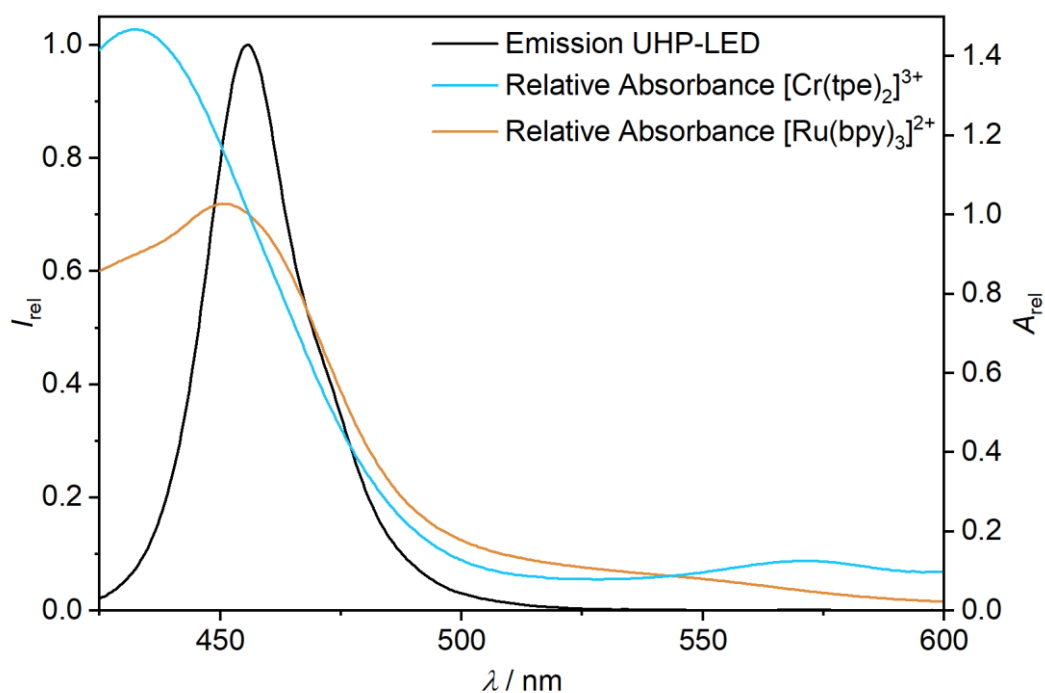


Figure S24. Emission spectrum of the employed LED (UHP-T-460-DI, black) overlaid with the relative absorbances of $[\text{Cr}(\text{tpe})_2]^{3+}$ (blue) and $[\text{Ru}(\text{bpy})_3]^{2+}$ (orange), normalized at $\lambda = 456$ nm.

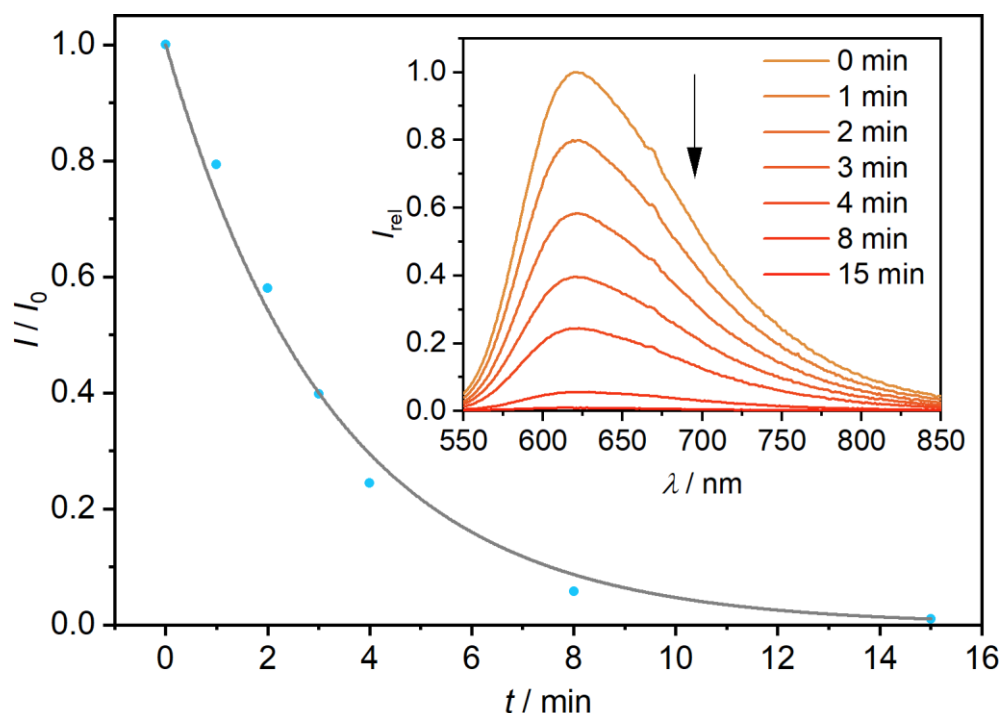


Figure S25. Normalized emission intensity of $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ in MeCN (80 mL) under argon after irradiating with a LED (UHP-T-460-DI, $\lambda_{\text{max}} = 456$ nm) in a 100 mL Schlenk-flask for time periods t , superimposed with a monoexponential fit (grey). Inset: corresponding emission spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ after excitation at $\lambda_{\text{exc}} = 450$ nm, normalized to the maximum intensity of the $t = 0$ min spectrum.

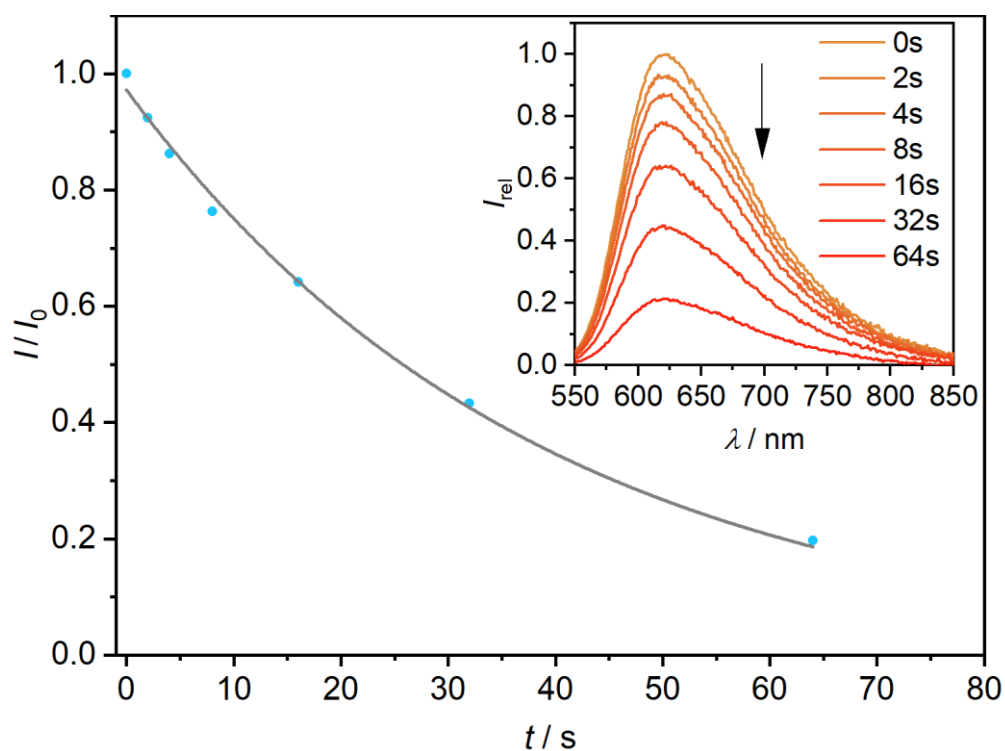


Figure S26. Normalized emission intensity of $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ in MeCN (3 mL) under argon after irradiating with a LED (UHP-T-460-DI, $\lambda_{\text{max}} = 456 \text{ nm}$) in a cuvette with a *Schott* valve for time periods t , superimposed with a monoexponential fit (grey). Inset: corresponding emission spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ after excitation at $\lambda_{\text{exc}} = 450 \text{ nm}$, normalized to the maximum intensity of the $t = 0 \text{ min}$ spectrum.

Absorption Spectra of Photocatalytic Experiments

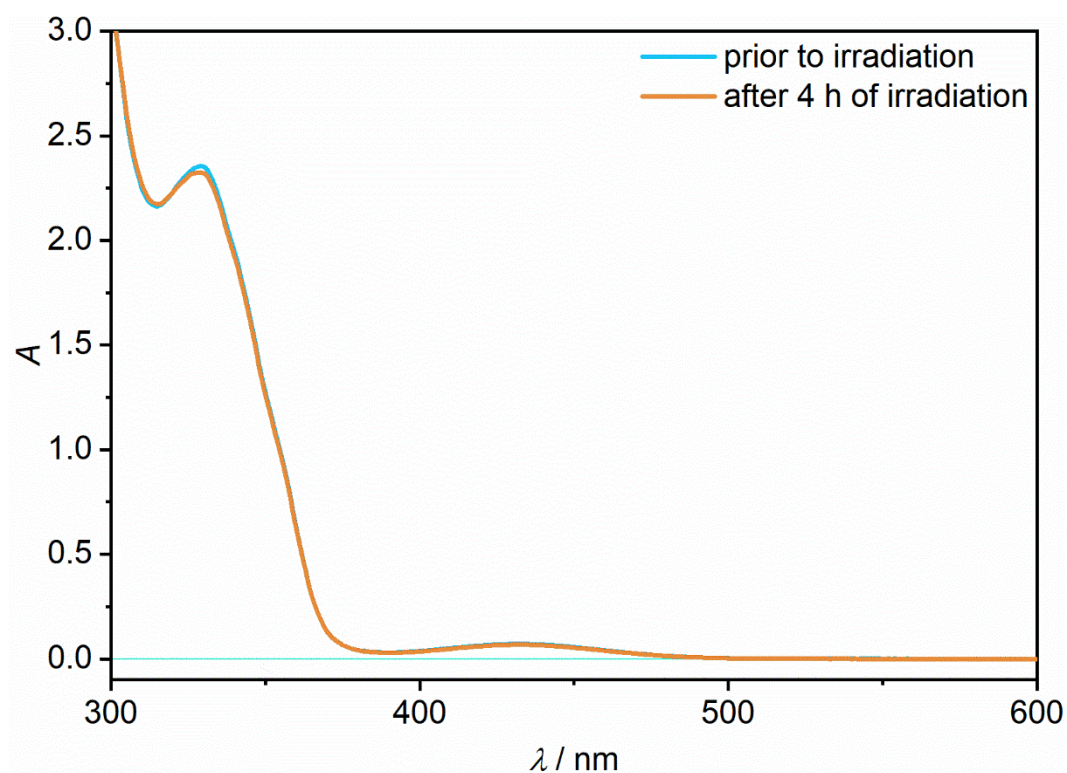


Figure S27. UV/vis absorption spectra of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ (2 mM) in a solution of oleic acid (50 mM) acetonitrile prior to irradiation (blue) and after 4 h of UHP-LED irradiation open to air ($\lambda_{\text{exc}} = 460$ nm; orange; corrected for solvent loss over the course of the irradiation).

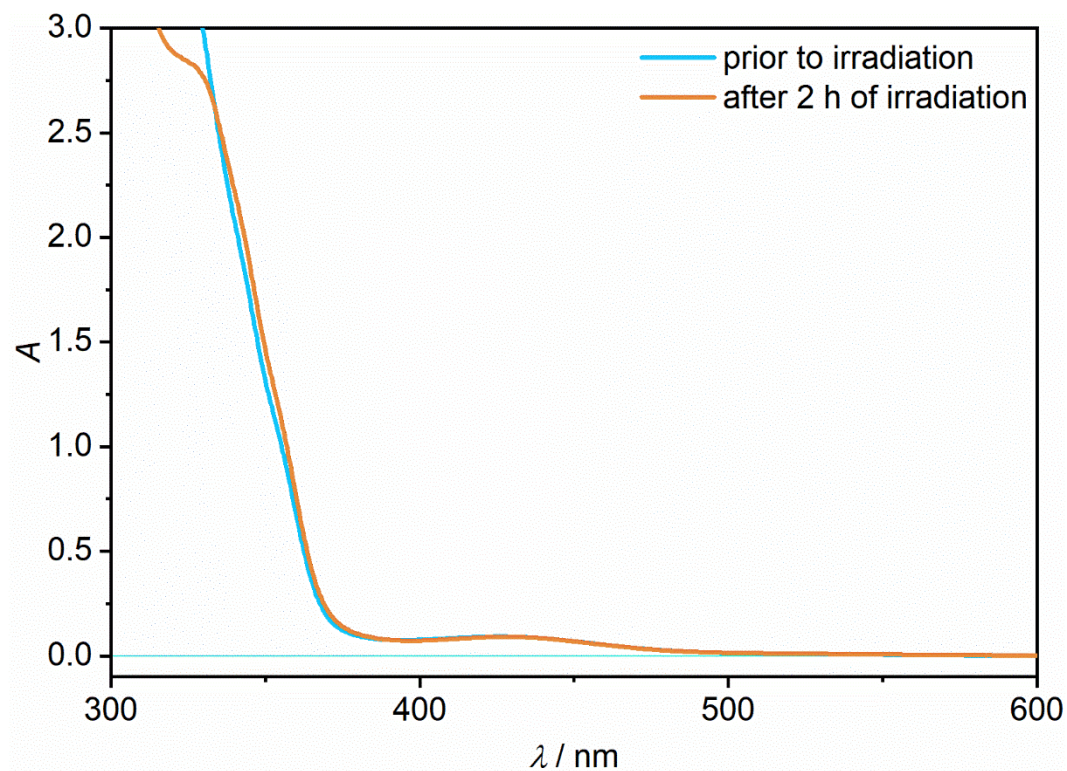


Figure S28. UV/vis absorption spectra of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ (2 mM) in a solution of O-(4-methoxyphenyl)-dimethylcarbamothioate (100 mM) in acetonitrile prior to irradiation (blue) and after 2 h of UHP-LED irradiation open to air ($\lambda_{\text{exc}} = 460$ nm; orange).

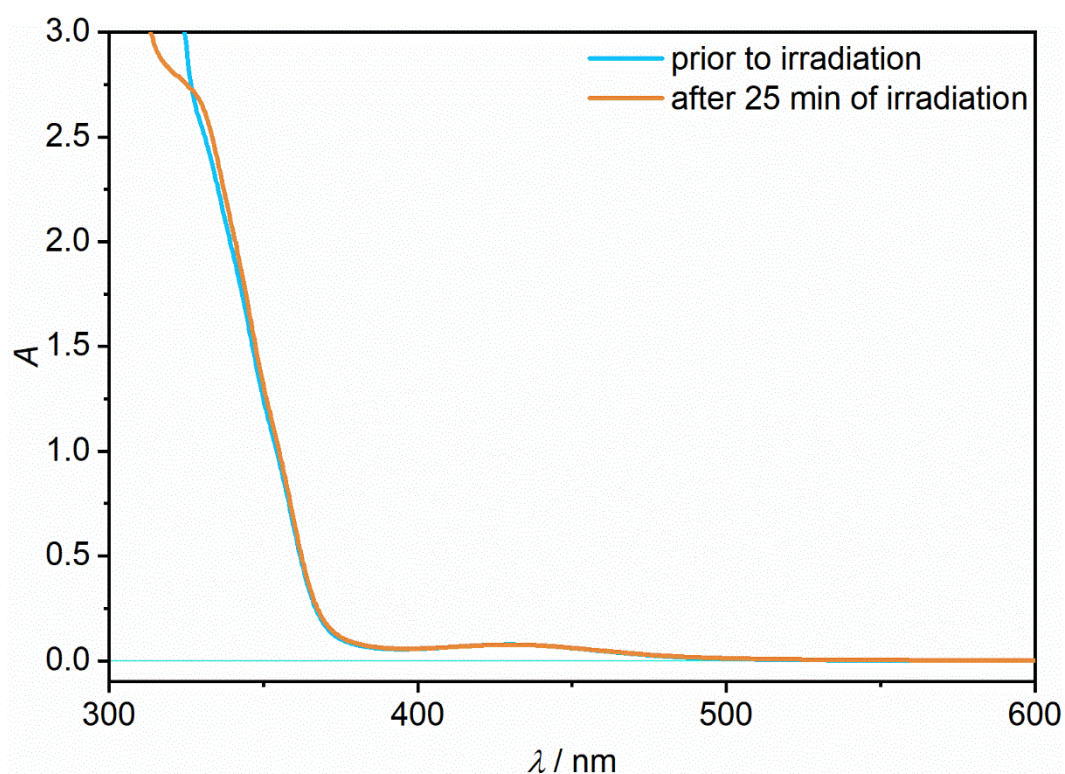


Figure S29. UV/vis absorption spectra of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ (2 mM) in a solution of *trans*-anethole (100 mM) and 2,3-dimethyl-1,3-butadiene (500 mM) in acetonitrile prior to irradiation (blue) and after 25 min of UHP-LED irradiation open to air ($\lambda_{\text{exc}} = 460$ nm; orange).

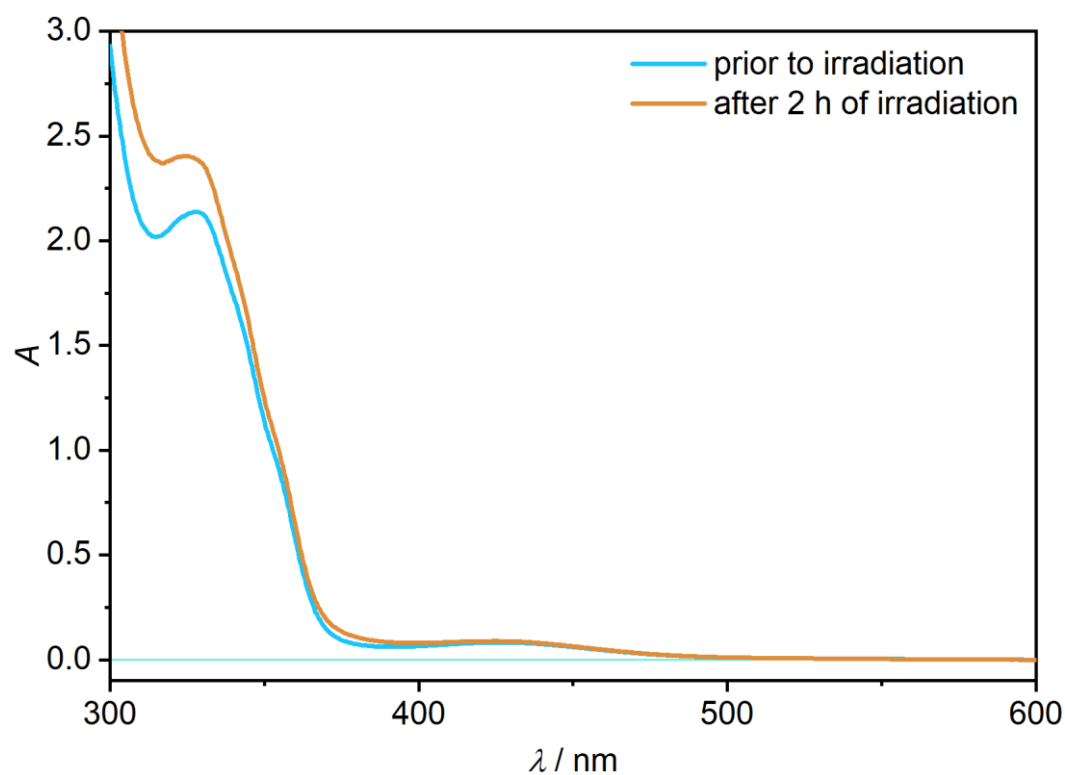


Figure S30. UV/vis absorption spectra of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ (2 mM) in an aerated solution of 2-phenylisobutyrate (100 mM) and Selectfluor® (300 mM) prior to irradiation (blue) and after 2 h of UHP-LED irradiation ($\lambda_{\text{exc}} = 460$ nm; orange).

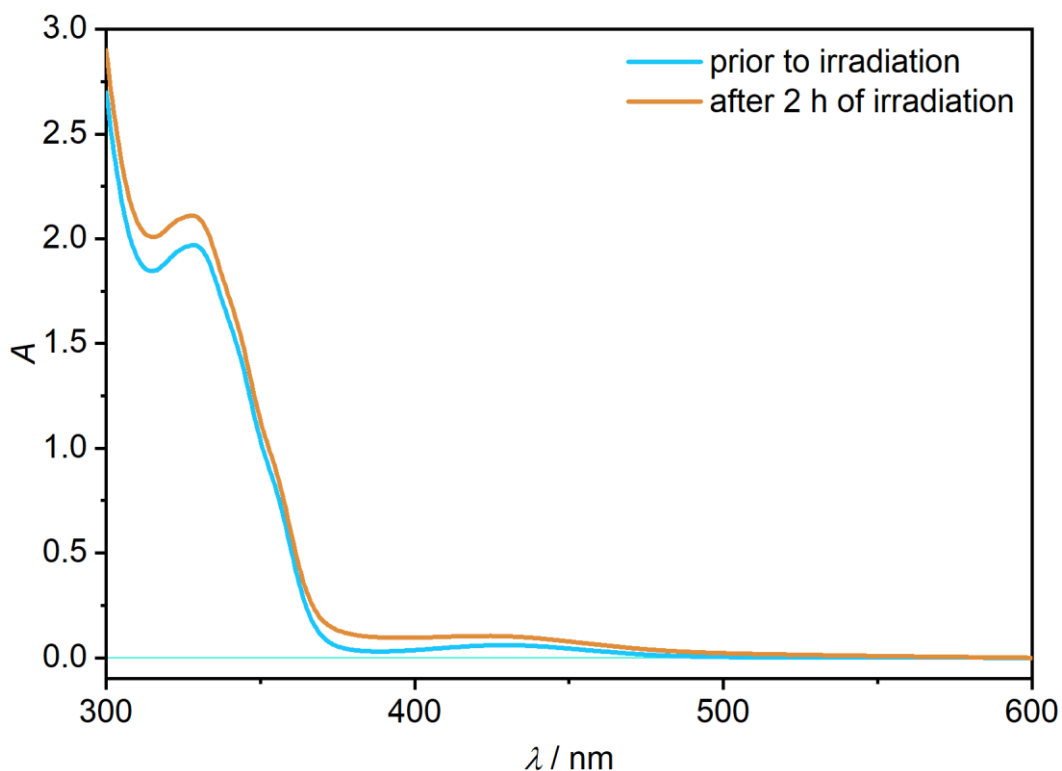


Figure S31. UV/vis absorption spectra of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ (2 mM) in a deaerated solution of 2-phenylisobutyrate (100 mM) and Selectfluor[®] (300 mM) prior to irradiation (blue) and after 2 h of UHP-LED irradiation ($\lambda_{\text{exc}} = 460$ nm; orange).

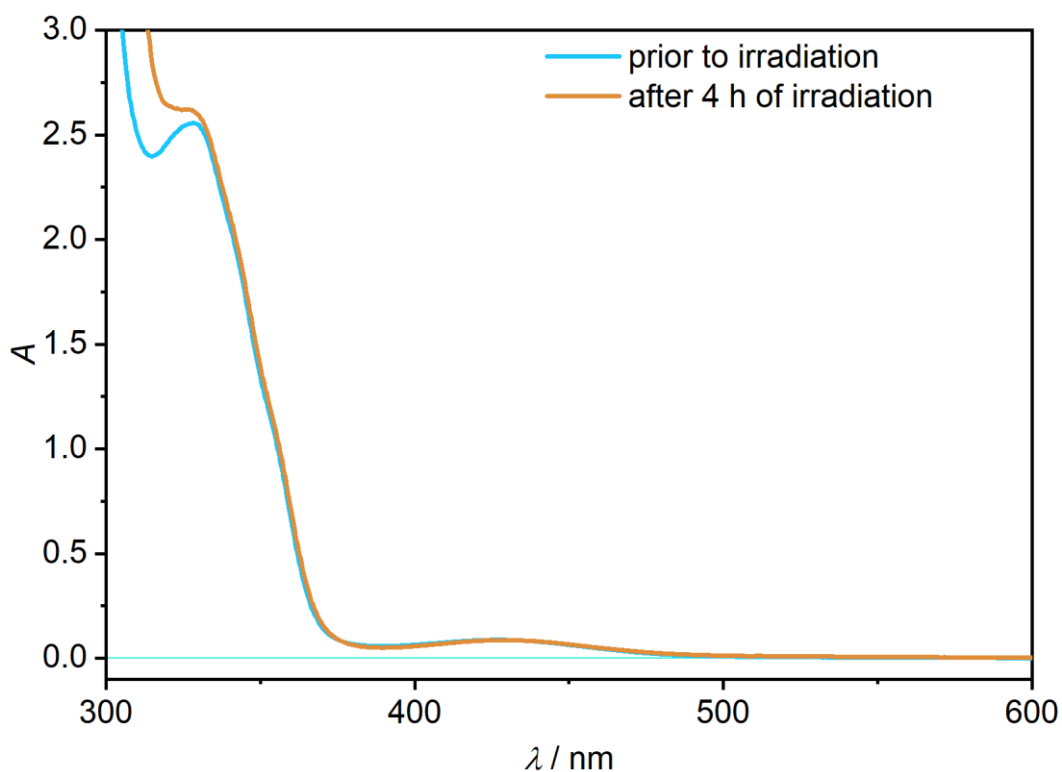


Figure S32. UV/vis absorption spectra of $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ (2 mM) in a deaerated solution of caffeine (10 mM), ammonium peroxodisulfate (10 mM) and sodium trifluoromethanesulfonate (30 mM) in D_2O prior to irradiation (blue) and after 4 h UHP-LED irradiation ($\lambda_{\text{exc}} = 460$ nm; orange).

NMR Spectra of tpe, Substrates and Products

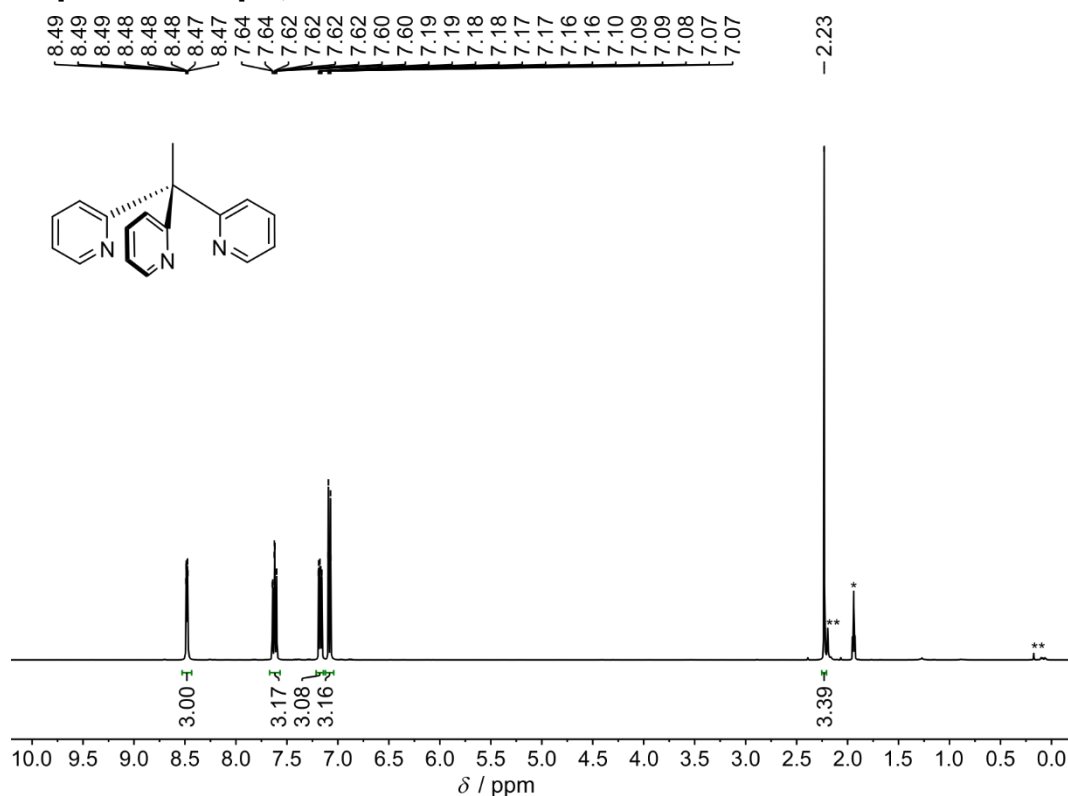


Figure S33. ¹H NMR spectrum of crude tpe in CD₃CN. * denotes acetonitrile solvent resonance; ** denotes resonances of water and grease.

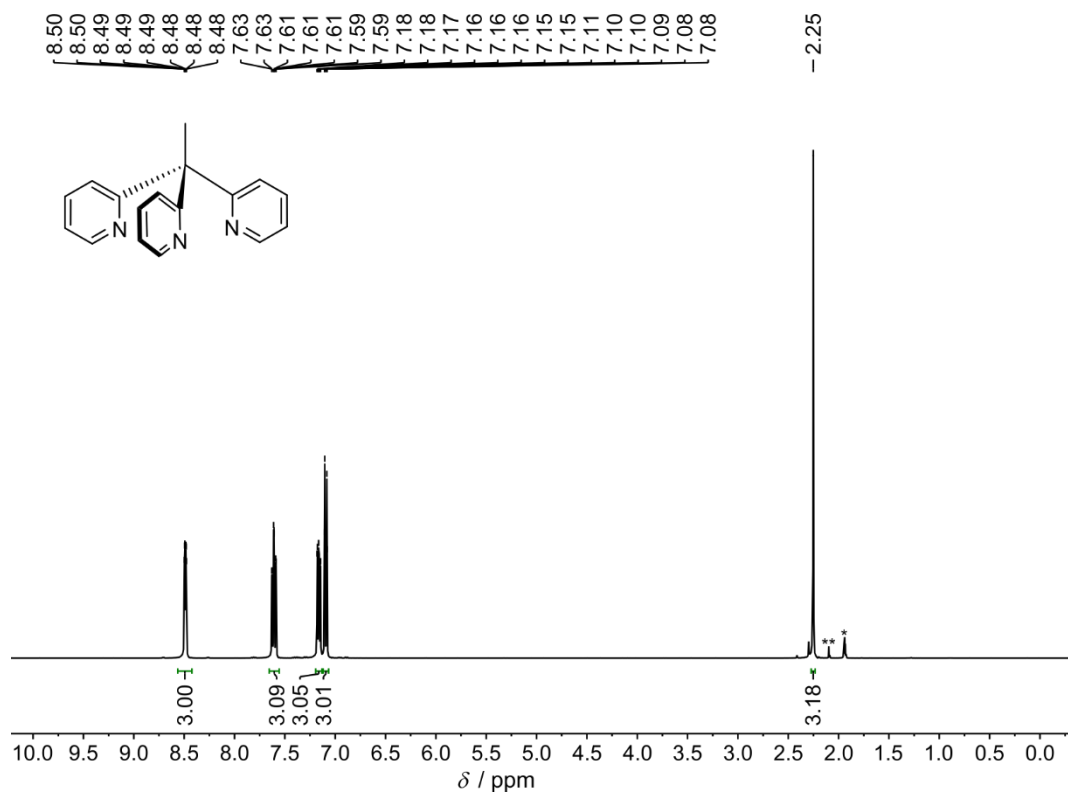


Figure S34. ¹H NMR spectrum of crude tpe in CD₃CN. * denotes acetonitrile solvent resonance; ** denotes resonance of residual water.

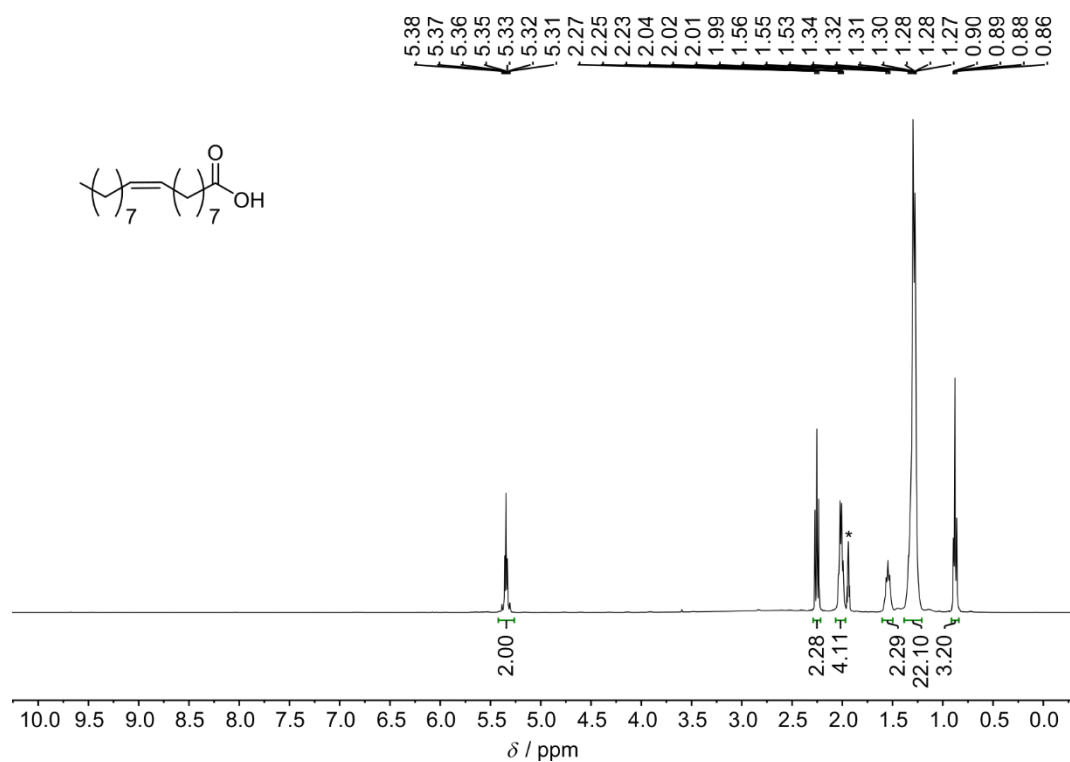


Figure S35. ¹H NMR spectrum of oleic acid in CD₃CN. * denotes acetonitrile solvent resonance.

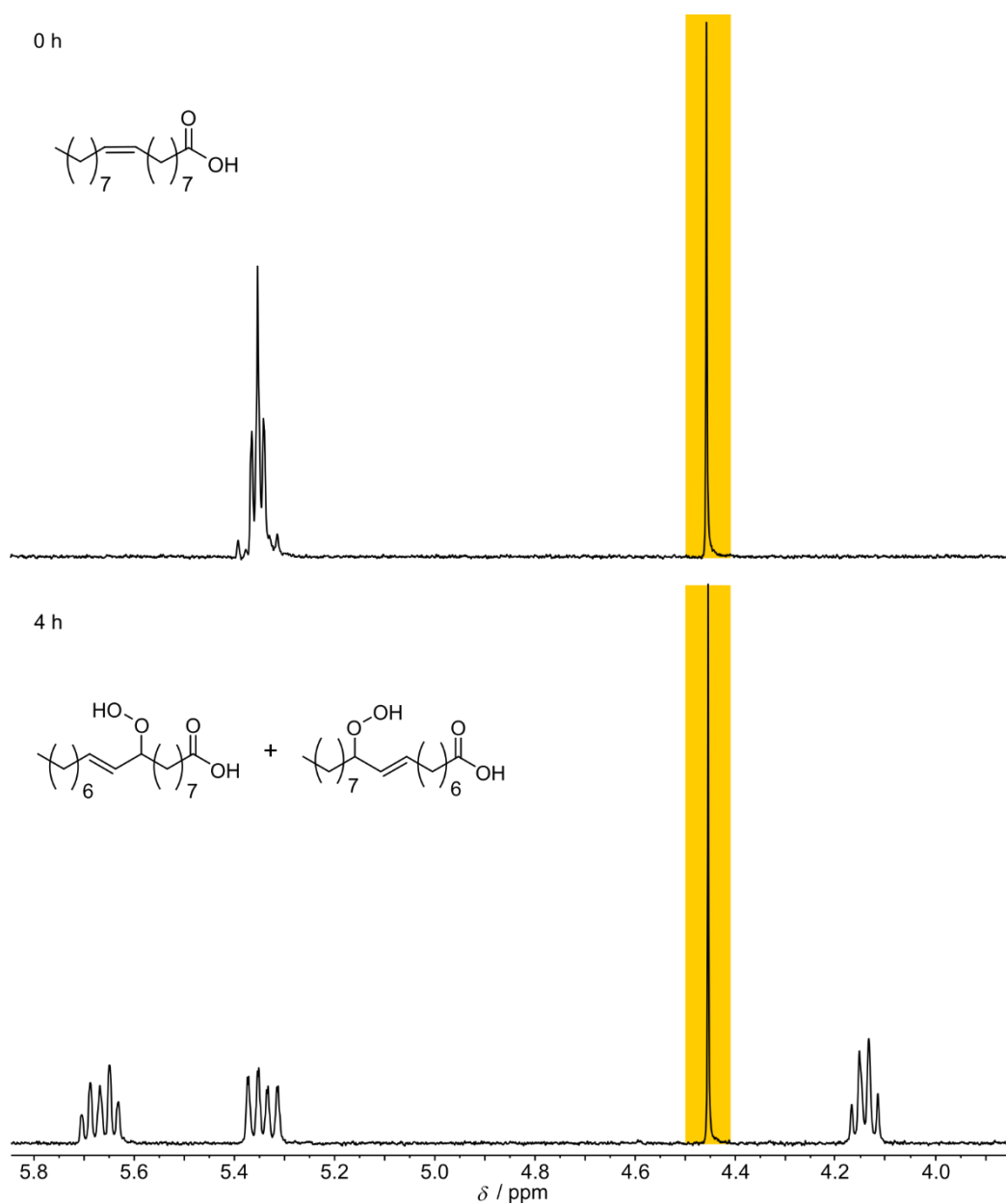


Figure S36. Exemplary partial ^1H NMR spectra of the laboratory-scale reaction using 50 mM oleic acid and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile with ethylene carbonate (yellow) as internal standard.

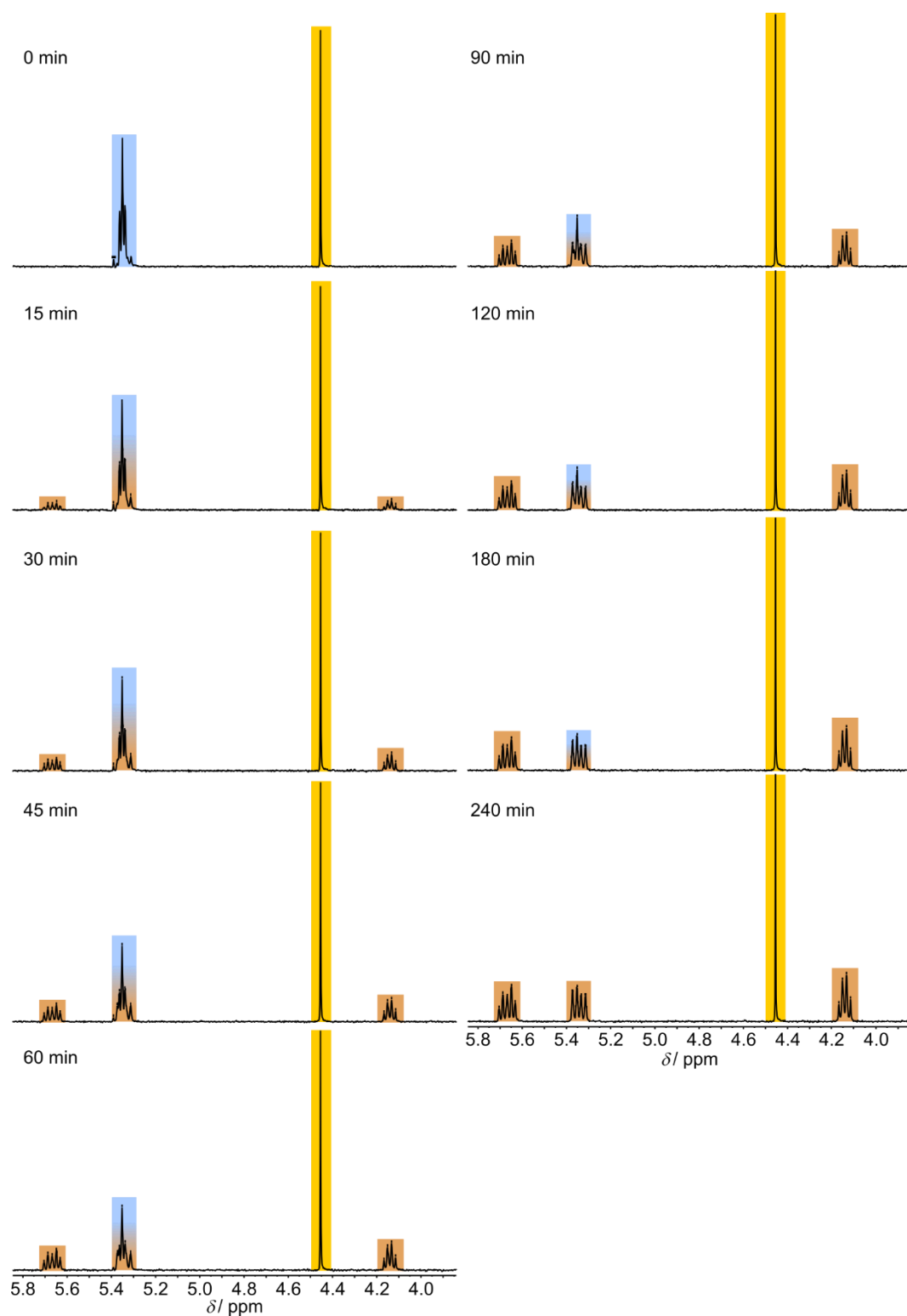


Figure S37. Exemplary partial ^1H NMR spectra of the laboratory-scale reaction using 50 mM oleic acid (blue) and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile recorded after different irradiation time periods. Product resonance highlighted in orange. Ethylene carbonate (yellow) was used as internal standard.

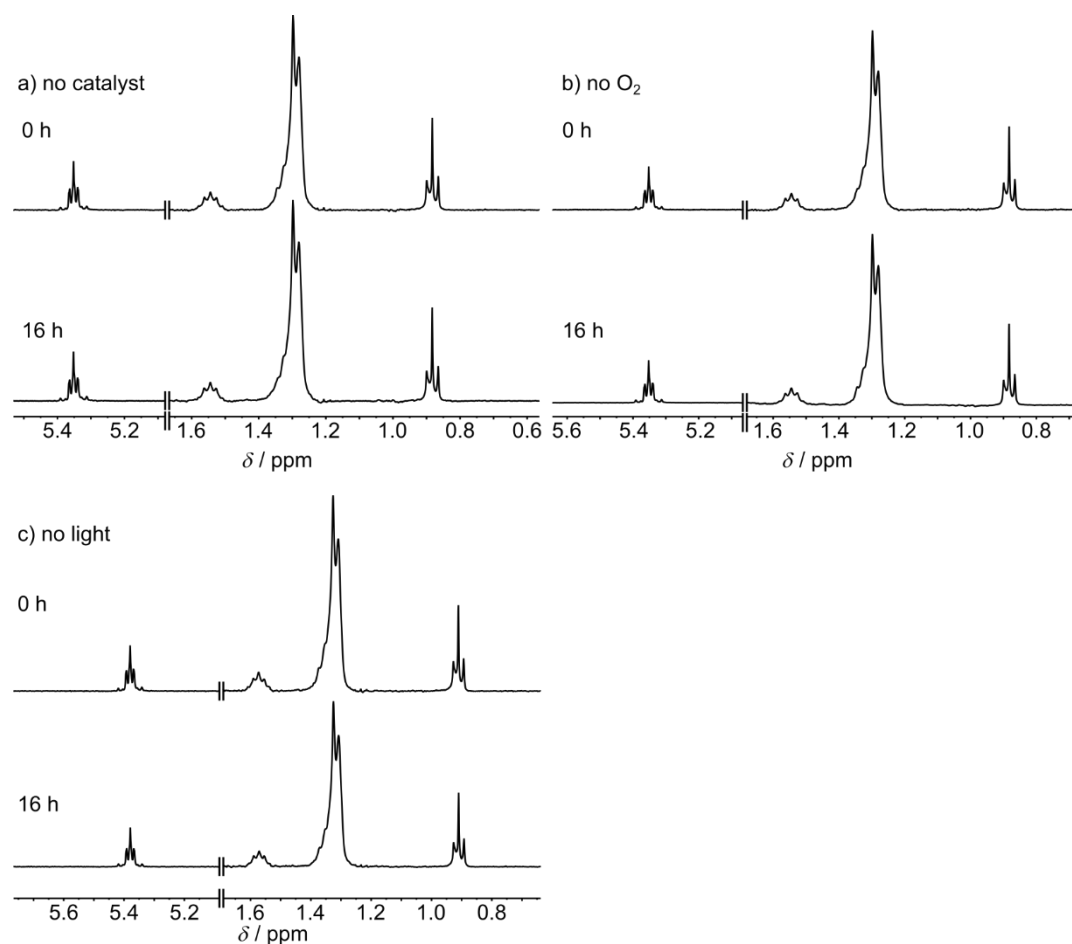


Figure S38. Partial ^1H NMR spectra of cuvette-scale control experiments using a) 50 mM oleic acid in acetonitrile without photocatalyst; b) 50 mM oleic acid and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile under deaerated conditions; c) 50 mM oleic acid and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ without light.

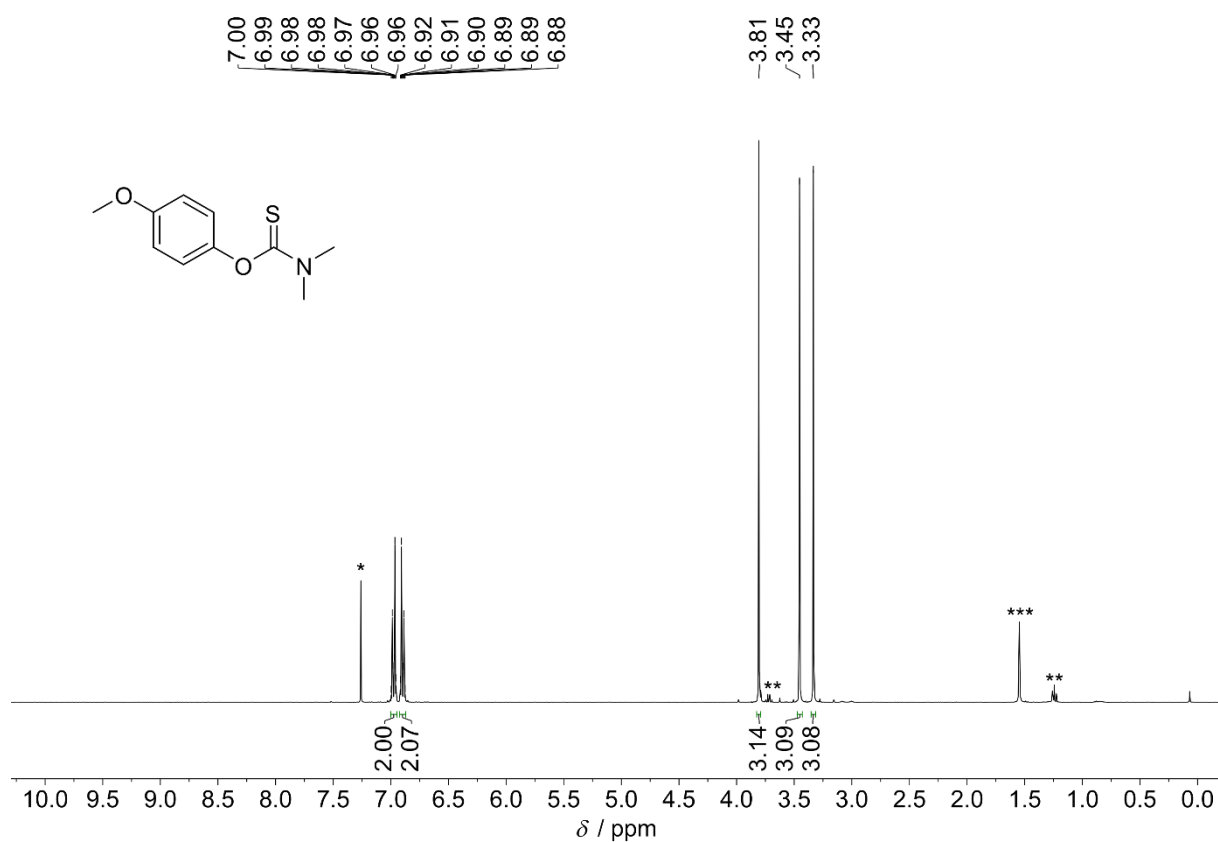


Figure S39. ¹H NMR spectrum of O-(4-methoxyphenyl)-dimethylcarbamothioate in CDCl₃. * denotes chloroform solvent resonance; ** denotes resonance of residual ethanol; *** denotes resonance of residual water.

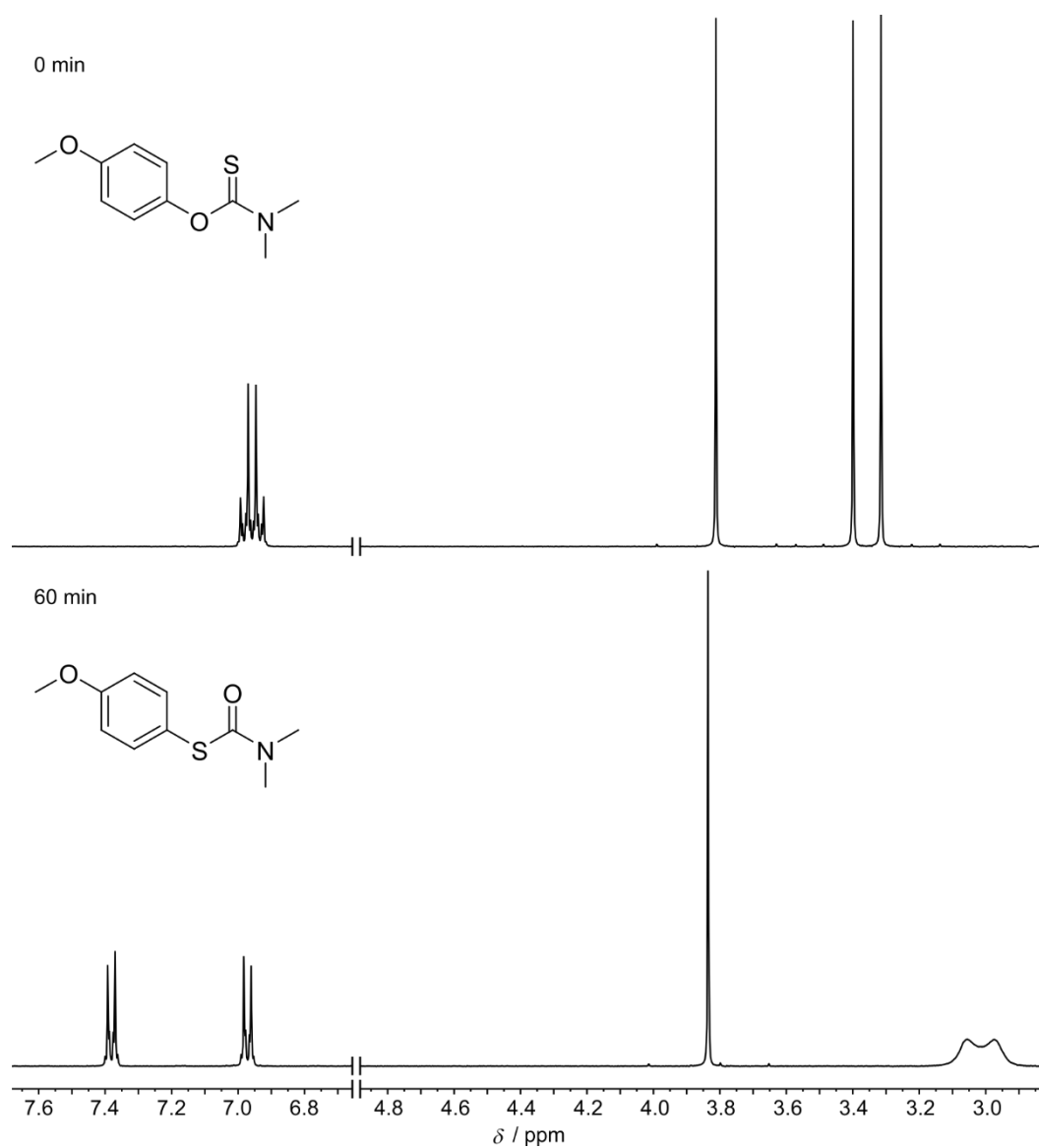


Figure S40. Exemplary partial ^1H NMR spectra of the laboratory-scale reaction using 100 mM O-(4-methoxyphenyl)-dimethylcarbamothioate and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile.

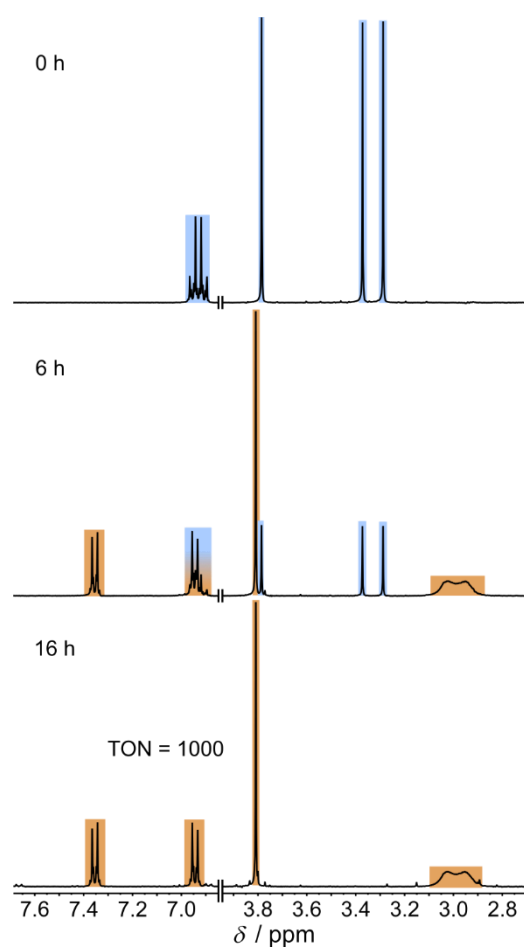


Figure S41. Exemplary partial ^1H NMR spectra of the laboratory-scale reaction using 100 mM O-(4-methoxyphenyl)-dimethylcarbamothioate (blue) and 0.1 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile. Product resonances highlighted in orange.

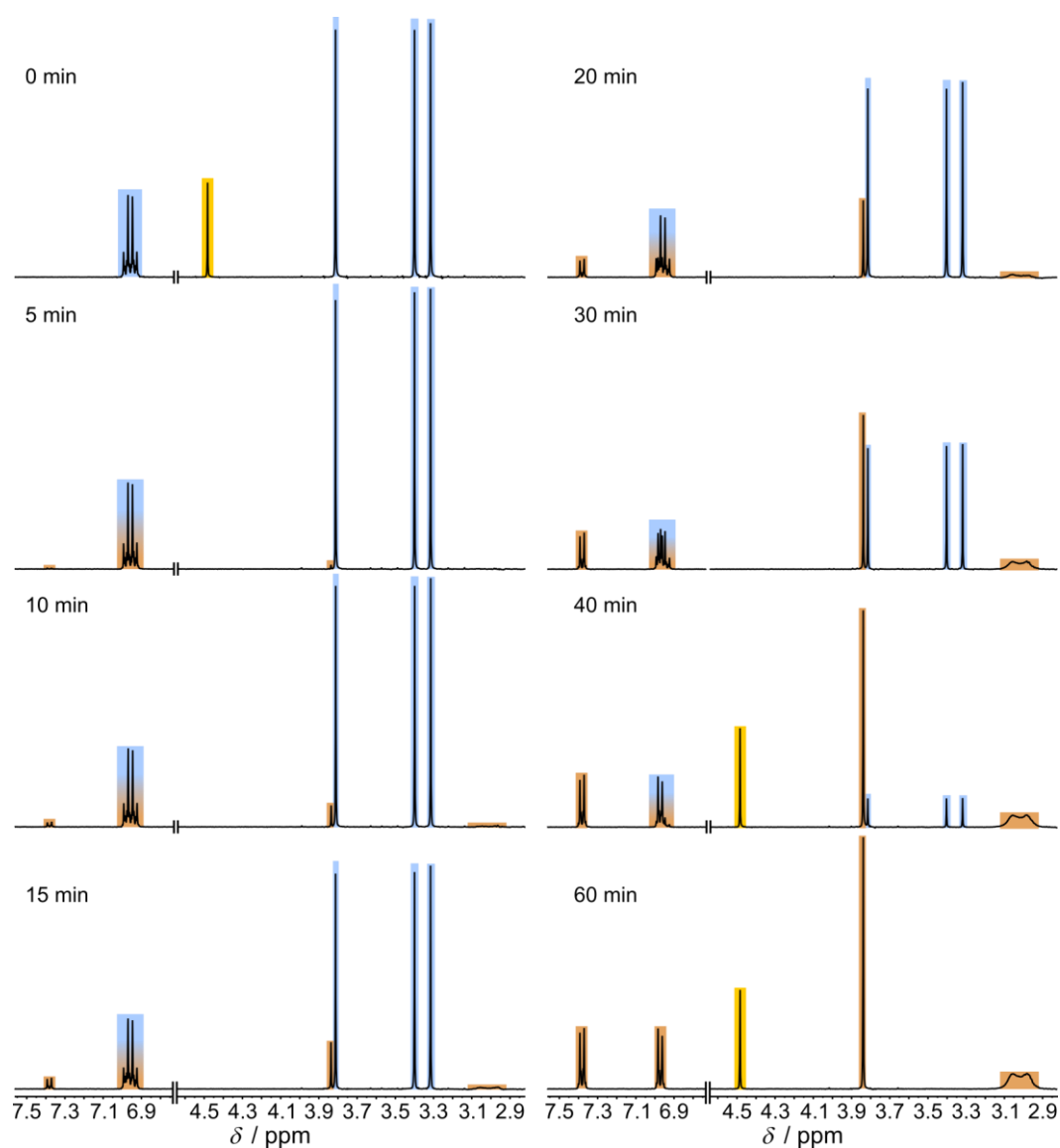


Figure S42. Exemplary partial ^1H NMR spectra of the laboratory-scale reaction using 100 mM O-(4-methoxyphenyl)-dimethylcarbamothioate (blue) and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile recorded after different irradiation time periods. Product resonances highlighted in orange. Ethylene carbonate (yellow) was used as internal standard.

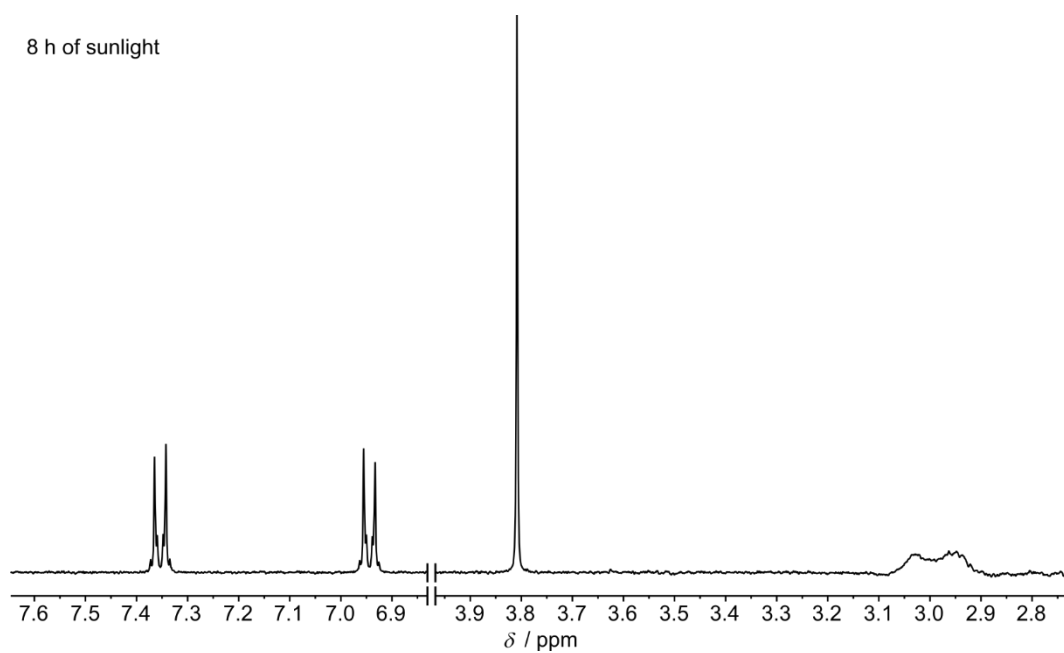


Figure S43. Partial ^1H NMR spectrum (in CD_3CN) of 20 mM O-(4-methoxyphenyl)-dimethylcarbamothioate and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ after irradiation with sunlight for 8 h in acetonitrile (Aug 28, 2024).

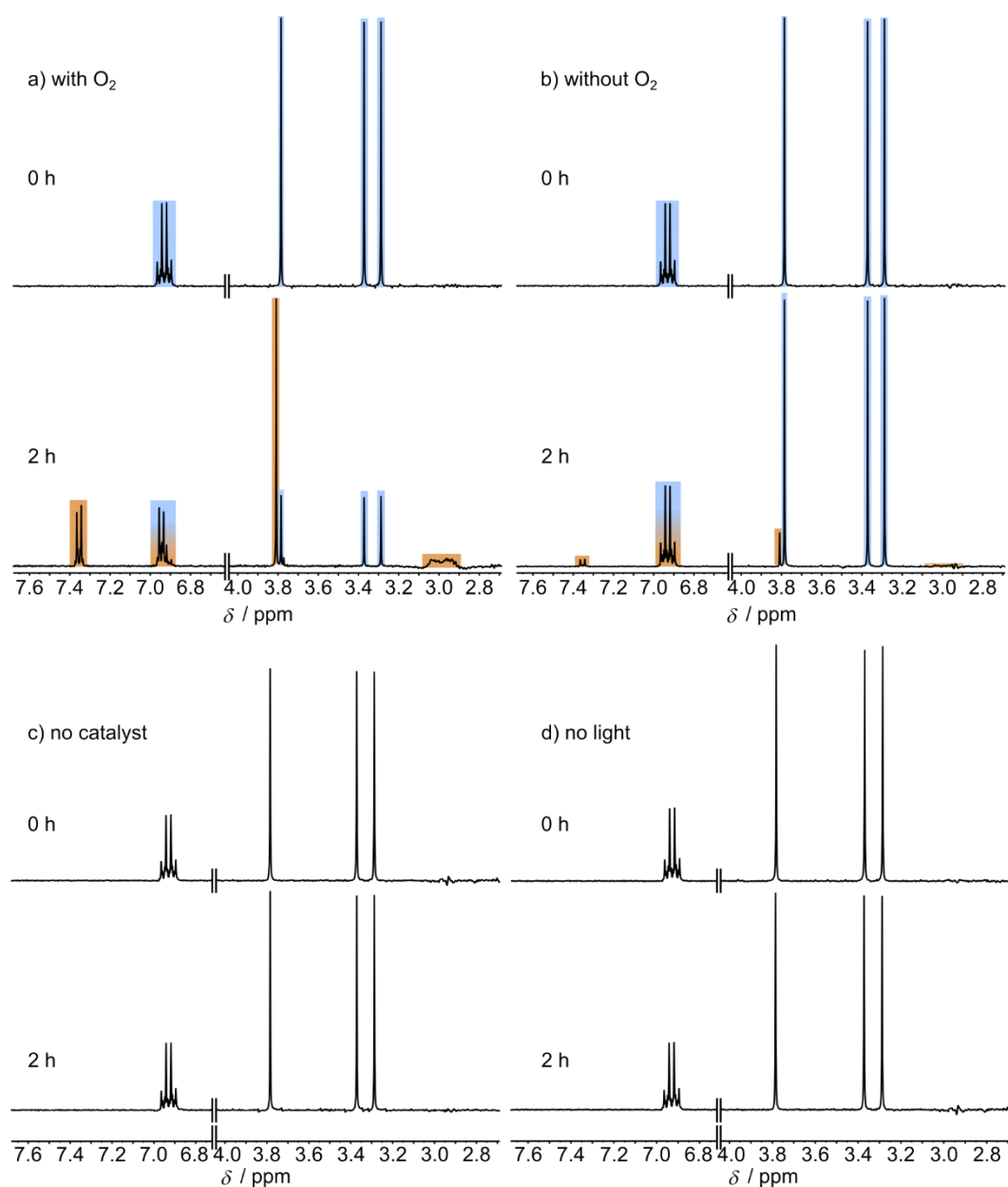


Figure S44. Exemplary partial ^1H NMR spectra of cuvette-scale control experiments using 20 mM O-(4-methoxyphenyl)-dimethylcarbamothioate (blue) and 1 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile under a) aerated and b) deaerated conditions (product resonances highlighted in orange); c) 20 mM O-(4-methoxyphenyl)-dimethylcarbamothioate in acetonitrile without photocatalyst; d) 20 mM O-(4-methoxyphenyl)-dimethylcarbamothioate and 1 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile without light.

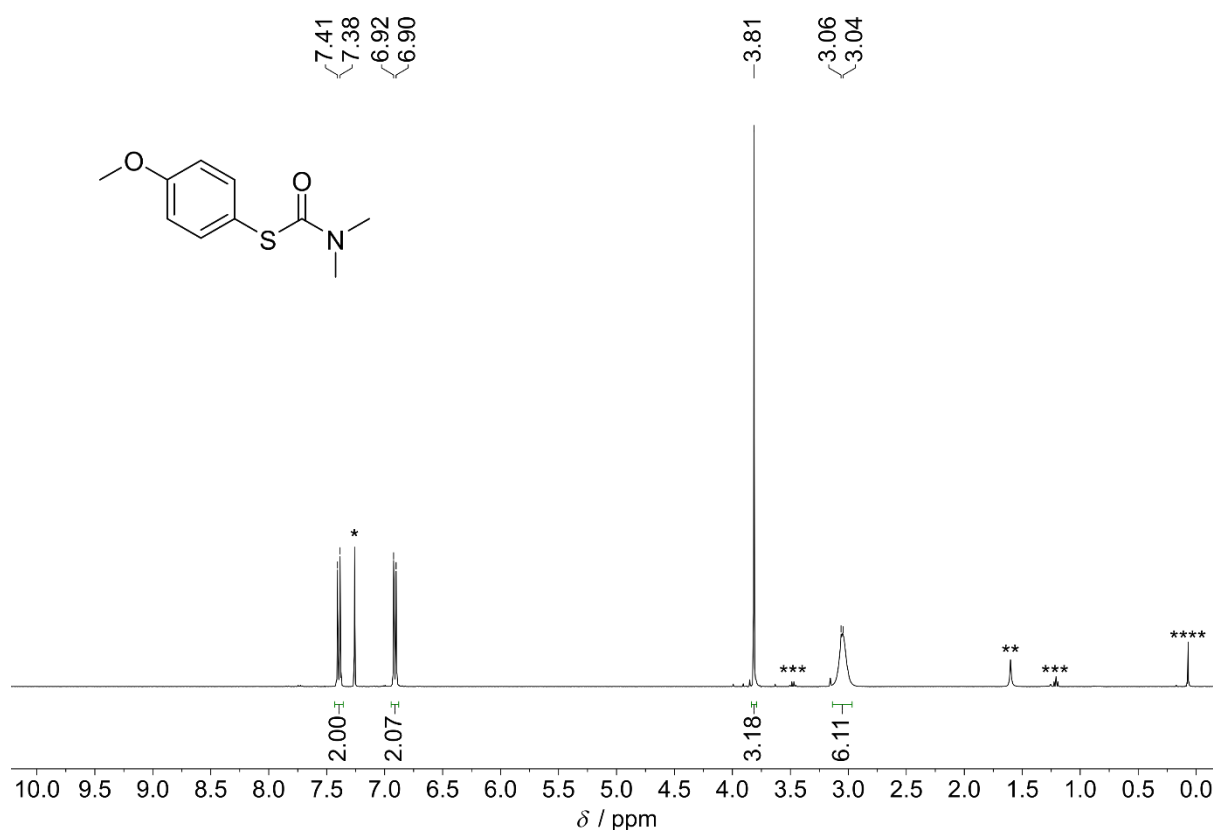


Figure S45. ^1H NMR spectrum of the isolated product S-(4-methoxyphenyl)dimethylcarbamothioate in CDCl_3 . * denotes chloroform solvent resonance; ** denotes residual water; *** denotes residual diethyl ether; **** denotes silicone grease.

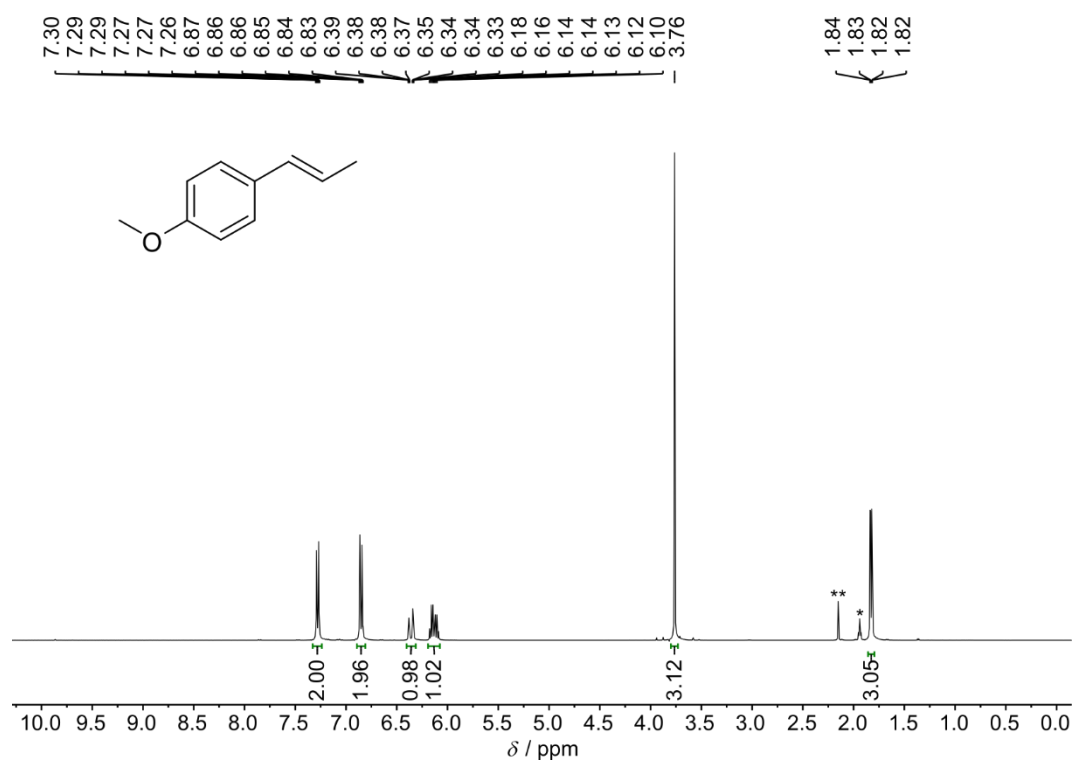


Figure S46. ^1H NMR spectrum of *trans*-anethole in CD_3CN . * denotes acetonitrile solvent resonance. ** denotes resonance of residual water.

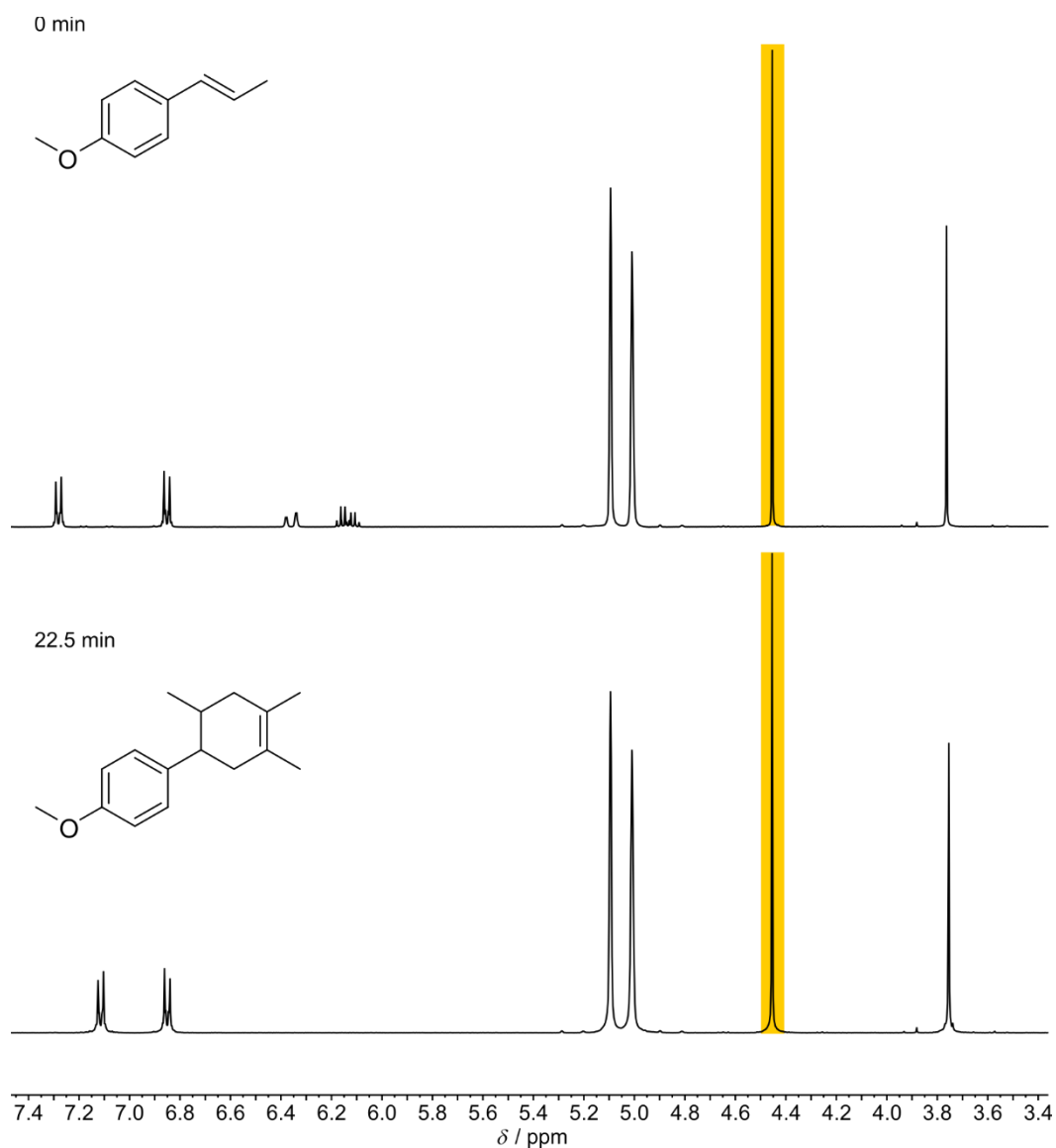


Figure S47. Exemplary partial ^1H NMR spectra of the laboratory-scale reaction using 100 mM *trans*-anethole, 500 mM 2,3-dimethyl-1,3-butadiene and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile. Ethylene carbonate (yellow) was used as internal standard.

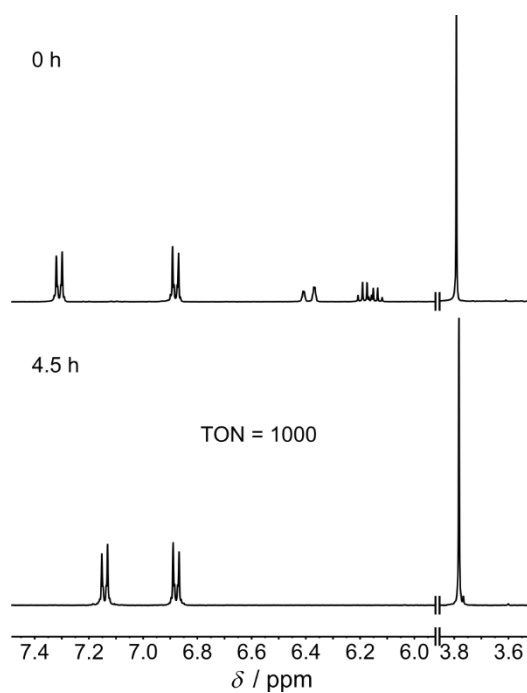


Figure S48. Exemplary partial ^1H NMR spectra of the laboratory-scale reaction using 100 mM *trans*-anethole, 500 mM 2,3-dimethyl-1,3-butadiene and 0.1 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile.

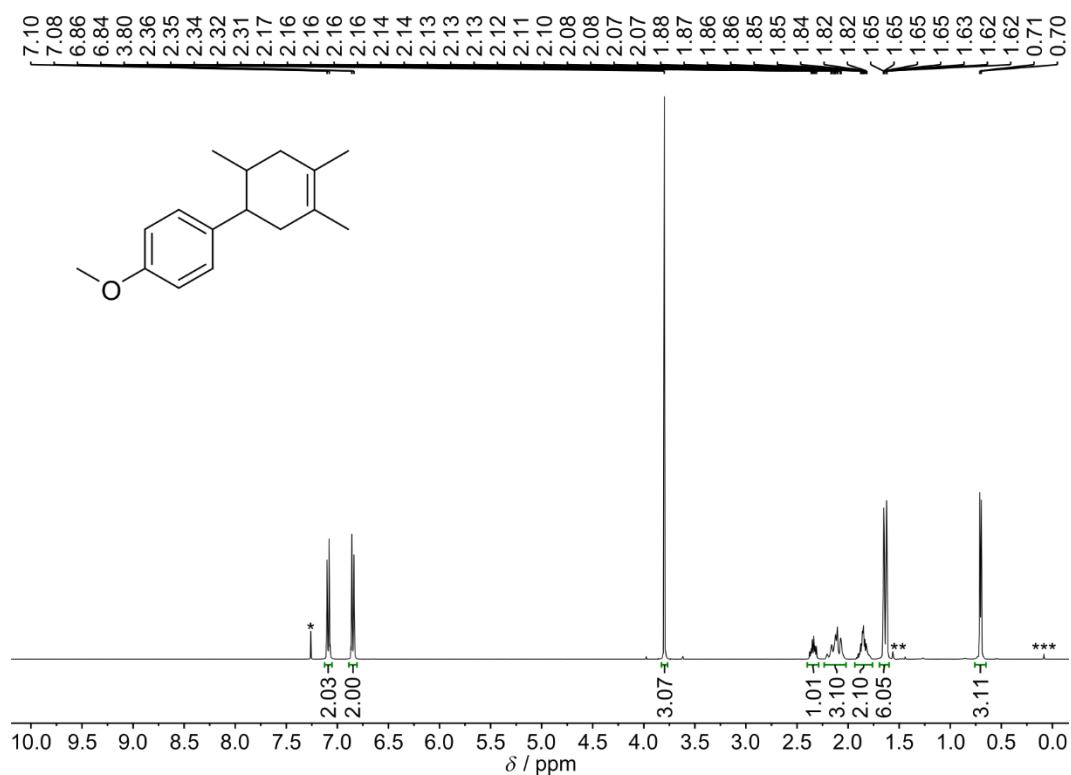


Figure S49. ^1H NMR spectrum of the isolated cycloaddition product in CDCl_3 . * denotes chloroform solvent resonance; ** denotes residual water; *** denotes silicone grease.

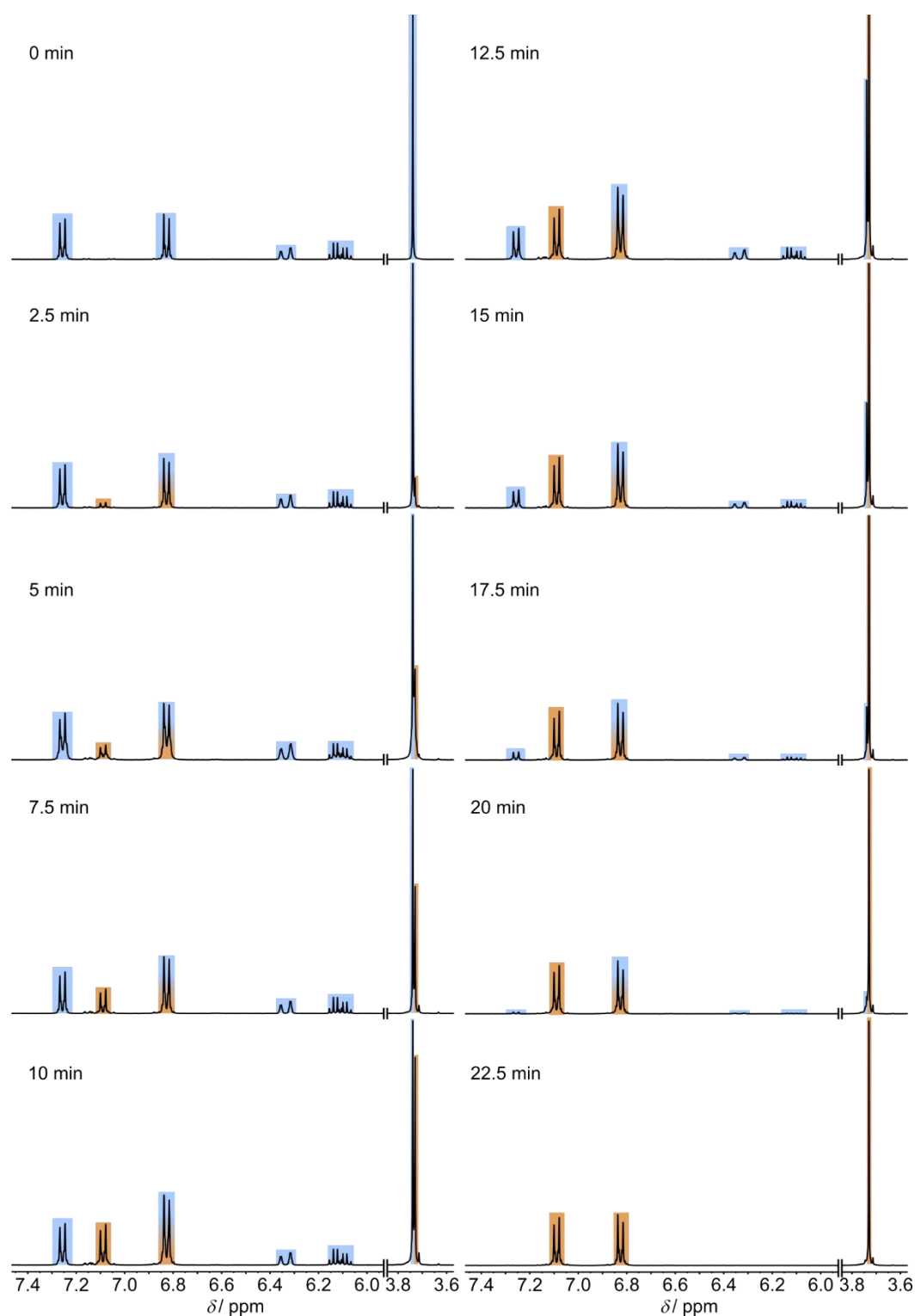


Figure S50. Exemplary partial ^1H NMR spectra of the laboratory-scale reaction using 100 mM *trans*-anethole, 500 mM 2,3-dimethyl-1,3-butadiene and 2 mM $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in acetonitrile recorded after different irradiation time periods. Product resonances highlighted in orange.

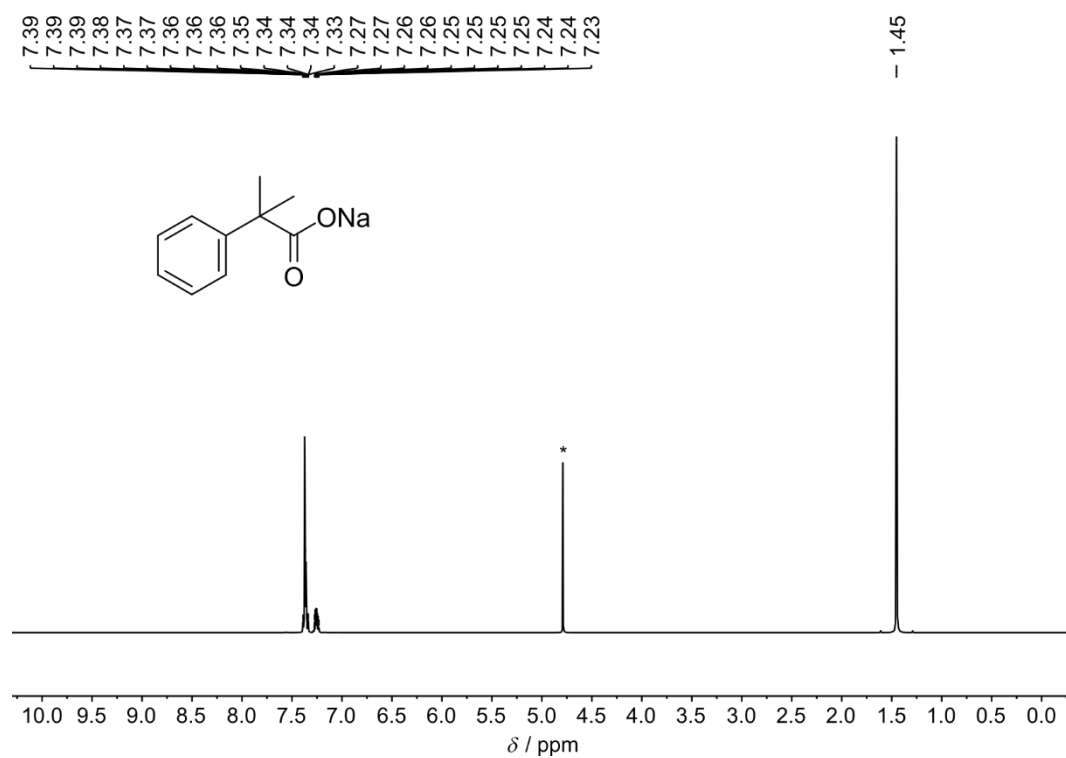


Figure S51. ¹H NMR spectrum of 2-phenylisobutrate in D₂O. * denotes water solvent resonance.

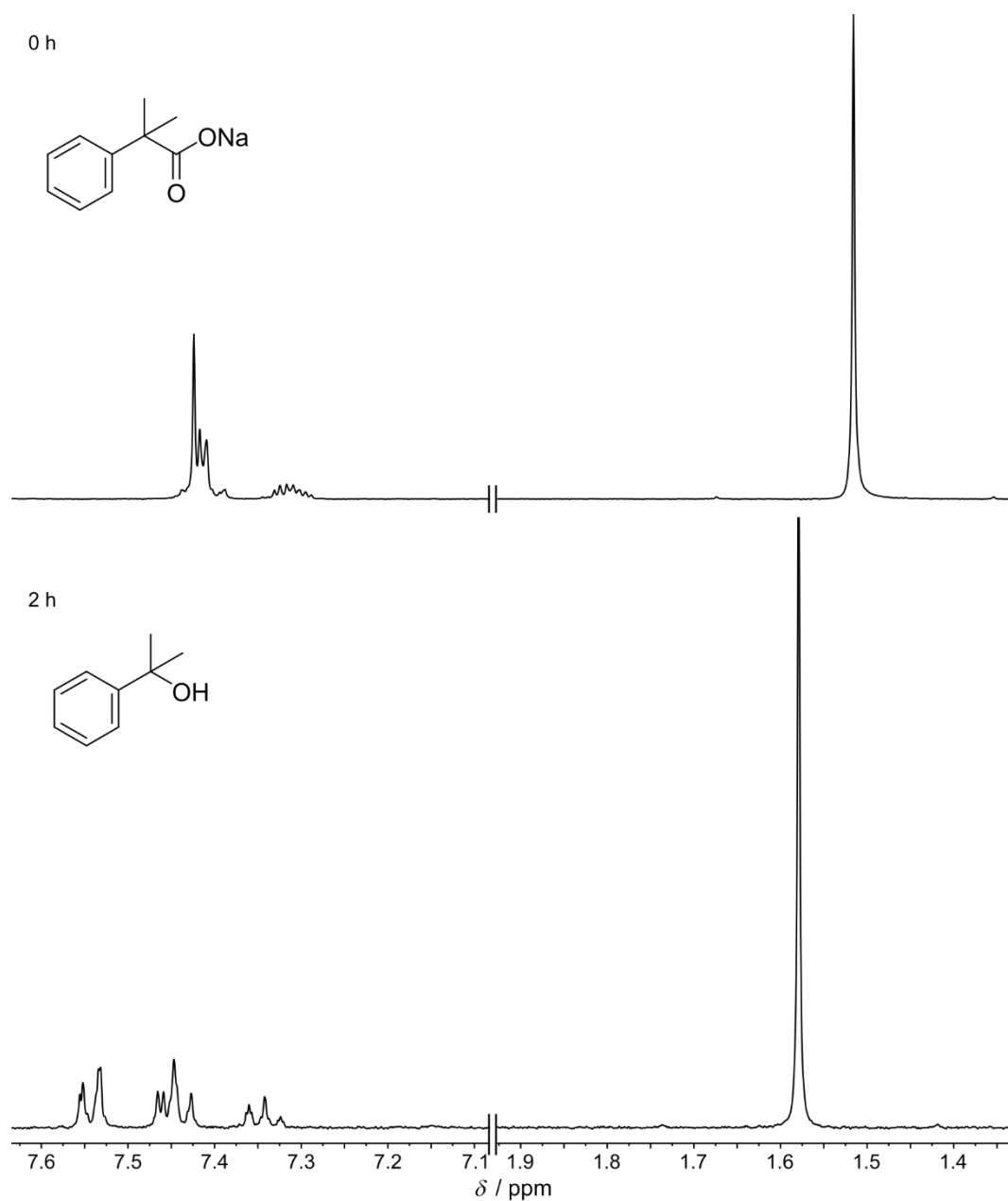


Figure S52. Exemplary partial ^1H NMR spectra (in D_2O) of the reaction using 100 mM 2-phenylisobutyrate, 300 mM Selectfluor[®] and 2 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in aerated water. The reaction control in D_2O after 2 h shows only the resonances of 2-phenyl-2-propanol but none of 2-fluoro-2-phenylpropane, since the fluorinated hydrocarbon is insoluble in water.

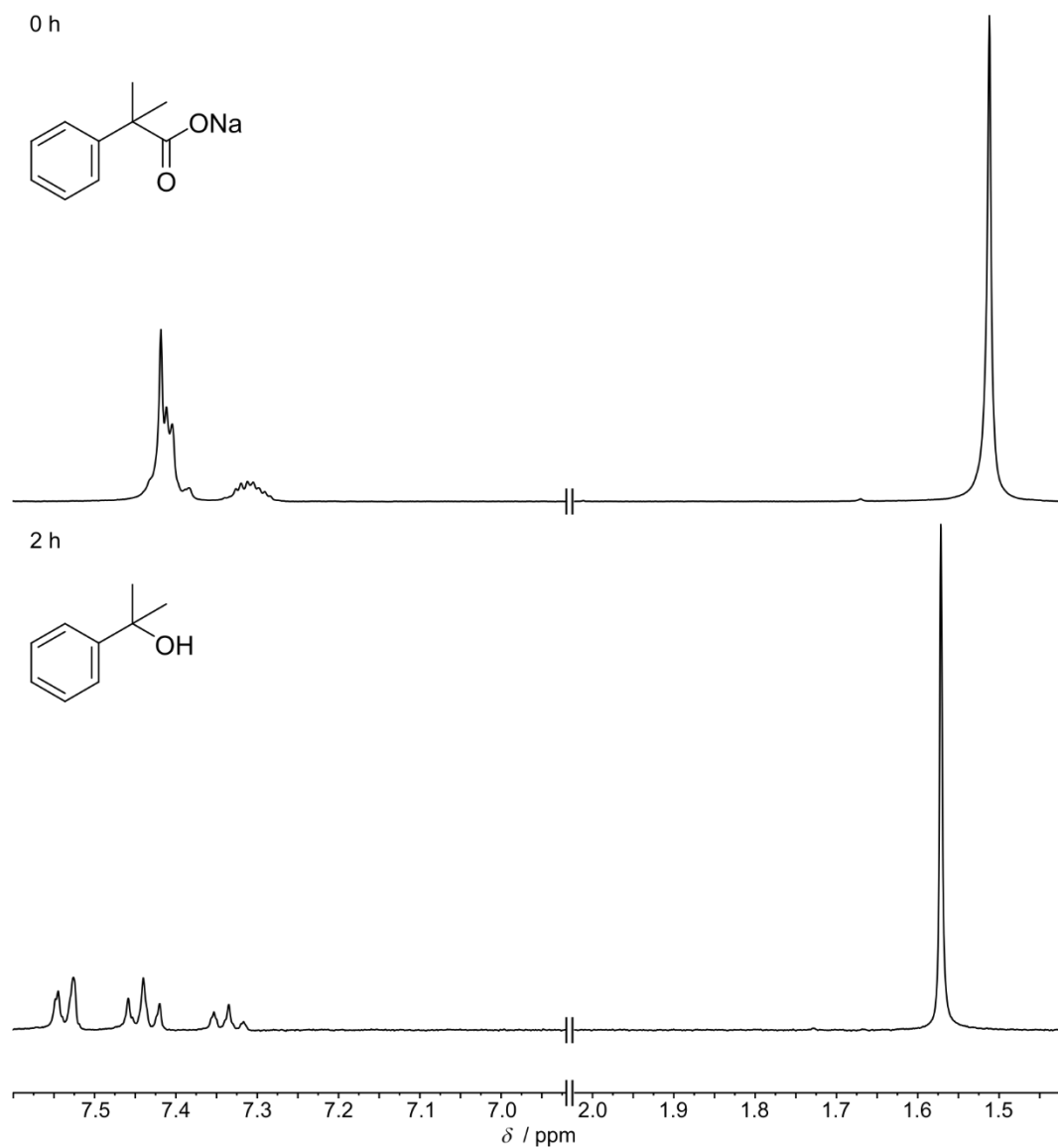


Figure S53. Exemplary partial ^1H NMR spectra of the reaction using 100 mM 2-phenylisobutyrate, 300 mM Selectfluor[®] and 2 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in deaerated water. The reaction control in D_2O after 2 h shows only the resonances of 2-phenyl-2-propanol but none of 2-fluoro-2-phenylpropane, since the fluorinated hydrocarbon is insoluble in water.

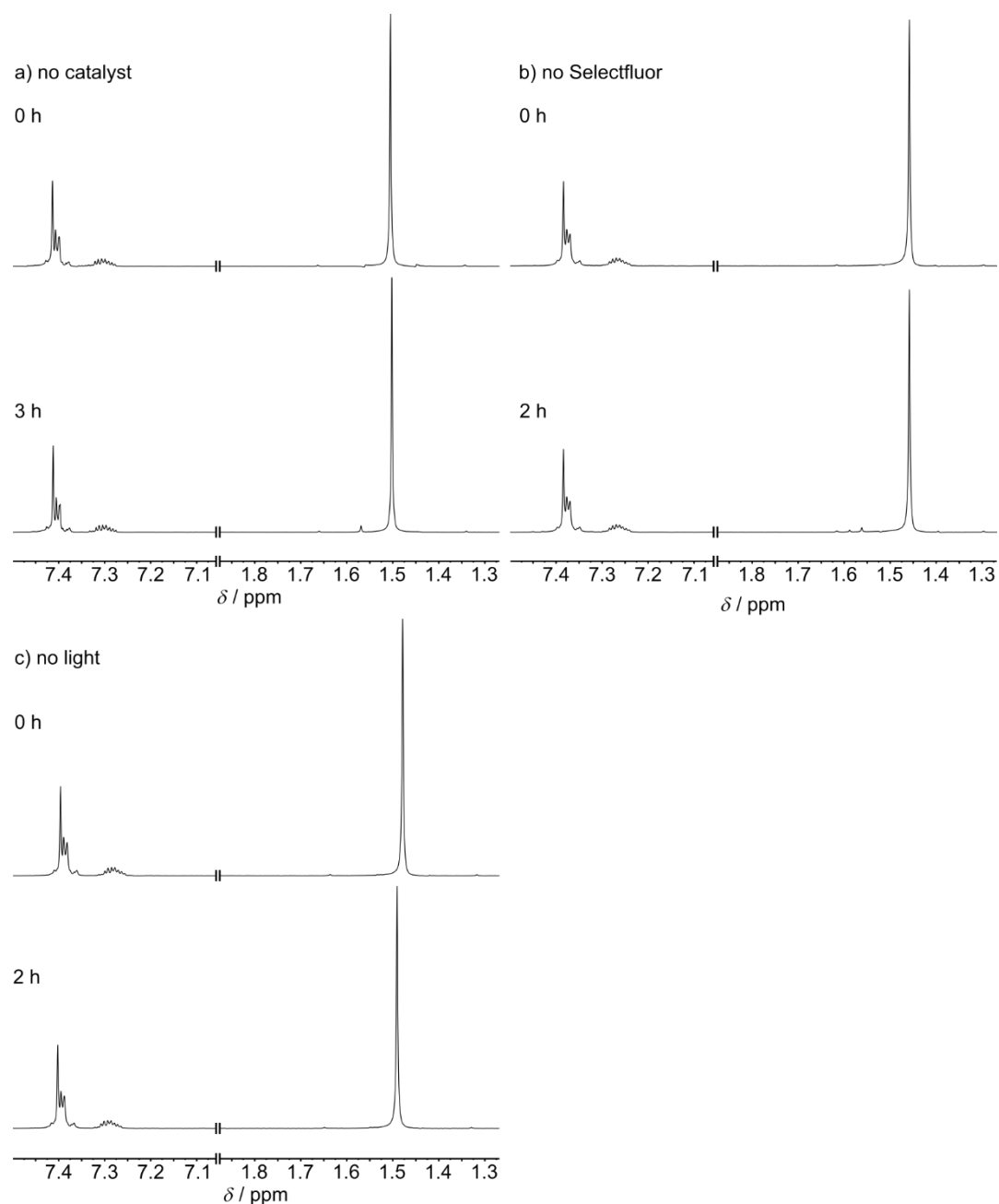


Figure S54. Exemplary partial ^1H NMR spectra of control experiments in D_2O using a) 100 mM 2-phenylisobutyrate and 300 mM Selectfluor[®] in water without photocatalyst; b) 100 mM 2-phenylisobutyrate and 2 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in water without Selectfluor[®]; c) 100 mM 2-phenylisobutyrate, 300 mM Selectfluor[®] and 2 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in water without light.

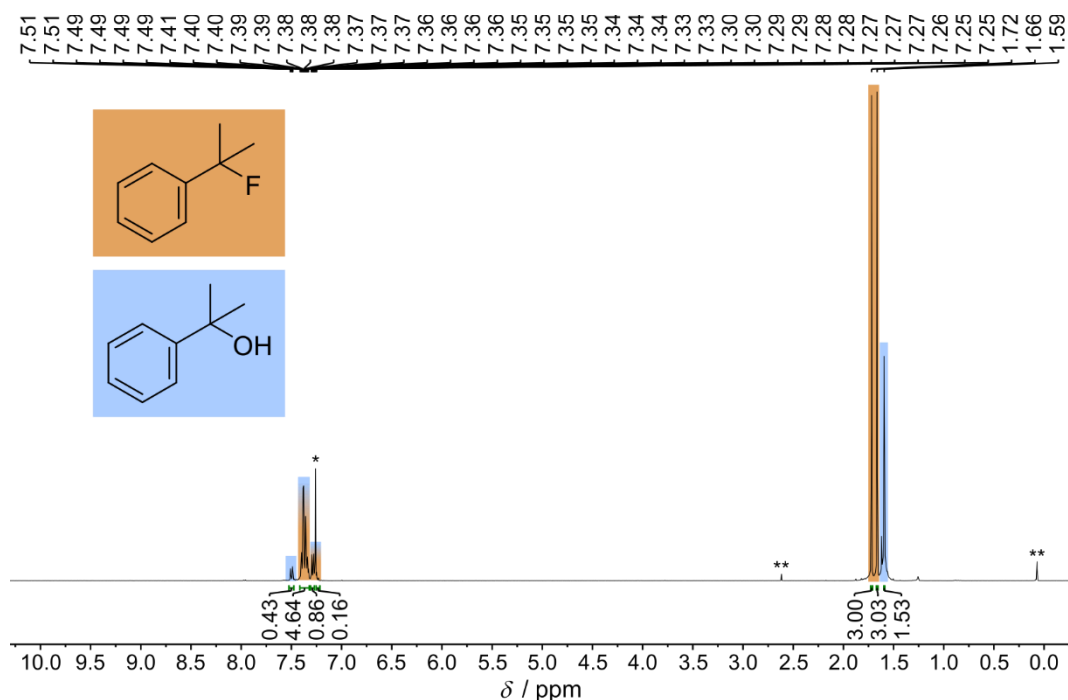


Figure S55. ^1H NMR spectrum of a mixture of 2-fluoro-2-phenylpropane (highlighted in orange) and 2-phenyl-2-propanol (blue) in CDCl_3 . Product mixture obtained from the photooxidative decarboxylation under aerated conditions. * denotes chloroform solvent resonance; ** denotes unidentified impurities. The multiplet from 7.31 to 7.24 ppm overlaps with the chloroform solvent resonance.

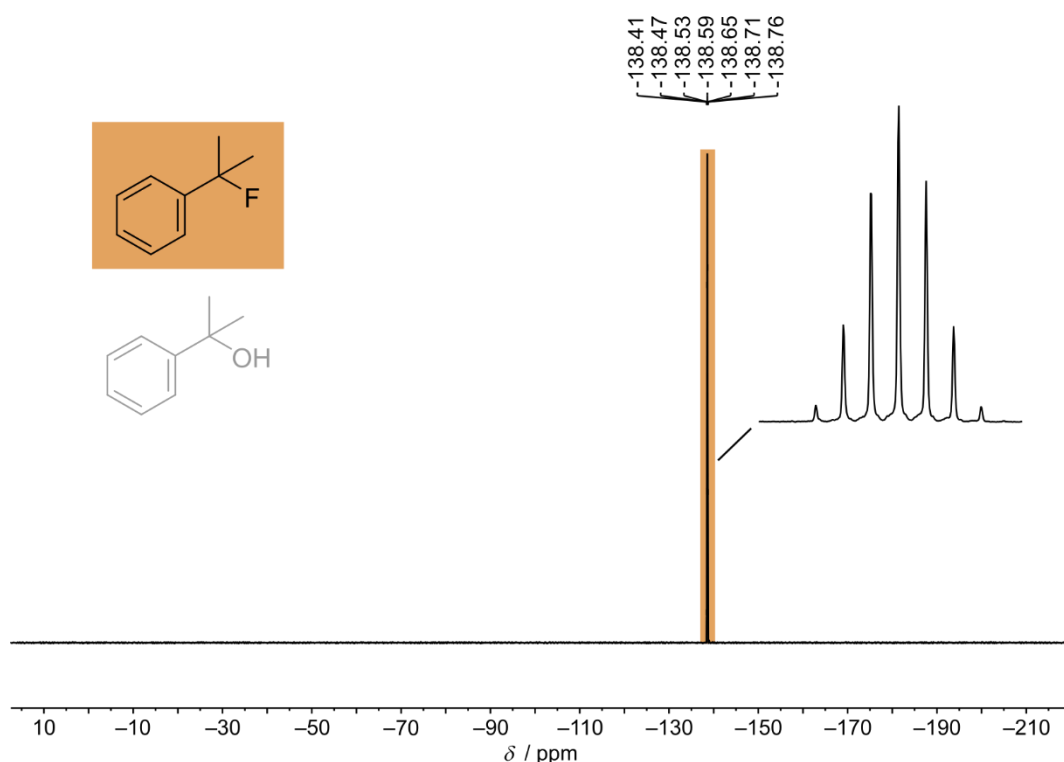


Figure S56. ^{19}F NMR spectrum of a mixture of 2-fluoro-2-phenylpropane (highlighted in orange) and 2-phenyl-2-propanol (no ^{19}F resonance) in CDCl_3 . Product mixture obtained from the photooxidative decarboxylation under aerated conditions. Inset: close-up of the heptet of the ^{19}F resonance.

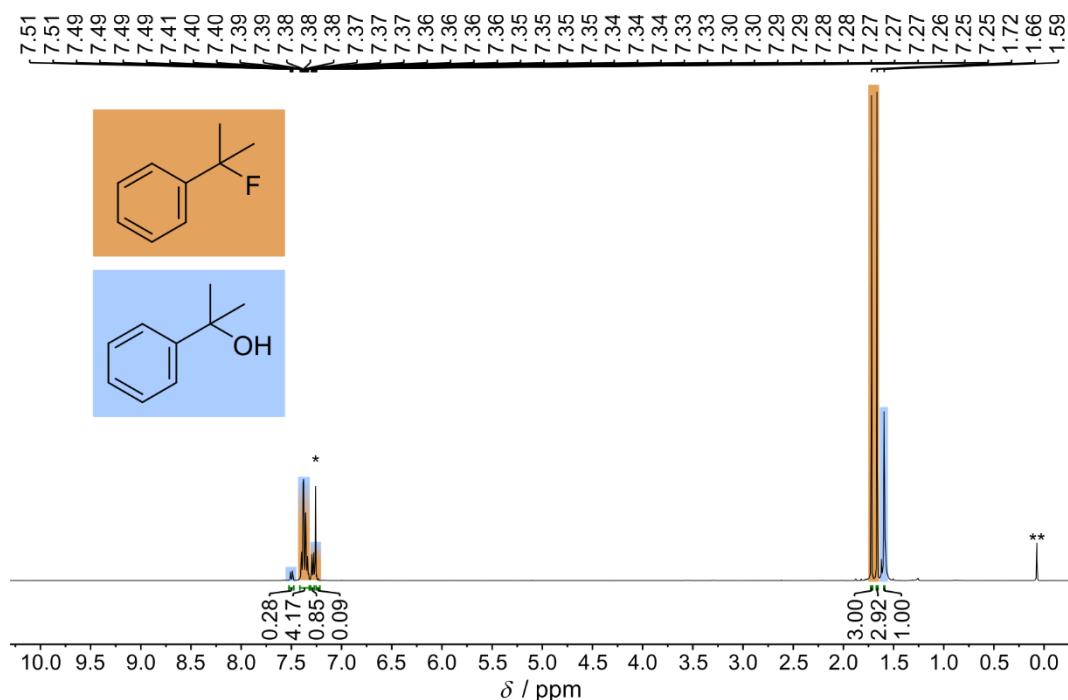


Figure S57. ¹H NMR spectrum of a mixture of 2-fluoro-2-phenylpropane (highlighted in orange) and 2-phenyl-2-propanol (blue) in CDCl₃. Product mixture obtained from the photooxidative decarboxylation under deaerated conditions. * denotes chloroform solvent resonance; ** denotes an unidentified impurity. The multiplet from 7.31–7.24 ppm overlaps with the chloroform solvent resonance.

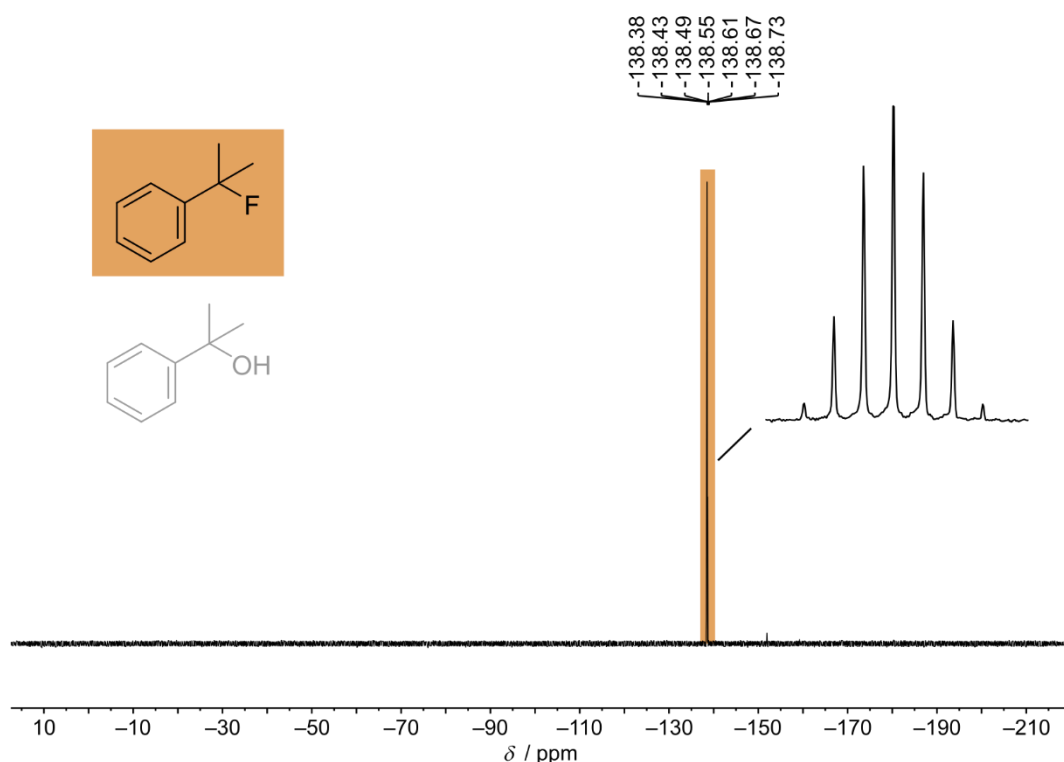


Figure S58. ¹⁹F NMR spectrum of a mixture of 2-fluoro-2-phenylpropane (highlighted in orange) and 2-phenyl-2-propanol (no ¹⁹F resonance) in CDCl₃. Product mixture obtained from the photooxidative decarboxylation under deaerated conditions. Inset: close-up of the heptet of the ¹⁹F resonance.

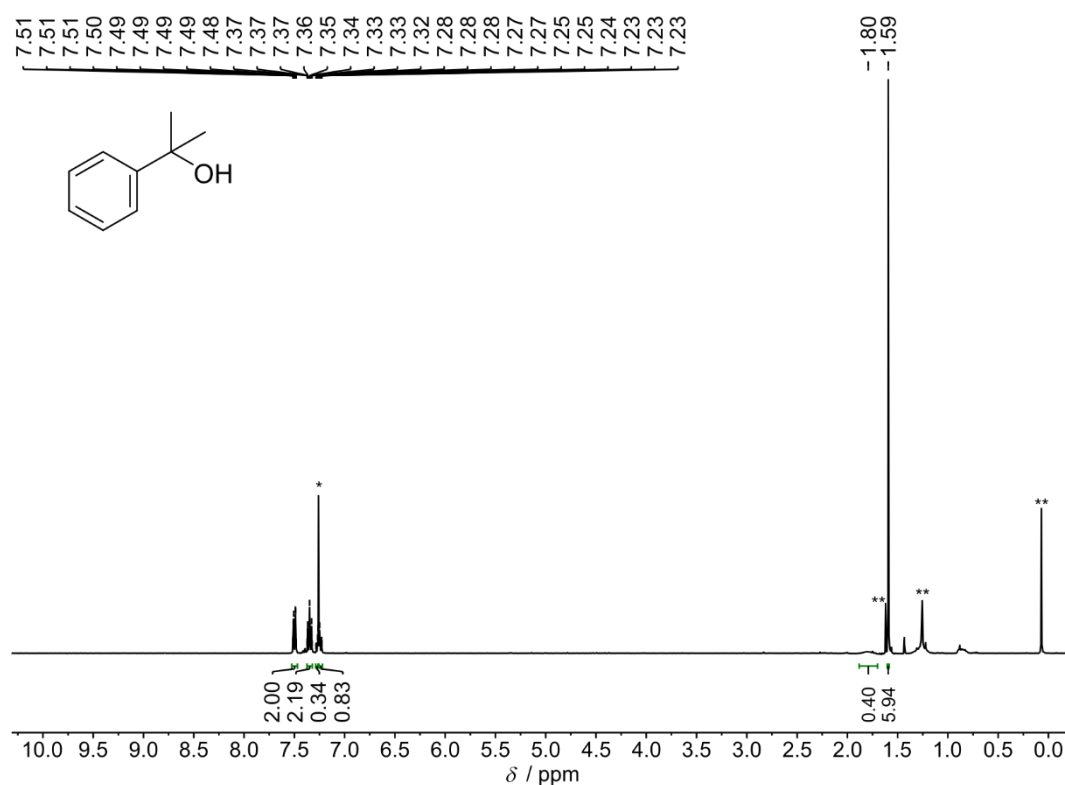


Figure S59. ^1H NMR spectrum of 2-phenyl-2-propanol in CDCl_3 . * denotes chloroform solvent resonance. ** denotes unidentified impurities. The multiplet from 7.27–7.23 ppm overlaps with the chloroform solvent resonance.

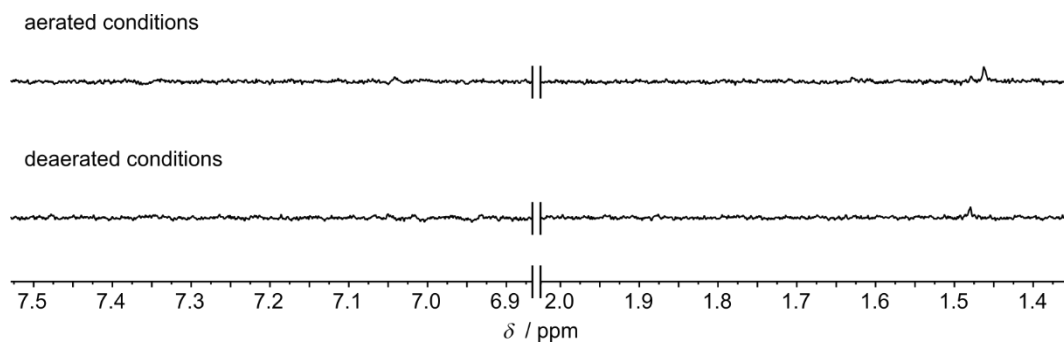


Figure S60. Exemplary partial ^1H NMR spectra (in D_2O) of the extracted aqueous phases after the photooxidative decarboxylation under aerated and deaerated conditions. In both cases no residual sodium 2-phenylisobutyrate is observed.

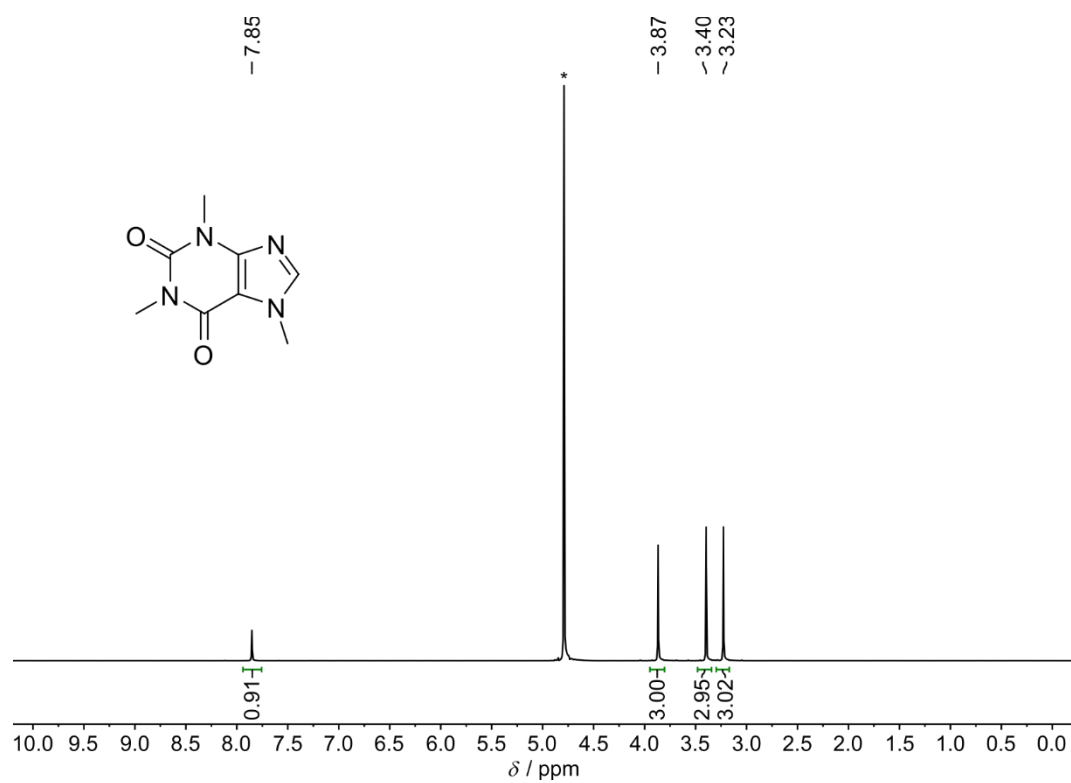


Figure S61. ¹H NMR spectrum of caffeine in D₂O. * denotes water solvent resonance.

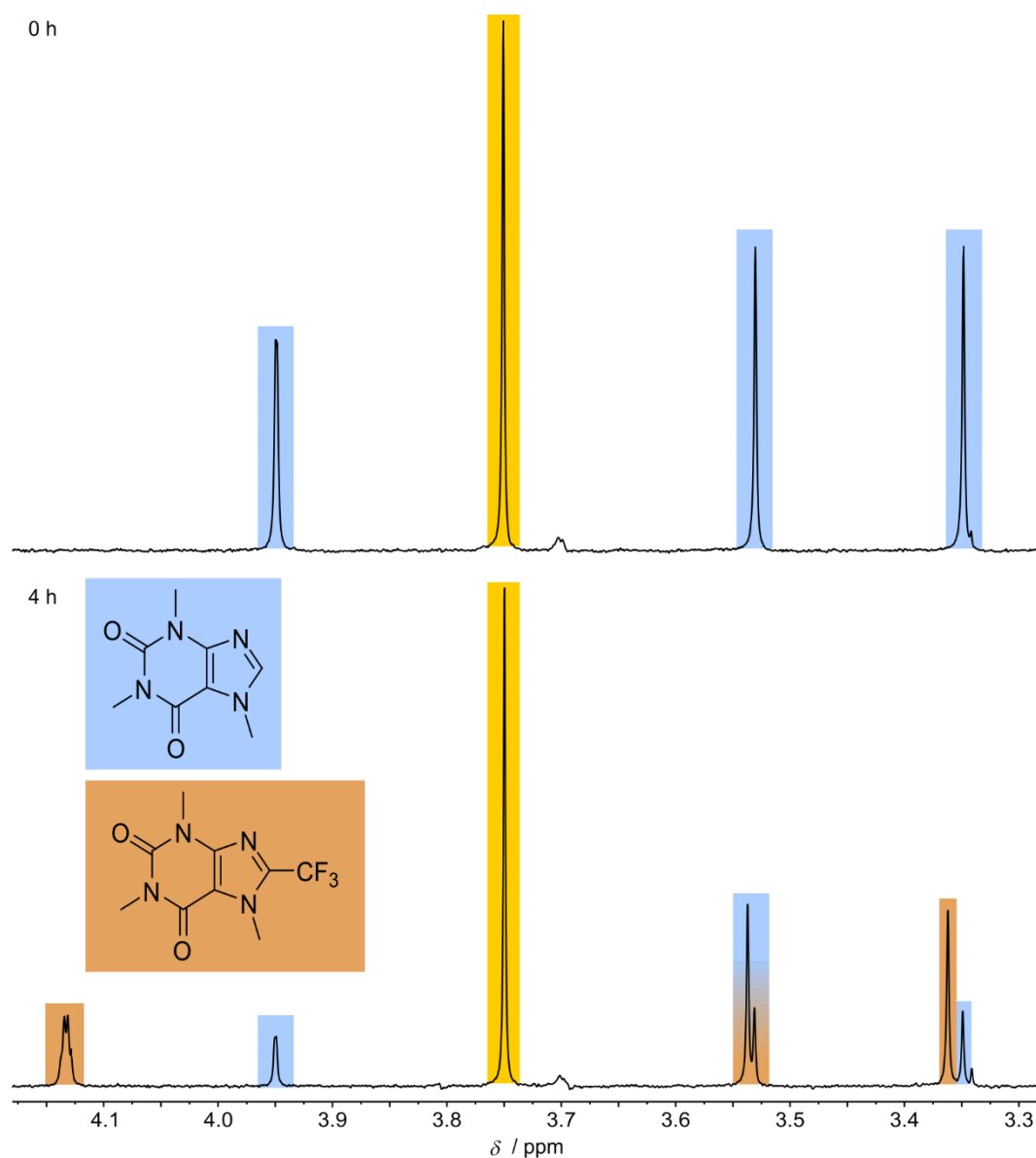


Figure S62. Exemplary partial ^1H NMR spectra of the reaction using 10 mM caffeine (blue), 10 mM ammonium peroxodisulfate, 30 mM Langlois reagent and 2 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in deaerated D_2O with 1,4-dioxane (yellow) as internal standard. Product resonances highlighted in orange.

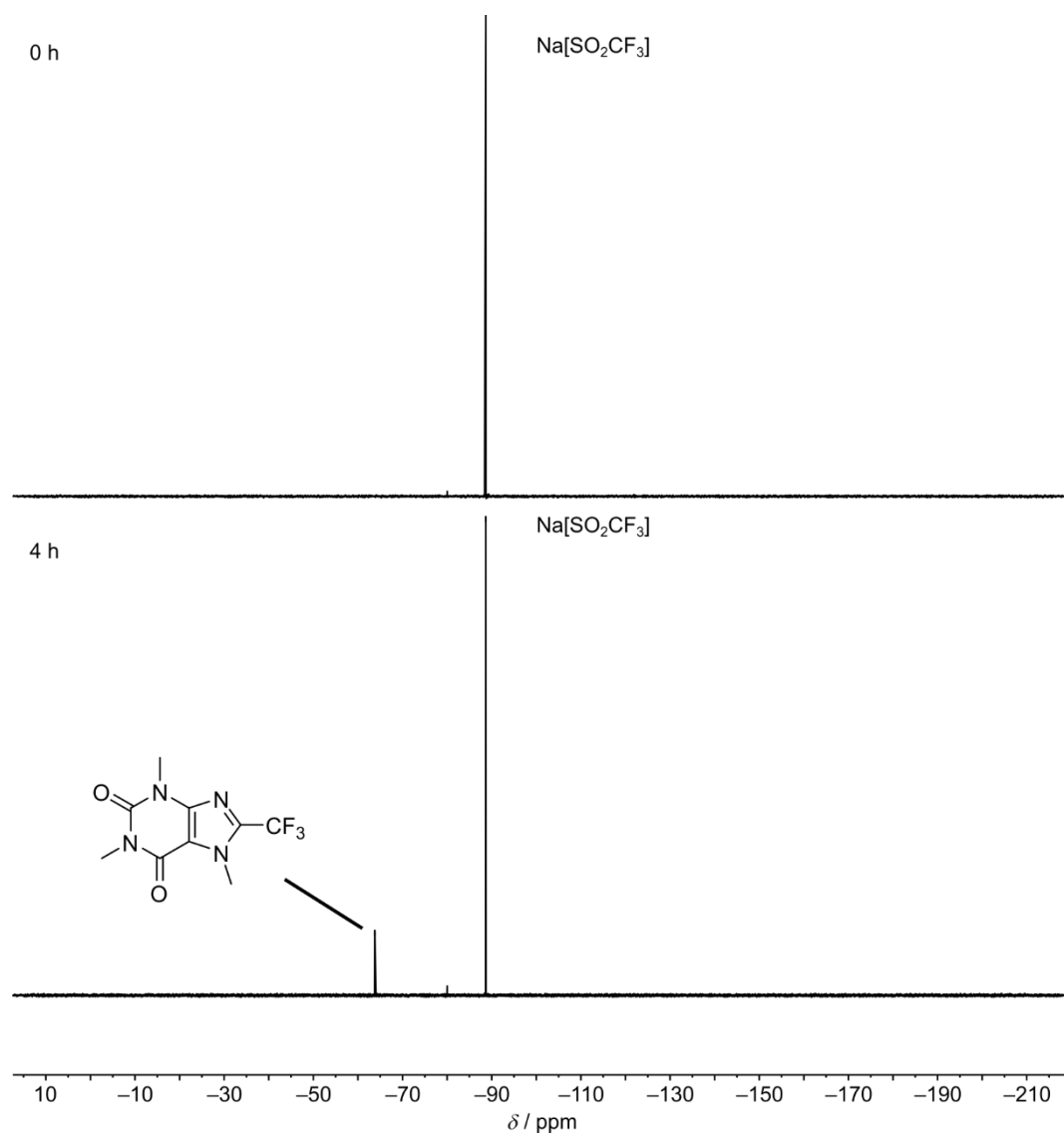


Figure S63. Exemplary ¹⁹F NMR spectra of the reaction using 10 mM caffeine, 10 mM ammonium peroxodisulfate, 30 mM Langlois reagent and 2 mM [Cr(tpe)₂][NO₃]₃ in D₂O.

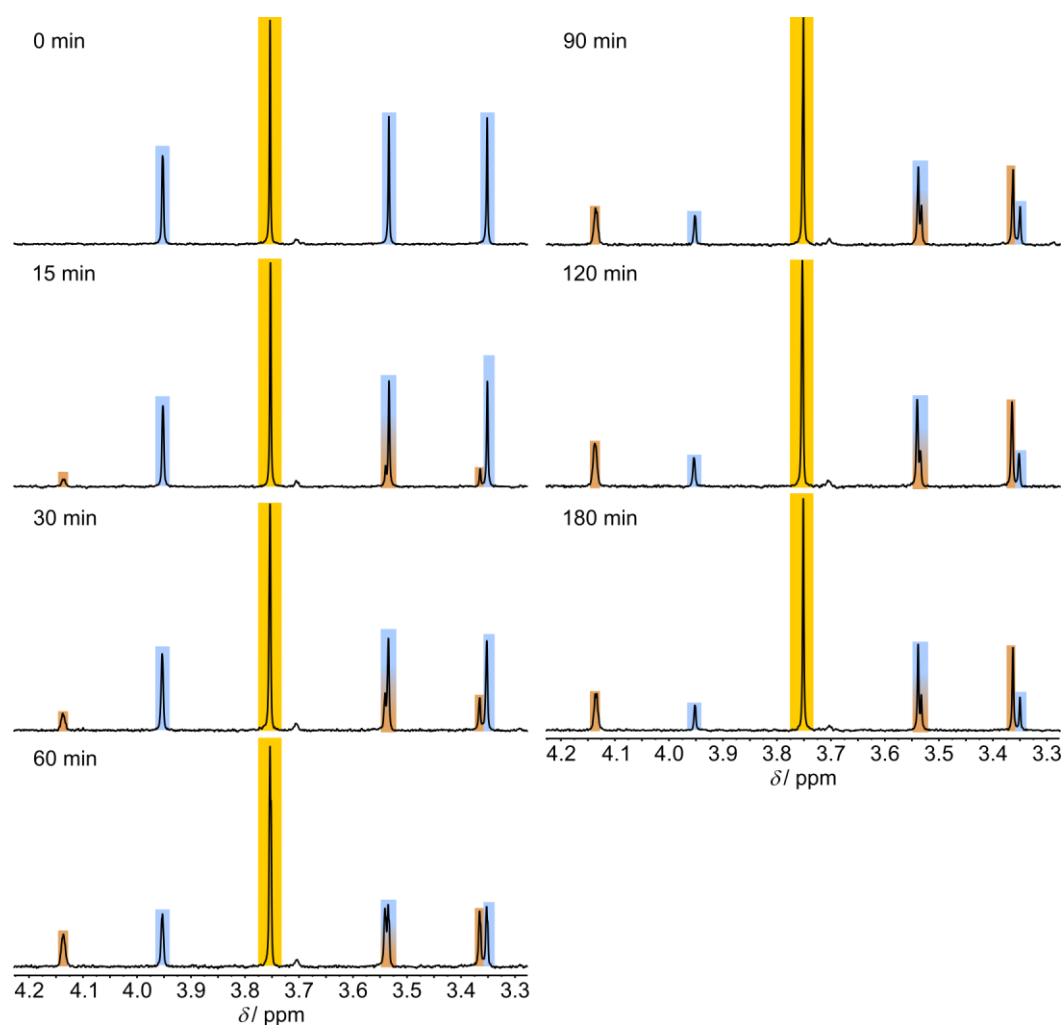


Figure S64. Exemplary partial ^1H NMR spectra of the reaction using 10 mM caffeine (blue), 10 mM ammonium peroxodisulfate, 30 mM Langlois reagent and 2 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in deaerated D_2O recorded after different irradiation time periods. 1,4-dioxane (yellow) was used as internal standard. Product resonances highlighted in orange.

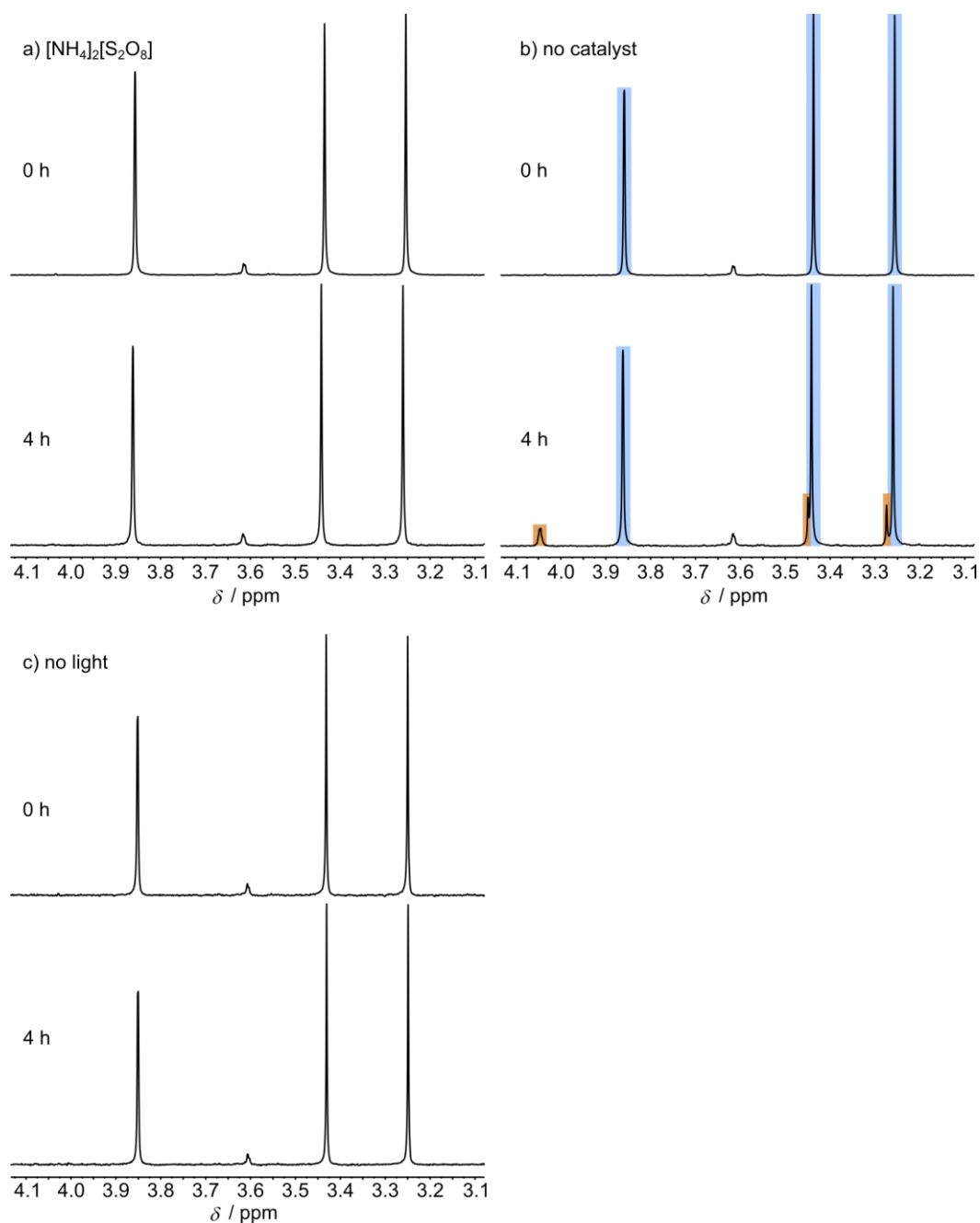


Figure S65. Exemplary partial ^1H NMR spectra of cuvette-scale control experiments using a) 10 mM caffeine, 30 mM Langlois reagent and 2 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in deaerated D_2O without the sacrificial oxidant ammonium peroxodisulfate; b) 10 mM caffeine (blue), 10 mM ammonium peroxodisulfate, 30 mM Langlois reagent in deaerated D_2O without photocatalyst (product resonances highlighted in orange); c) 10 mM caffeine, 10 mM ammonium peroxodisulfate, 30 mM Langlois reagent and 2 mM $[\text{Cr}(\text{tpe})_2][\text{NO}_3]_3$ in deaerated D_2O without light.

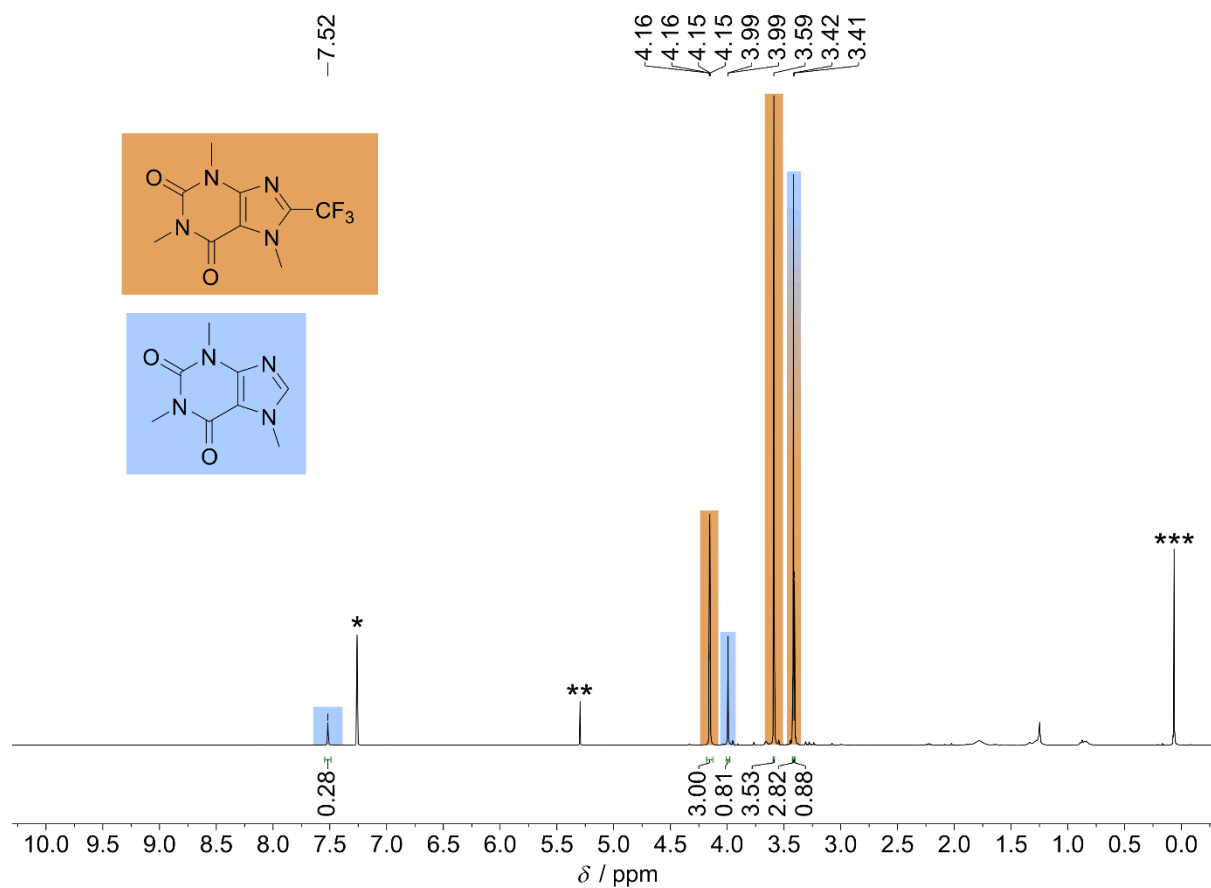


Figure S66. ¹H NMR spectrum of a mixture of 1,3,7-trimethyl-8-(trifluoromethyl)-7H-purine-2,6-dione (highlighted in orange) and caffeine (blue) in CDCl₃. * denotes chloroform solvent resonance; ** denotes residual dichloromethane; *** denotes silicone grease.

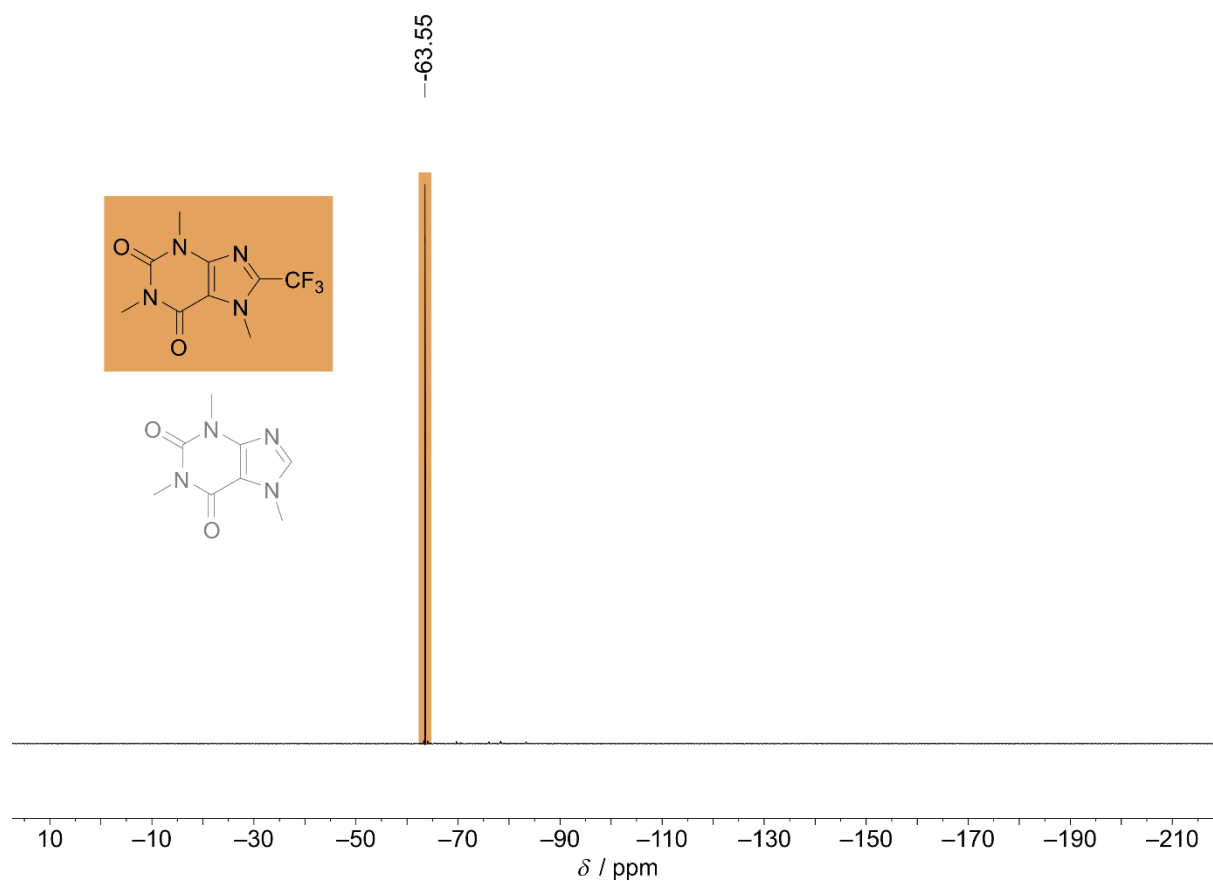


Figure S67. ^{19}F NMR spectrum of a mixture of 1,3,7-trimethyl-8-(trifluoromethyl)-7H-purine-2,6-dione (orange) and caffeine (no ^{19}F resonance) in CDCl_3 .

References

- [1] V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta* **2000**, 298, 97.
- [2] I. Ahmad, Z. Anwar, S. A. Ali, K. A. Hasan, M. A. Sheraz, S. Ahmed, *J. Photochem. Photobiol. B* **2016**, 157, 113.
- [3] J. N. Brönsted, *Z. Phys. Chem.* **1922**, 102, 169.
- [4] N. Bjerrum, *Z. Phys. Chem.* **1924**, 108, 82.
- [5] *STOE & Cie, X-Area*, STOE & Cie GmbH: Darmstadt, Germany.
- [6] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, 51, 33.
- [7] A. L. Spek, *Acta Crystallogr. Sect. D* **2009**, 65, 148.
- [8] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, 71, 3.
- [9] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, 71, 3.
- [10] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, 64, 112.
- [11] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, 44, 1281.
- [12] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, 29, 2176.
- [13] W. R. Kitzmann, M.-S. Bertrams, P. Boden, A. C. 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, 16597.
- [14] S. Treiling, C. Wang, C. Förster, F. Reichenauer, J. Kalmbach, P. Boden, J. P. Harris, L. M. Carrella, E. Rentschler, U. Resch-Genger, C. Reber, M. Seitz, M. Gerhards, K. Heinze, *Angew. Chem. Int. Ed.* **2019**, 58, 18075.
- [15] D. M. Arias-Rotondo, J. K. McCusker, *Chem. Soc. Rev.* **2016**, 45, 5803.
- [16] A. J. Perkowski, C. L. Cruz, D. A. Nicewicz, *J. Am. Chem. Soc.* **2015**, 137, 15684.
- [17] P. J. Larkin, *Infrared and Raman Spectroscopy*, Elsevier, **2018**.
- [18] N. A. Porter, J. S. Wujek, *J. Org. Chem.* **1987**, 52, 5085.
- [19] S. Lin, M. A. Ischay, C. G. Fry, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, 133, 19350.
- [20] E. W. Webb, J. B. Park, E. L. Cole, D. J. Donnelly, S. J. Bonacorsi, W. R. Ewing, A. G. Doyle, *J. Am. Chem. Soc.* **2020**, 142, 9493.
- [21] D. Arnodo, M. Ramos-Martín, L. Cicco, V. Capriati, N. Ríos-Lombardía, J. González-Sabín, A. Presa Soto, J. García-Álvarez, *Org. Biomol. Chem.* **2023**, 21, 4414.
- [22] I. Abdiaj, C. Bottecchia, J. Alcazar, T. Noël, *Synthesis* **2017**, 49, 4978.

6.4 Supporting Information: Decoupling Redox Potentials and Excited State Energies in Substituted Chromium(III) Chromophores

Decoupling Redox Potentials and Excited State Energies in Substituted Chromium(III) Chromophores

Steven Sittel, [REDACTED]
[REDACTED]

Supporting Information

General. $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$,^[24-26] $\text{Cr}(\text{OTf})_3$ ^[44] and 1,1-bis(2-pyridyl)ethane^[40] were synthesized according to literature procedures. 2-Fluoro-4-(trifluoromethyl)pyridine (Angene Chemical, 98%), $\text{CrCl}_3 \times 6\text{H}_2\text{O}$ (Alfa Aesar, >99.5%), $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ for synthesis (>98%, TCI), trimethylsilyl trifluoromethanesulfonate (TMSOTf; TCI, >98%), NaCl (Thermo Fisher Scientific, ≥99.5%), cobaltocene (Sigma-Aldrich), ferrocenium hexafluorophosphate (Sigma-Aldrich), methanol, isopropanol, acetonitrile, diethylether, bis(2-methoxyethyl)ether, acetonitrile for spectroscopy (Supelco, hypergrade), water, CD_3CN (Deutero[®]) were commercially available and used as received. $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ for electrochemical experiments (≥99% for electrochemical analysis, Sigma-Aldrich) was dried at 80 °C at reduced pressure (10^{-3} mbar) for three days and stored under argon. Syntheses and handling of air-sensitive compounds were either conducted using Schlenk techniques or a glovebox (UniLab/Mbraun – Ar 5.0; O_2 <0.1 ppm; H_2O <0.1 ppm). Microwave syntheses were conducted using a CEM Discover microwave in 10 mL glass vials with Teflon seal caps under stirring.

Intensity data for crystal structure determination of $\text{Cr}(\text{OTf})_3(\text{tpe})$ were collected with a STOE IPDS-2T diffractometer from STOE & CIE GmbH with an Oxford cooling using Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The diffraction frames were integrated using the STOE X-AREA^[71] software package and were corrected for absorption with MULABS^[72] of the PLATON software package.^[73] The structures were solved with SHELXT^[74] and refined by the full-matrix method based on F^2 using SHELXL^[75] of the SHELX^[76] software package and the ShelXle^[77] graphical interface. 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 structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2479151.

Crystallographic data of $\text{Cr}(\text{OTf})_3(\text{tpe})$: $\text{C}_{20}\text{H}_{15}\text{CrF}_9\text{N}_3\text{O}_9\text{S}_3$ (760.53); monoclinic; $P2_1/c$, $a = 10.781(2)$ Å, $b = 13.484(3)$ Å, $c = 18.923(4)$ Å, $\beta = 102.31(3)^\circ$; $V = 2687.8(10)$ Å³, $Z = 4$; density (calculated) = 1.879 g cm⁻³; $T = 120(2)$ K; $\mu = 0.778$ mm⁻¹; $F(000) = 1524$; crystal size $0.900 \times 0.380 \times 0.070$ mm³; $\theta = 2.454$ to 28.129 deg.; $-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-25 \leq l \leq 24$; rfln collected = 32444; rfln unique = 6505 [$R(\text{int}) = 0.0613$]; completeness to $\theta = 25.242$ deg. = 99.9 %; semi empirical absorption correction from equivalents; max. and min. transmission 1.20201 and 0.84693; Data 6505; restraints 682; parameters 553; goodness-of-fit on $F^2 = 1.064$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0398$, $wR_2 = 0.1002$; R indices (all data) $R_1 = 0.0522$, $wR_2 = 0.1075$; largest diff. peak and hole 1.051 and -0.445 e Å⁻³.

HPLC purification and analysis was carried out using a Jasco LC-NetII/ADC control unit, two Jasco PU-2087 Plus pumps, a Jasco CO-4060 column oven and a Jasco UV-2075 Plus absorption detector. Fractions were collected using an Advantec CHF122SC fraction collector. Eluents were degassed by a Gastorr AG-42 degassing unit and subsequently mixed with a high-pressure mixing unit. Analytical runs were conducted on a Macherey-Nagel EC Nucleodur HILIC column (5 μ m, 4.6 $\times$ 250 mm), while semipreparative separations were conducted on a Macherey-Nagel VP Nucleodur HILIC column (5 μ m, 21 $\times$ 250 mm). Discrimination between *cis* and *trans* isomers was achieved using a chiral column ChiralPAK IC (5 μ m, 4.6 $\times$ 250 mm) column from Daicel.

Electrochemical experiments were carried out on a BioLogic SP-200 voltammetric analyzer. Platinum wires were used as working and counter electrodes and 10 mM Ag/AgNO₃ (100 mM [*n*-Bu₄N][ClO₄] in MeCN) was used as the reference electrode. For [Cr(tpe)₂][PF₆]₃, a glassy carbon working electrode was used. 100 mM [*n*-Bu₄N][PF₆] as supporting electrolyte in MeCN and 1 mM of the sample were used. Cyclic voltammetry experiments were carried out at scan rates of 50–100 mV s⁻¹. Potentials were referenced relative to the ferrocenium/ferrocene couple. Potentials were converted to the saturated calomel electrode (SCE).^[63]

IR spectra were recorded with a Bruker Alpha II FTIR spectrometer with an ATR unit containing a diamond crystal. The intensities are qualitatively indicated with weak (w), medium (m) and strong (s). Assignments were accomplished according to the literature.^[78]

NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 400.13 MHz (¹H), 100.70 MHz (¹³C{¹H}) or 376.50 MHz (¹⁹F). Resonances are reported in ppm versus the solvent signal as an internal standard (¹H/¹³C: δ (CD₃CN) = 2.13, 1.94/118.26, 1.32).^[79] ¹⁹F NMR resonances are reported in ppm versus CFCl₃ (δ (CFCl₃) = 0) as external standard. (s) = singlet, (d) = doublet, (t) = triplet, (m) = multiplet.

ESI⁺ mass spectra were measured on an Agilent 6545 HPLC-ESI-QTOF-MS spectrometer in MeCN.

UV/vis absorption spectra were recorded on an Agilent Cary 5000 UV/vis/NIR spectrophotometer using 1.0 cm quartz cells. 1.00 cm quartz cells with a Schott valve were used to maintain an inert atmosphere.

Emission spectra and luminescence decay curves were recorded with a FLS1000 spectrometer from Edinburgh Instruments equipped with the cooled red and NIR sensitive photomultiplier detectors PMT-980 and N-G09 PMT-1700, together covering the entire spectral range between 200 nm and 1700 nm. A xenon arc lamp Xe2 (450 W) was used for excitation in steady-state measurements. Time-resolved luminescence experiments were performed in the multi-channel scaling mode employing a variable pulsed laser VPL-450 (λ_{exc} = 451.3 nm) as excitation source. The absolute luminescence quantum yield Φ was determined using an integrating sphere from Edinburgh Instruments. Relative uncertainty of Φ is estimated to be $\pm 10\%$. Due to the extremely long excited state lifetimes in the millisecond range and the high excited state redox potentials of the complexes, their luminescence is quenched efficiently even by trace impurities. Therefore, it is very challenging to reproducibly obtain the natural lifetime τ_0 . Highly purified samples and a particularly cautious conduction of the experiments is

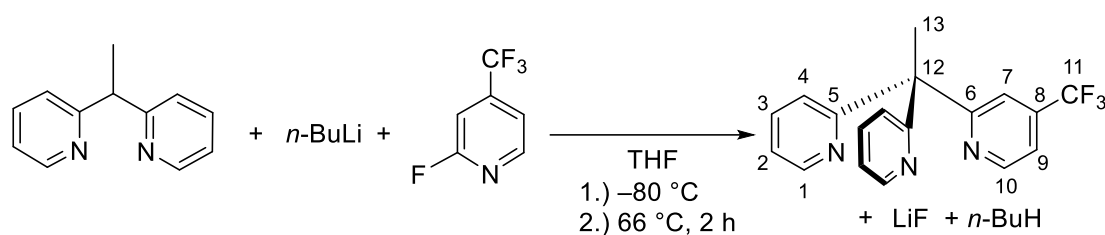
mandatory, otherwise erroneous τ_0 values much lower than milliseconds are obtained. Trace impurities that quench the emission will also affect the luminescence quantum yield Φ , which is proportional to the lifetime τ according to $\Phi = k_r \tau$.

Density functional theory and CASSCF-NEVPT2 calculations were carried out using the ORCA program package 5.0.3.^[80,81]

The **DFT** calculations were performed using the B3LYP functional^[82,83] employing the RIJCOSX approximation^[84,85] and the SARC/J auxiliary basis.^[86] Tight convergence criteria were chosen for DFT-UKS calculations (keywords *tightscf* and *tightopt*). Relativistic effects were calculated at the zeroth order regular approximation (ZORA) level.^[86] The ZORA keyword automatically invokes relativistically adjusted basis sets. To account for solvent effects, a conductor-like screening model (CPCM) modeling acetonitrile was used in all calculations.^[87,88] Geometry optimizations were performed using Ahlrichs' polarized valence triple- ζ basis set (def2-TZVPP).^[89,90] Atompairwise dispersion correction was performed with the Becke-Johnson damping scheme (D3BJ).^[91,92] The energy of the electronic states and the presence of energy minima were checked by numerical frequency calculations. Explicit counter ions and/or solvent molecules were not taken into account. TD-DFT calculations were performed at the same level of theory. Fifty vertical spin-allowed transitions were calculated.

The **CASSCF(7,12)-SC-NEVPT2** calculations of ground and excited state properties with respect to metal-centered (MC) states were performed using the complete-active-space self-consistent field method (CASSCF).^[93,94] To accelerate the calculation, the RI-JK approximation was used,^[95,96] with an automatically generated auxiliary basis (*AutoAux*). To recover the missing dynamic electron correlation, the strongly contracted variant of N-electron valence perturbation theory to second order (SC-NEVPT2) was used.^[97,98] All electronic states are classified by irreducible representations of the *O* point group, despite the lower actual symmetry of the considered complex. To accurately model the ligand field, the active space was expanded to encompass the dominant bonding/antibonding orbitals formed between chromium and the ligand. In addition to the minimal active space of (3,5), two occupied Cr–N σ bonding orbitals and a second d shell^[99] were included in these calculations giving an active space of (7,12). 10 quartet and 10 doublet roots were calculated with this active space.

Synthesis of the tpe^{CF₃} ligand



The following procedure was carried out under an inert atmosphere until the quenching step. Glassware was oven-dried and flushed with inert gas.

In a 250 mL three-neck round-bottom flask, 1,1-bis(2-pyridyl)ethane (5.0 g, 27 mmol, 1.0 eq.) was dissolved in dry THF (100 mL). The solution was cooled to $-78\text{ }^{\circ}\text{C}$ using an ethanol/dry ice bath. *n*-Butyllithium (1.8 g, 29 mmol, 12 mL of 2.5 M solution in hexanes, 1.1 eq.) was added dropwise to this solution, yielding a red solution. After addition, the mixture was stirred for 30 min at $-78\text{ }^{\circ}\text{C}$. 2-Fluoro-4-(trifluoromethyl)pyridine (1.3 g, 30 mmol, 1.1 eq.) was dissolved in dry THF (20 mL) and added to the reaction solution over the course of 5 min, which led to a deeper red color. The reaction mixture was allowed to reach to room temperature and refluxed for 2 h. The red solution was cooled to room temperature and poured onto ice (100 g), causing a color change to yellow. The organic solvents were removed by rotary evaporation. The remaining aqueous phase was filtered under reduced pressure to remove precipitated LiF and then extracted with diethyl ether (4×100 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and the solvent was removed by rotary evaporation. The residue was dried under reduced pressure (10^{-3} mbar) and the product was obtained as a yellow oil (8.1 g, 25 mmol, 91 %). Upon standing at room temperature for three days, large colorless crystals formed from the oil. The crystals were washed with hexanes (4×5 mL) and dried under reduced pressure (3.2 g, 9.7 mmol, 36 %).

¹H NMR (400 MHz, CD₃CN): δ / ppm = 8.71 (1H, dt, $^3J_{\text{HH}} = 5.2\text{ Hz}$, $^5J_{\text{HH}} = 0.8\text{ Hz}$, H¹⁰), 8.48 (2H, ddd, $^3J_{\text{HH}} = 4.8\text{ Hz}$, $^4J_{\text{HH}} = 1.9\text{ Hz}$, $^5J_{\text{HH}} = 1.0\text{ Hz}$, H¹), 7.67 (2H, ddd, $^3J_{\text{HH}} = 8.0\text{ Hz}$, $^3J_{\text{HH}} = 7.5\text{ Hz}$, $^4J_{\text{HH}} = 1.9\text{ Hz}$, H³), 7.47 (1H, m, H⁹), 7.35 (1H, m, H⁷), 7.21 (2H, ddd, $^3J_{\text{HH}} = 7.5\text{ Hz}$, $^3J_{\text{HH}} = 4.5\text{ Hz}$, $^4J_{\text{HH}} = 1.1\text{ Hz}$, H²), 7.14 (2H, ddd, $^3J_{\text{HH}} = 8.0\text{ Hz}$, $^4J_{\text{HH}} = 1.1\text{ Hz}$, H⁴), 2.25 (3H, s, H¹³).

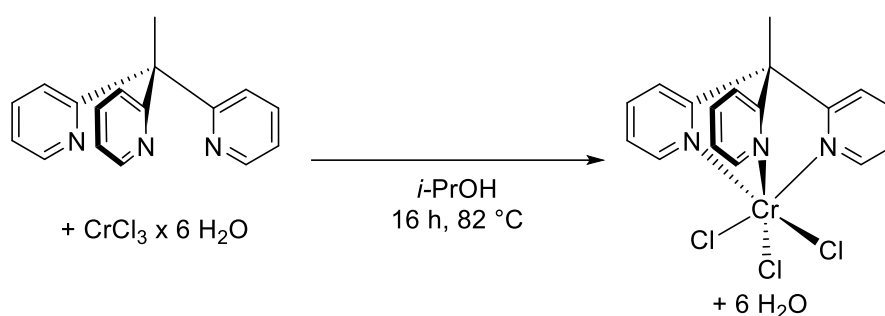
¹³C{¹H} NMR (100 MHz, CD₃CN): δ / ppm = 168.83 (s, C⁶), 166.21 (s, C⁵), 150.51 (s, C¹⁰), 149.51 (s, C¹), 137.28 (s, C³), 124.35 (s, C⁴), 122.66 (s, C²), 120.40 (s, C⁷), 117.83 (s, C⁹), 61.27 (s, C¹²), 27.54 (s, C¹³). The ¹³C NMR resonance of C¹¹ was not detected.

¹⁹F NMR (377 MHz, CD₃CN): δ / ppm = -65.28 (s).

MS (ESI⁺, MeCN): m/z (%) = calcd for [tpe^{CF₃}+H; C₁₈H₁₅F₃N₃]⁺: $m/z = 330.121$; found: m/z (%) = 330.121 (100) [M+H]⁺.

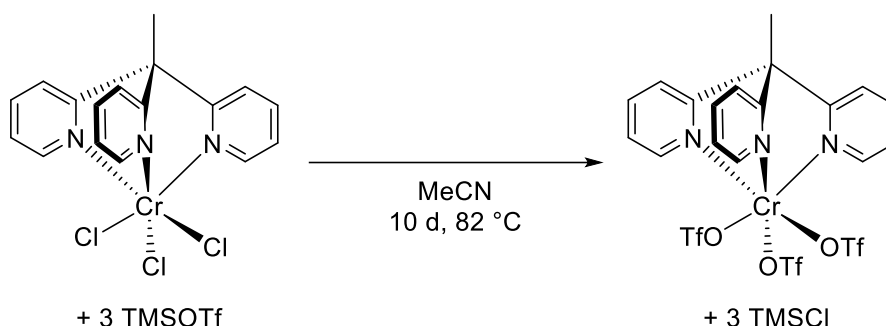
IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 3067 (w, CH), 3012 (w, CH), 2995 (w, CH), 2940 (w, CH), 1583 (m), 1567 (m), 1472 (m), 1430 (m), 1390 (m), 1329 (s, CF), 1293 (m), 1239 (w), 1181 (s), 1131 (s, CF), 1088 (m), 1065 (m), 1046 (m), 990 (m), 912 (w), 896 (w), 874 (m), 843 (m), 800 (w), 785 (m), 769 (w), 750 (s), 727 (w), 665 (s), 631 (w), 620 (m), 611 (m), 587 (w), 570 (m), 525 (w), 512 (w), 472 (w), 455 (w), 416 (w), 402 (w).

Synthesis of CrCl₃(tpe)



The precursor complex CrCl₃(tpe) was prepared analogously to the preparation of CrCl₃(tpy) (tpy = 2,2':6',2''-terpyridine).^[47] CrCl₃×6 H₂O (2.14 g, 8.06 mmol, 1.05 eq.) was dissolved in isopropanol (50 mL). To the resulting deep green solution was added a pale-yellow solution of tpe (2.00 g, 7.66 mmol, 1.00 eq.) in isopropanol (50 mL). The mixture was heated to 82 °C for 16 h. A fine green solid precipitated. The suspension was cooled to room temperature and filtered under reduced pressure. The remaining green solid was washed with warm isopropanol (60 °C; 3×50 mL), acetonitrile (2×50 mL) and diethyl ether (2×50 mL). The obtained green powder (2.06 g, 4.94 mmol, 64 %) was dried under reduced pressure and used without further purification.

Synthesis of Cr(OTf)₃(tpe)



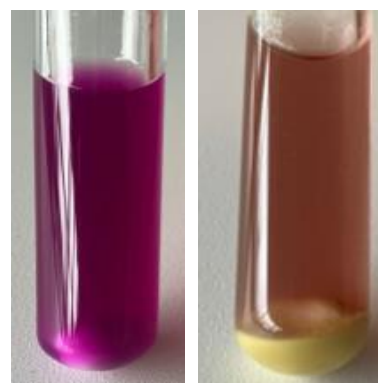
The precursor complex Cr(OTf)₃(tpe) was prepared analogously to the preparation of Cr(ddpd)(OTf)₃ (ddpd = *N,N'*-dimethyl-*N,N'*-dipyridine-2-yl-pyridine-2,6-diamine).^[49] All steps were carried out using dry solvents and inert conditions using Schlenk techniques or a glovebox. CrCl₃(tpe) (2.26 g, 3.02 mmol, 1.00 eq.) was suspended in MeCN (50 mL) and TMSOTf (10.0 g, 45.0 mmol, 15.0 eq.) was added. The green suspension immediately became purple-brown and the green solid partially dissolved. The mixture was heated to 82 °C for ten days and then cooled to room temperature.^a The solvent and the TMSCl byproduct were removed under reduced pressure at 40 °C until a dark-purple residue remained. The crude product was further dried under reduced pressure for 16 h, washed with diethyl ether (2×50 mL), petroleum ether (2×50 mL) and ground using a spatula. The residue was dissolved in 10 mL MeCN and the purple product was precipitated via slow addition of diethyl ether (120 mL).^b The supernatant was decanted and the purple solid was washed with MeOH (2×20 mL), petroleum ether (2×20 mL) and diethyl ether (20 mL). After drying for 16 h under reduced pressure, the product was obtained as a purple solid and used without further purification (1.11 g, 1.46 mmol, 49 %). Dark purple single crystals suitable for XRD analysis were obtained via diffusion of diethyl ether into a solution of Cr(OTf)₃(tpe) in MeCN (50 mg/5 mL).

^a Before proceeding with the workup, it is recommended to grease the stopcock of the flask again, since it is prone to getting stuck.

^b Occasionally, the precipitate clotted again during this process. Washing the residue with diethyl ether and repeating the precipitation proved useful in these cases.

Synthesis of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_3$

In a glovebox, $\text{Cr}(\text{OTf})_3(\text{tpe})$ (100 mg, 0.13 mmol, 1.0 eq.) was dissolved in dry, deaerated MeCN (0.5 mL), resulting in a purple solution. A colorless solution of tpe^{CF_3} (52.0 mg, 0.16 mmol, 1.2 eq.) in bis(2-methoxyethyl)ether (diglyme, 4 mL) was added. The purple mixture (see photo) was transferred to a microwave vial and heated in a microwave oven at 200 °C for 3 h. A yellow solid with an orange supernatant was obtained (see photo). The liquid was decanted and discarded. The solid was washed with diethyl ether (4×5 mL) and dried under ambient conditions. The product was obtained as a pale-yellow powder (128 mg, 0.11 mmol, 89 % yield). As determined by analytical HPLC, the crude product was contaminated with $[\text{Cr}(\text{tpe})_2]^{3+}$ and presumably $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (Figure S9).



before (left) and after (right) the microwave reaction.

The desired heteroleptic complex (several combined batches) was purified by HPLC (H_2O (300 mM NaCl)/MeCN (40/60 v/v); $R_t = 6.8$ min). The solvent mixture was removed by rotary evaporation. To separate the product from NaCl, the solid residue was extracted with MeCN (4×50 mL). The solvent was removed by rotary evaporation. The remaining pale-yellow solid was dissolved in MeOH (5 mL) and added dropwise to a saturated solution of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ in MeOH (3 mL) under strong stirring, yielding $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_3$ as a fine precipitate. The solid was washed with MeOH (5×10 mL) and diethyl ether (5 mL) and dried under ambient conditions. Finally, the product was dissolved in MeCN (3 mL) and crystallized by diffusion of diethyl ether. Crude $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})_2][\text{OTf}]_3$ (680 mg) yielded purified $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_3$ (432 mg).

MS (MeCN/ESI⁺): calcd for $[[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_2]^+$: $m/z = 932.108$, found: m/z (%) = 932.108 (77.0); calcd for $[[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]]^{2+}$: $m/z = 393.572$, found: m/z (%) = 393.571 (100); calcd for $[[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]]^{3+}$: $m/z = 214.060$, found: m/z (%) = 214.061 (20.2).

IR (ATR): $\tilde{\nu} / \text{cm}^{-1} = 3145$ (w, CH), 3103 (w, CH), 1663 (w), 1631 (w), 1605 (w), 1579 (w), 1496 (w), 1472 (w), 1442 (w), 1413 (w), 1392 (w), 1335 (w, CF), 1307 (w), 1249 (w), 1210 (w), 1188 (w), 1159 (w, CF), 1113 (w), 1062 (w), 1037 (w), 874 (m), 826 (vs, PF), 757 (m), 723 (w), 685 (w), 662 (w), 640 (w), 619 (w), 556 (vs, PF), 509 (w), 465 (w), 445 (w), 411 (w).

UV/vis/NIR absorption (MeCN): λ / nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) = 332 (1200), 433 (35).

Emission (MeCN): λ / nm (I_{rel}) = 719 (0.50), 723 (0.53), 730 (0.75), 743 (1.00), 748 (0.90), 767 (0.28), 790 (0.23), 818 (0.10), 826 (0.11).

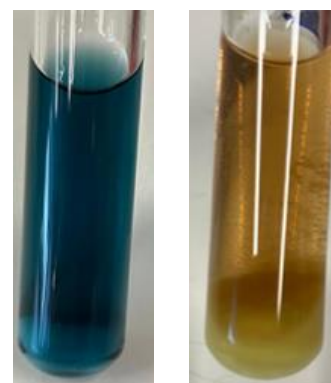
Emission Lifetime (MeCN): $\tau / \mu\text{s} = 2600$ (deaerated); 330 (aerated).

Quantum Yield (MeCN): $\Phi / \% = 4.9$.

CV (MeCN, 100 mM $[n\text{-Bu}_4\text{N}][\text{PF}_6]$): $E_{1/2} / \text{V}$ vs. SCE = −0.40 V, −1.06 V.

Synthesis of $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$

$\text{Cr}(\text{OTf})_3$ (200 mg, 0.40 mmol, 1.0 eq.) was dissolved in MeCN (0.5 mL) in a glovebox, resulting in a turquoise solution. A colorless solution of tpe^{CF_3} (277 mg, 0.84 mmol, 2.1 eq.) in bis(2-methoxyethyl)ether (diglyme, 4 mL) was added. The turquoise mixture (see photo) was transferred to a microwave vial and heated in a microwave oven at 200 °C for 3 h. A yellow solid with an orange supernatant was obtained (see photo). The liquid was decanted and discarded. The solid was washed with diethyl ether (4×5 mL) and dried under ambient conditions. The crude product was obtained as a pale-yellow powder (329 mg, 0.28 mmol, 71 % yield). As determined by analytical HPLC, the mixture consisted of *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ in a 2:1 ratio (Figure S11).



before (left) and after (right) the microwave reaction.

The isomers (several combined batches) were separated by HPLC (H_2O (75 mM NaCl)/MeCN (17.5/82.5 v/v); $R_t(\text{trans}) = 28.9$ min; $R_t(\text{cis}) = 31.6$ min). For both fractions, the solvent mixture was removed by rotary evaporation. To separate the product from NaCl, the solid residue was extracted with MeCN (4×50 mL). The solvent was removed by rotary evaporation. The remaining pale-yellow solid was dissolved in MeOH (5 mL) and added dropwise to a saturated solution of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ in MeOH (3 mL) under strong stirring, yielding the respective isomer as a fine precipitate. The solid was washed with MeOH (5×10 mL) and diethyl ether (5 mL) and dried under ambient conditions. Finally, the product was dissolved in MeCN (3 mL) and crystallized by diffusion of diethyl ether. Crude $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{OTf}]_3$ (632 mg) yielded *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_3$ (180 mg) and *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_3$ (139 mg), respectively.

***cis*-[Cr(tpe^{CF3})₂][PF₆]₃:**

MS (MeCN/ESI⁺): calcd for [[Cr(tpe)(tpe^{CF3})]][PF₆]₂⁺: m/z = 1000.096, found: m/z (%) = 1000.098 (42.5); calcd for [[Cr(tpe)(tpe^{CF3})]][PF₆]₂²⁺: m/z = 427.566, found: m/z (%) = 427.566 (100); calcd for [[Cr(tpe)(tpe^{CF3})]]³⁺: m/z = 236.722, found: m/z (%) = 236.722 (64.6).

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 3147 (w, CH), 3104 (w, CH), 1633 (w), 1605 (w), 1578 (w), 1498 (w), 1474 (w), 1444 (w), 1412 (w), 1395 (w), 1334 (m, CF), 1299 (w), 1243 (w), 1213 (w), 1184 (m), 1144 (m, CF), 1116 (w), 1090 (w), 1073 (w), 1063 (w), 1037 (w), 878 (m), 824 (vs, PF), 774 (m), 759 (m), 741 (w), 724 (w), 684 (m), 666 (w), 642 (w), 620 (w), 596 (w), 555 (vs, PF), 509 (w), 489 (w), 463 (w), 446 (w), 439 (w), 424 (w), 408 (w).

UV/vis/NIR absorption (MeCN): λ / nm (ϵ / M⁻¹ cm⁻¹) = 333 (1200), 432 (35).

Emission (MeCN): λ / nm (I_{rel}) = 719 (0.51), 730 (0.78), 738 (0.75), 743 (1.00), 748 (0.95), 768 (0.27), 790 (0.22), 819 (0.10), 828 (0.10).

Emission Lifetime (MeCN): τ / μ s = 3000 (deaerated), 360 (aerated).

Quantum Yield (MeCN): Φ / % = 6.0.

CV (MeCN, 100 mM [*n*-Bu₄N][PF₆]): $E_{1/2}$ / V vs. SCE = -0.30 V, -0.90 V.

***trans*-[Cr(tpe^{CF3})₂][PF₆]₃:**

MS (MeCN/ESI⁺): calcd for [[Cr(tpe)(tpe^{CF3})]][PF₆]₂⁺: m/z = 1000.096, found: m/z (%) = 1000.097 (32.5); calcd for [[Cr(tpe)(tpe^{CF3})]][PF₆]₂²⁺: m/z = 427.566, found: m/z (%) = 427.566 (100); calcd for [[Cr(tpe)(tpe^{CF3})]]³⁺: m/z = 236.722, found: m/z (%) = 236.725 (32.6).

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 3145 (w, CH), 3102 (w, CH), 1635 (w), 1605 (w), 1590 (w), 1500 (w), 1472 (w), 1441 (w), 1414 (w), 1337 (w, CF), 1301 (w), 1245 (w), 1210 (w), 1179 (w), 1149 (m, CF), 1117 (w), 1090 (w), 1070 (w), 1064 (w), 1037 (w), 877 (m), 828 (vs, PF), 772 (m), 759 (m), 742 (w), 724 (w), 687 (m), 666 (w), 643 (w), 621 (w), 596 (w), 556 (vs, PF), 515 (w), 468 (w), 448 (w), 432 (w).

UV/vis/NIR absorption (MeCN): λ / nm (ϵ / M⁻¹ cm⁻¹) = 333 (1300), 432 (35).

Emission (MeCN): λ / nm (I_{rel}) = 731 (0.76), 744 (0.98), 748 (1.00), 791 (0.21), 819 (0.09), 826 (0.10).

Emission Lifetime (MeCN): τ / μ s = 3300 (deaerated), 360 (aerated).

Quantum Yield (MeCN): Φ / % = 6.2.

CV (MeCN, 100 mM [*n*-Bu₄N][PF₆]): $E_{1/2}$ / V vs. SCE = -0.28 V, -1.00 V.

Chemical reduction of chromium(III) complexes

Reduction of the chromium(III) complexes was accomplished in a glovebox using cobaltocene in dry and degassed MeCN.

In an exemplary procedure, a stock solution of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ (3.30 mg, 3.27 mmol) was prepared in MeCN (1.9 mL, 1.72 mmol L⁻¹). An aliquot of this stock solution (100 μL) was diluted with MeCN (2.9 mL) in an inert gas cuvette yielding a 0.06 mM solution. Separately, a cobaltocene stock solution (13.1 mg) was prepared in MeCN (25 mL, 2.74 mmol L⁻¹). An aliquot of the cobaltocene stock solution (64 μL) was added to the cuvette (0.06 mM in the cuvette) to reduce the chromium(III) complex. The solution immediately turned green. The cuvette was locked, removed from the glovebox and UV/vis/NIR absorption spectra were recorded.

UV/vis/NIR absorption of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_2$ (MeCN): λ / nm (ϵ / M⁻¹ cm⁻¹) = 416 (6000), 689 (6700), 890 (13400, sh), 944 (25000).

UV/vis/NIR absorption of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_2$ (MeCN): λ / nm (ϵ / M⁻¹ cm⁻¹) = 436 (4800), 685 (3600), 795 (4200, sh), 983 (17800).

UV/vis/NIR absorption of *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_2$ (MeCN): λ / nm (ϵ / M⁻¹ cm⁻¹) = 432 (5200), 690 (3500), 830 (6000, sh), 915 (10200, sh), 994 (19000).

UV/vis/NIR absorption of *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_2$ (MeCN): λ / nm (ϵ / M⁻¹ cm⁻¹) = 437 (4900), 660 (3800), 761 (3600), 910 (5000, sh), 1048 (26700).

Reoxidation of reduced complexes

Reductions of the chromium(III) complexes were carried out as described above. For re-oxidation, a stock solution of ferrocenium hexafluorophosphate (10.4 mg) in MeCN (10 mL, 3.14 mmol L⁻¹) was prepared. Exemplary, the solution of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ in MeCN was treated with an aliquot of the ferrocenium hexafluorophosphate solution (57 μL) in the cuvette (0.06 mM in the cuvette). The cuvette was locked, removed from the glovebox and UV/vis/NIR absorption spectra were recorded. These matched the spectra of the tricationic complexes.

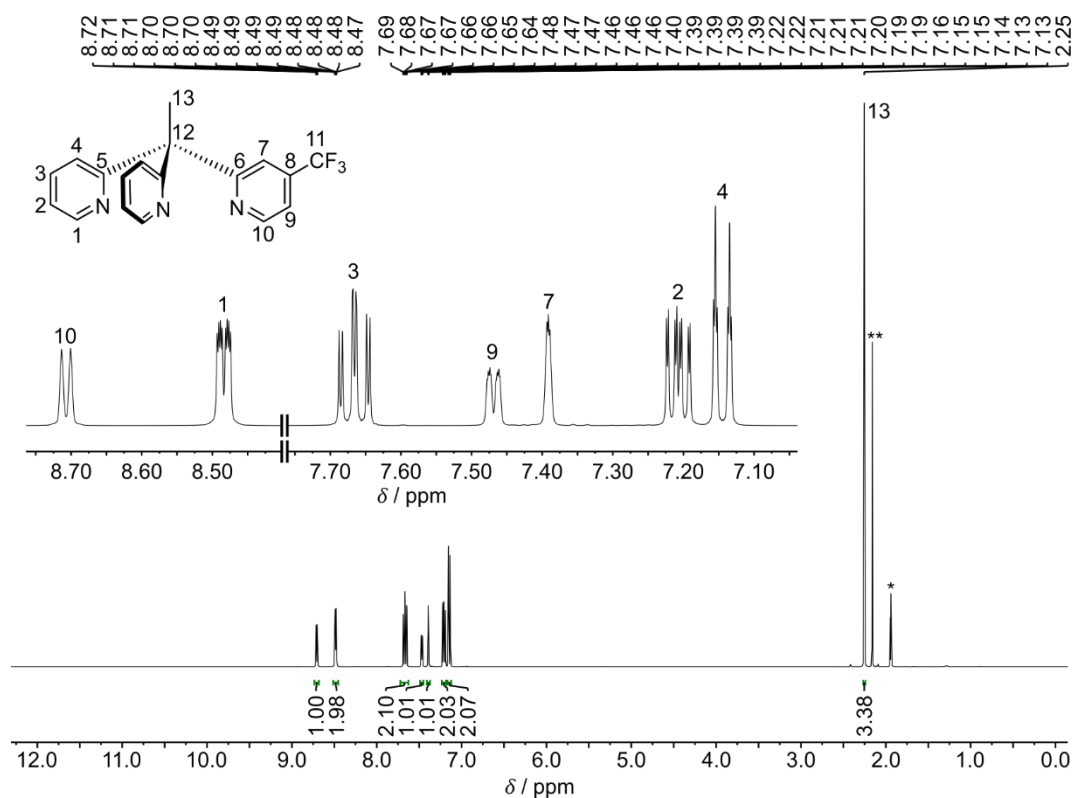


Figure S1. ^1H NMR spectrum of tpe^{CF_3} in CD_3CN . The inset shows a zoom in the aromatic region. The asterisk * denotes solvent resonance. The double asterisk ** denotes water resonance.

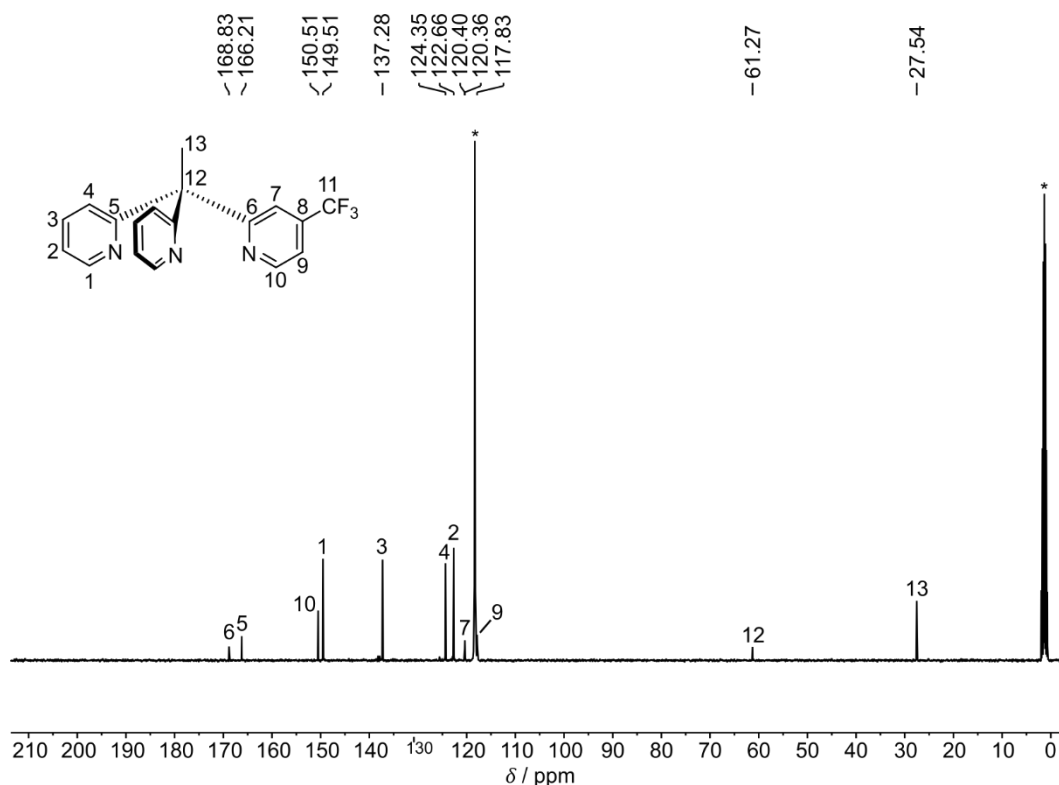


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of tpe^{CF_3} in CD_3CN . The asterisks * denote solvent resonances.

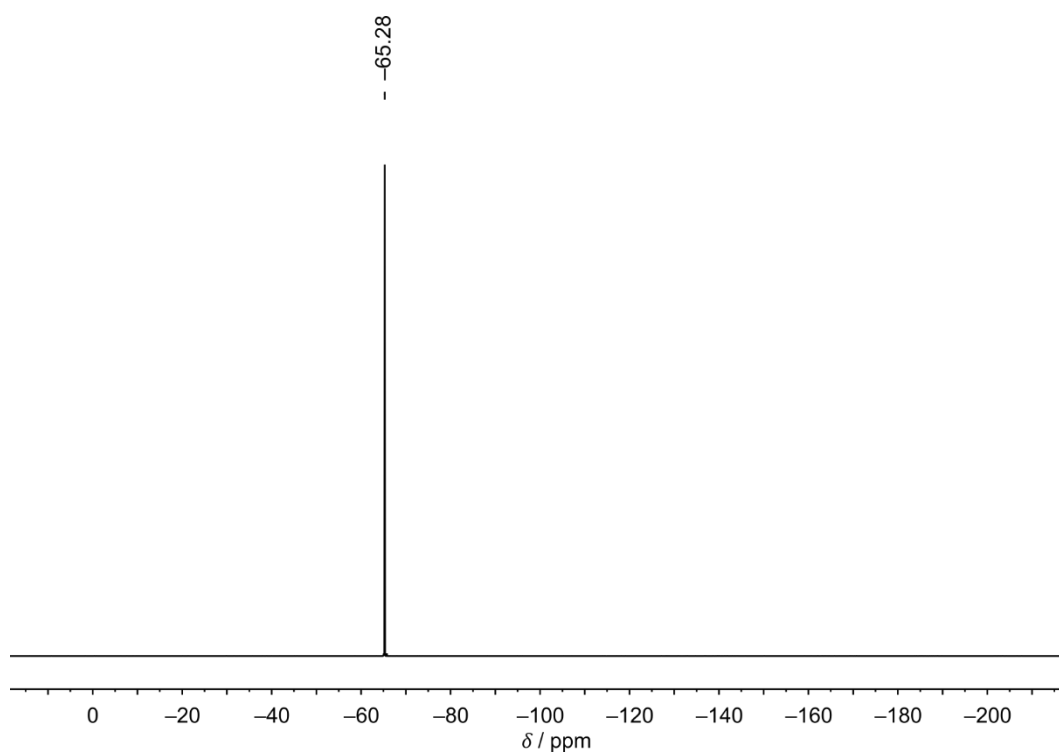


Figure S3. ^{19}F NMR spectrum of tpe^{CF_3} in CD_3CN .

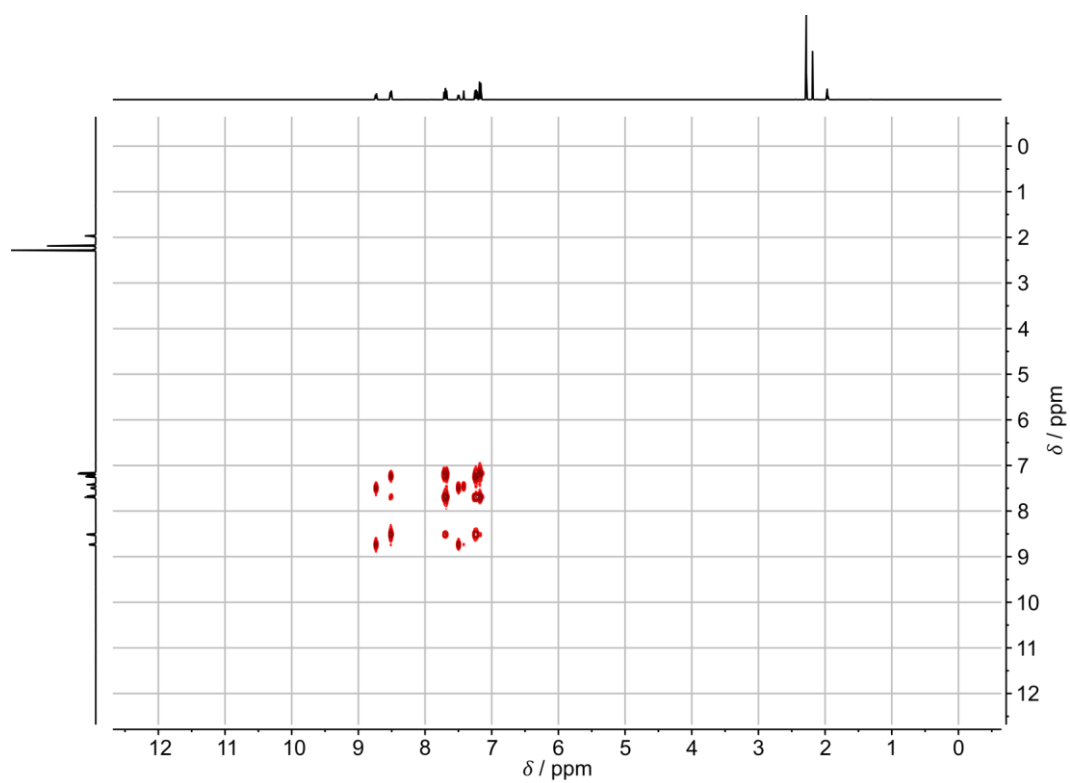


Figure S4. ^1H - ^1H -COSY NMR spectrum of tpe^{CF_3} in CD_3CN .

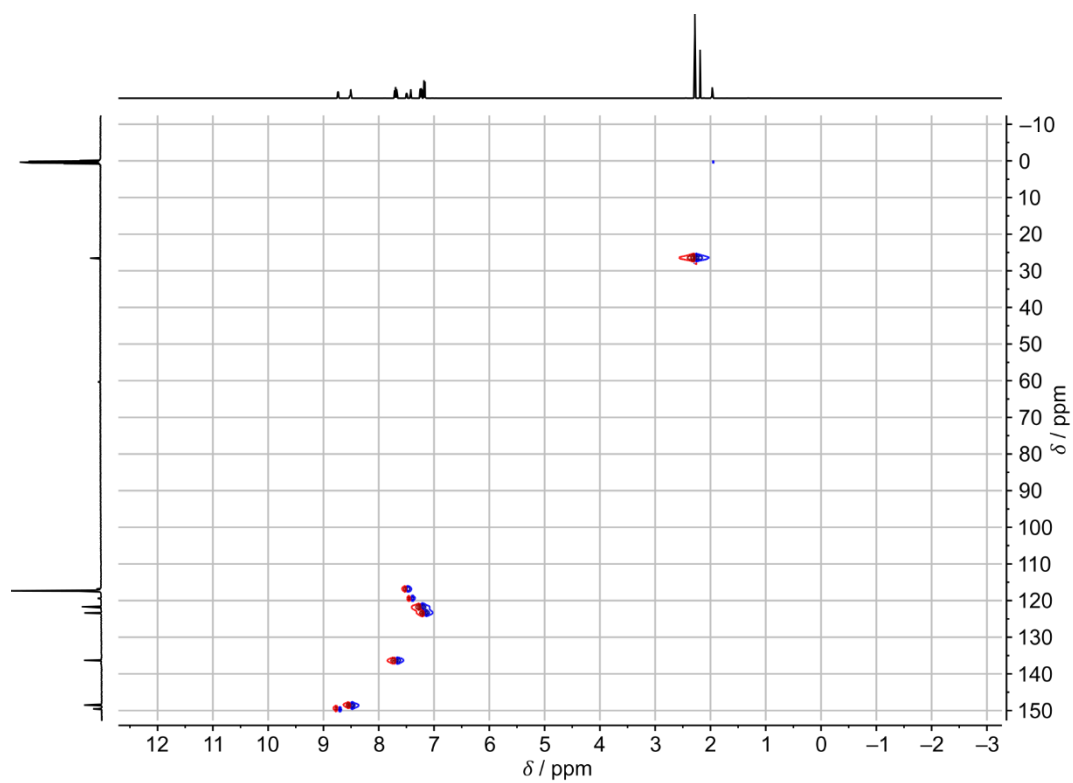


Figure S5. ^1H - ^{13}C -HSQC NMR spectrum of tpe^{CF_3} in CD_3CN .

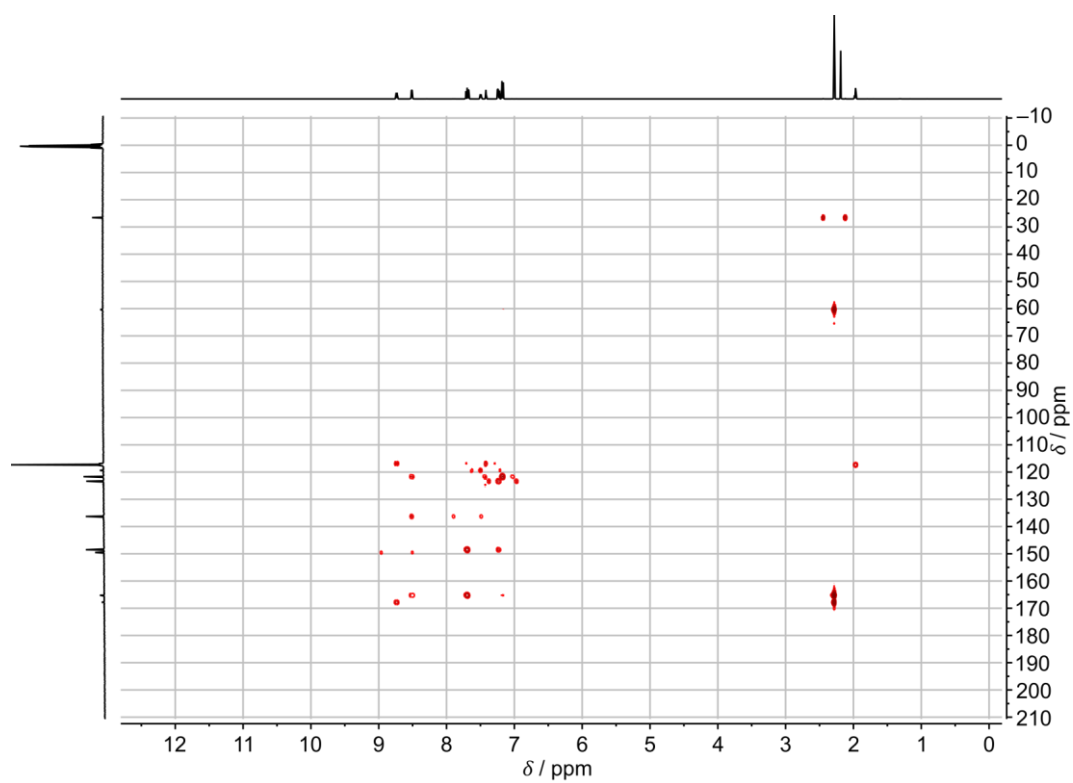


Figure S6. ^1H - ^{13}C -HMBC NMR spectrum of tpe^{CF_3} in CD_3CN .

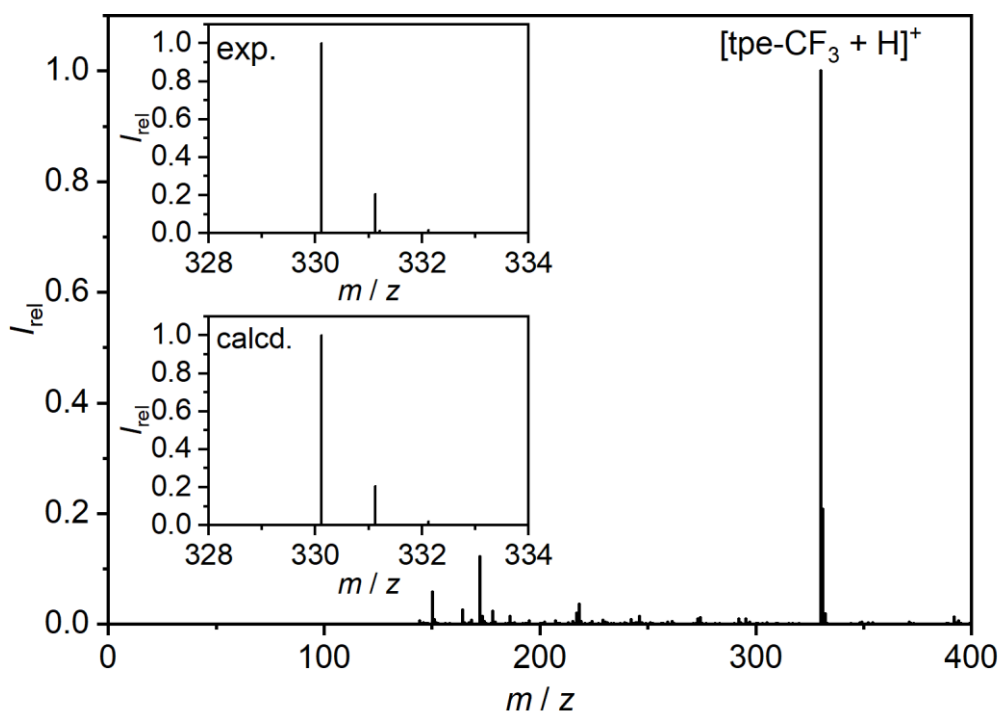


Figure S7. ESI⁺ mass spectrum of tpe^{CF₃} in MeCN. Insets show experimental and calculated ($C_{18}H_{15}F_3N_3$) isotope patterns of the $[tpe^{CF_3} + H]^+$ peak, respectively.

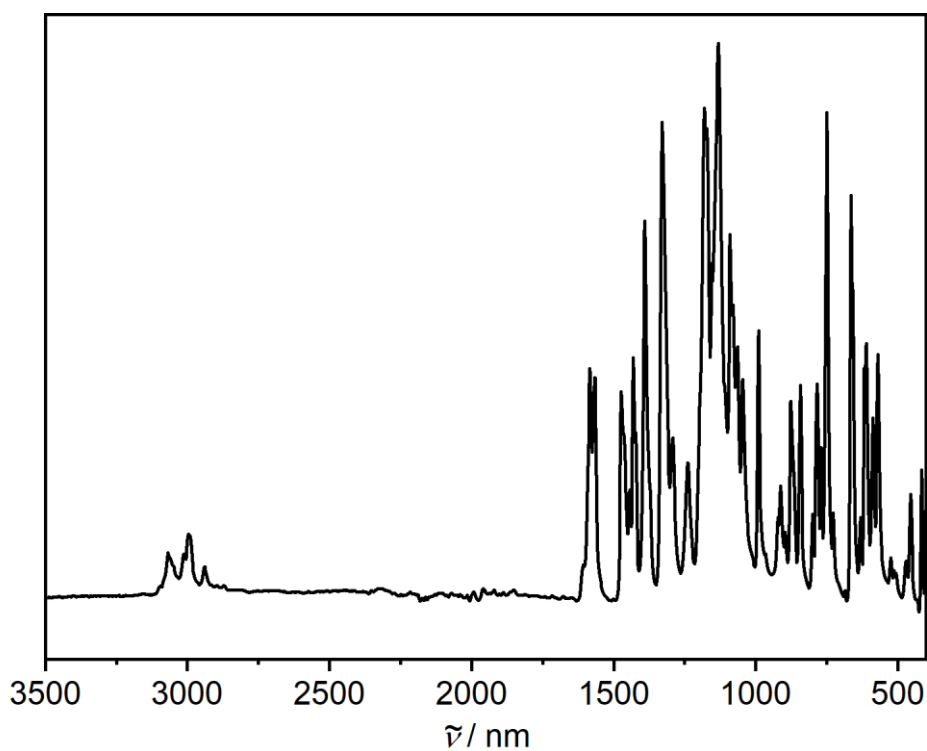


Figure S8. ATR-IR spectrum of tpe^{CF₃}.

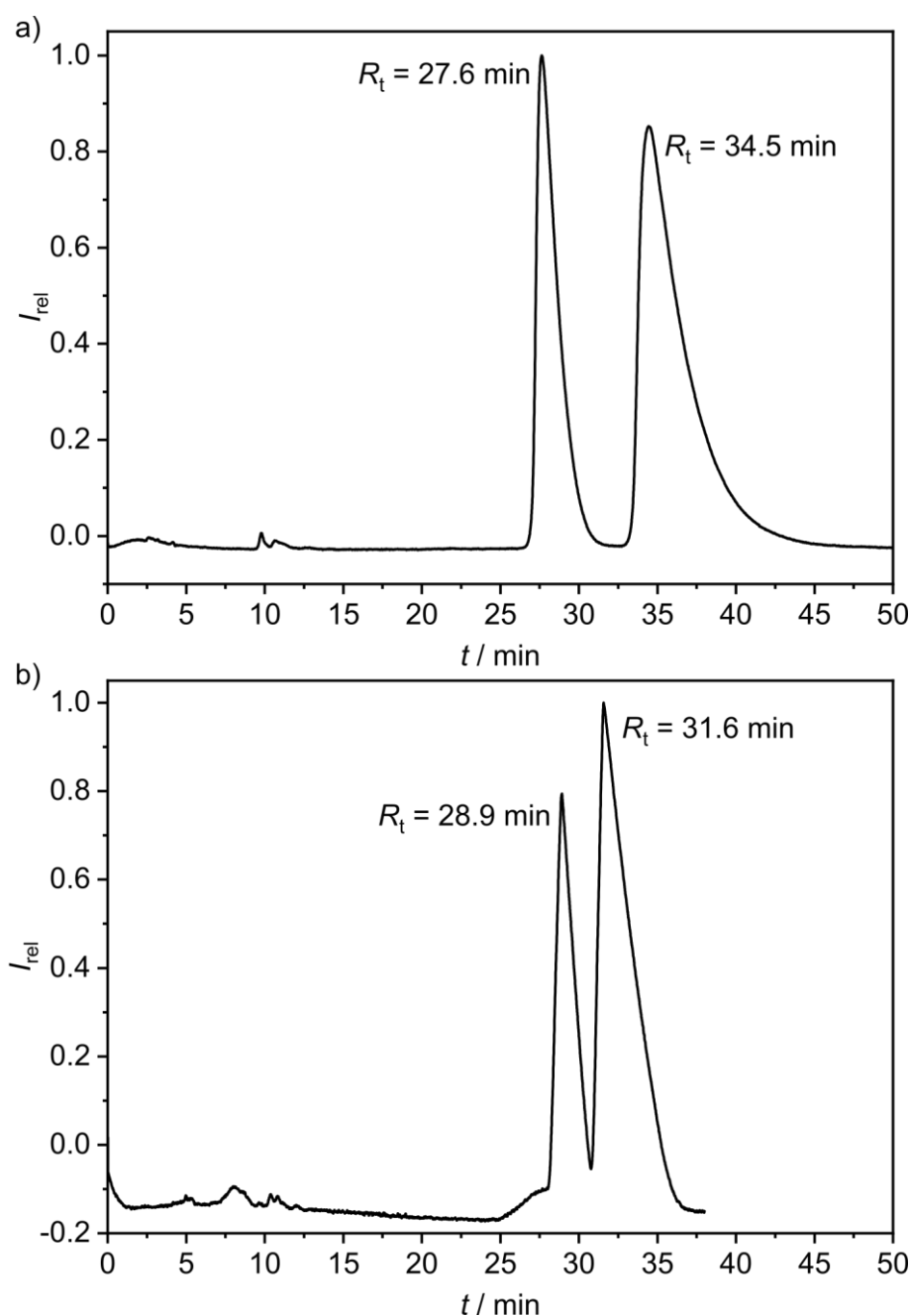


Figure S9. a) Analytical HPLC chromatogram (H_2O (75 mM NaCl)/MeCN (17.5/82.5 v/v)) of the crude product obtained from the synthesis of $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$. The peaks at $R_t = 27.6$ min and $R_t = 34.5$ min integrate as 1:2 and correspond to *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ and *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$, respectively. b) Preparative HPLC chromatogram (H_2O (75 mM NaCl)/MeCN (17.5/82.5 v/v)) of the crude product obtained from the synthesis of $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$. The peaks at $R_t = 28.9$ min and $R_t = 31.6$ min correspond to *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ and *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$, respectively.

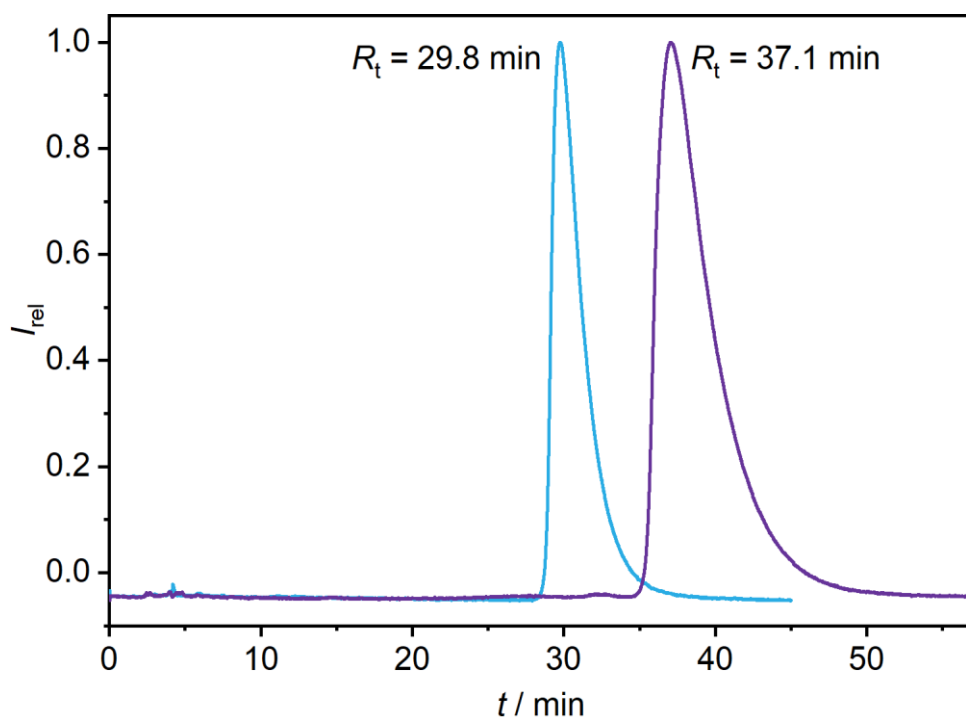


Figure S10. Analytical HPLC chromatograms (H_2O (75 mM NaCl)/MeCN (17.5/82.5 v/v)) of *trans*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (blue; $R_t = 29.0$ min) and *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (purple; $R_t = 37.1$ min).

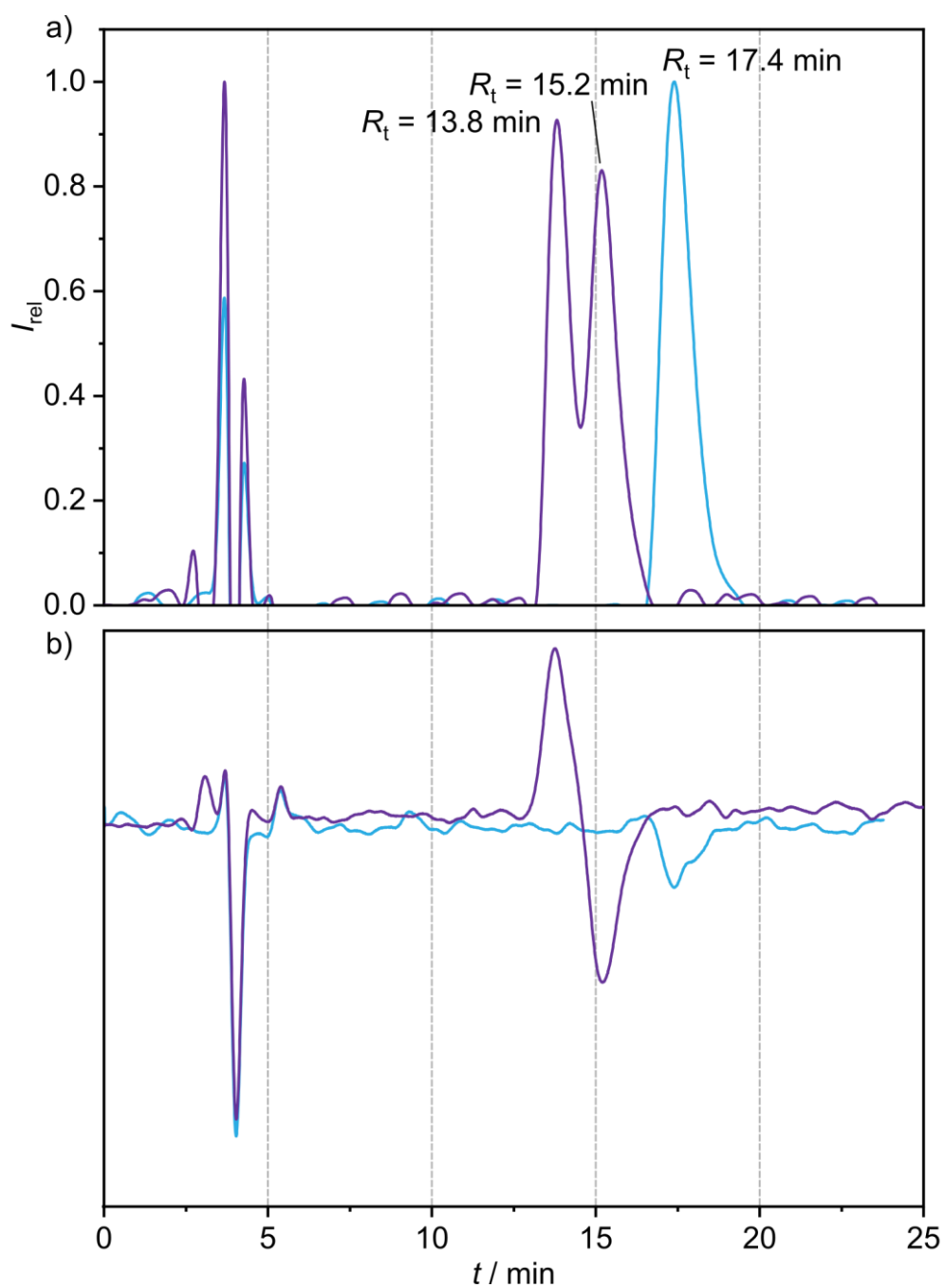


Figure S11. HPLC chromatograms (MeOH (40 mM [$n\text{-Bu}_4\text{N}$]Cl)/ CH_2Cl_2 (40 mM [$n\text{-Bu}_4\text{N}$]Cl; 10/90 v/v); 0.1 % formic acid) of $trans\text{-[Cr(tpe}^{CF_3})_2]^{3+}$ (blue; $R_t = 17.4 \text{ min}$) and $cis\text{-[Cr(tpe}^{CF_3})_2]^{3+}$ (purple; $R_t = 13.8/15.2 \text{ min}$) using a chiral column and detection via CD spectroscopy.

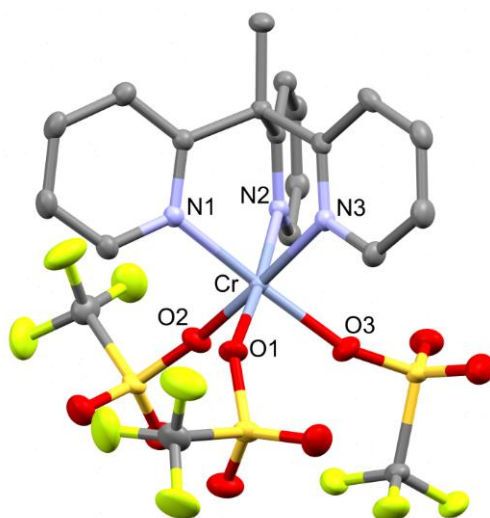


Figure S12. Molecular structure of $\text{Cr}(\text{OTf})_3(\text{tpe})$ obtained from single-crystal XRD. Thermal ellipsoids set to 50% probability. Hydrogen atom omitted.

Table S1. Bond lengths [$\text{\AA}$] and angles [deg] of $\text{Cr}(\text{OTf})_3(\text{tpe})$ obtained from XRD analysis.

bond lengths/ $\text{\AA}$	
Cr-N1	2.023(18)
Cr-N2	2.031(18)
Cr-N3	2.023(19)
Cr-O1	1.963(17)
Cr-O2	1.959(17)
Cr-O3	1.969(17)
bond angles/deg	
N1-Cr-N2	86.91(8)
N1-Cr-N3	85.53(7)
N1-Cr-O1	88.06(9)
N1-Cr-O2	93.76(8)
N1-Cr-O3	175.74(7)
N2-Cr-N3	87.58(7)
N2-Cr-O1	174.94(9)
N2-Cr-O2	87.04(7)
N2-Cr-O3	94.49(8)
N3-Cr-O1	91.59(9)
N3-Cr-O2	174.60(7)
N3-Cr-O3	90.50(8)
O1-Cr-O2	93.74(9)
O1-Cr-O3	90.50(10)
O2-Cr-O3	90.33(8)

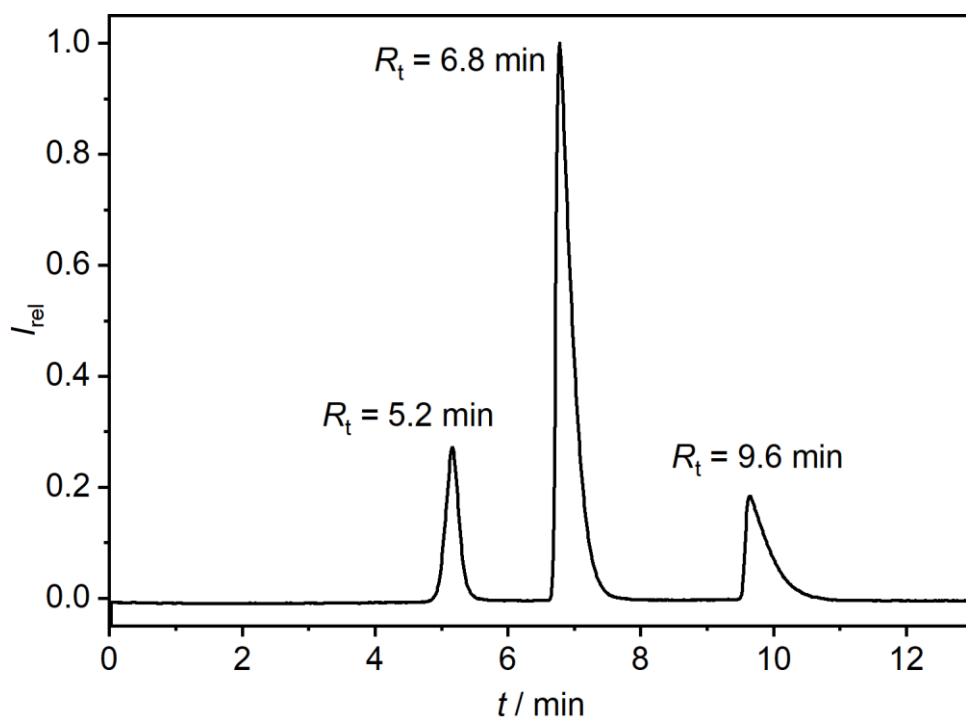


Figure S13. Preparative HPLC chromatogram (H_2O (300 mM NaCl)/MeCN (40/60 v/v)) of the crude product obtained from the synthesis of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ ($R_t = 6.8 \text{ min}$). The peaks at $R_t = 5.2 \text{ min}$ and $R_t = 9.6 \text{ min}$ stem from homoleptic $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (presumably) and $[\text{Cr}(\text{tpe})_2]^{3+}$, respectively.

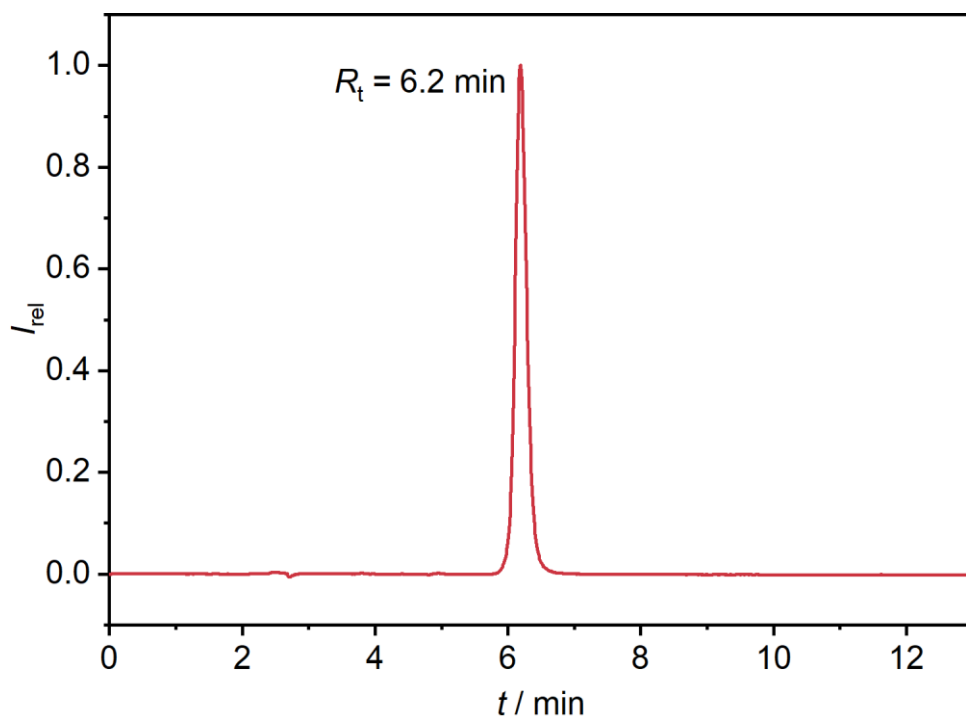


Figure S14. Analytical HPLC chromatogram (H_2O (300 mM NaCl)/MeCN (40/60 v/v)) of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ ($R_t = 6.2 \text{ min}$).

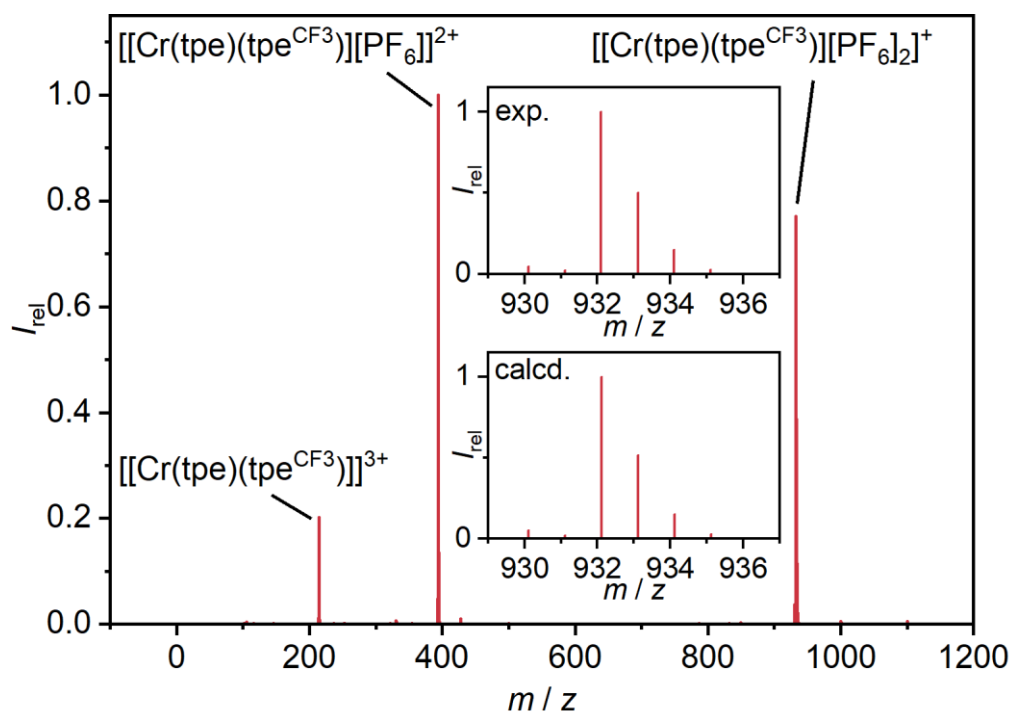


Figure S15. ESI⁺ mass spectrum of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_3$ in MeCN. Insets show experimental and calculated isotope patterns of the $\{[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_2\}^+$ peak, respectively.

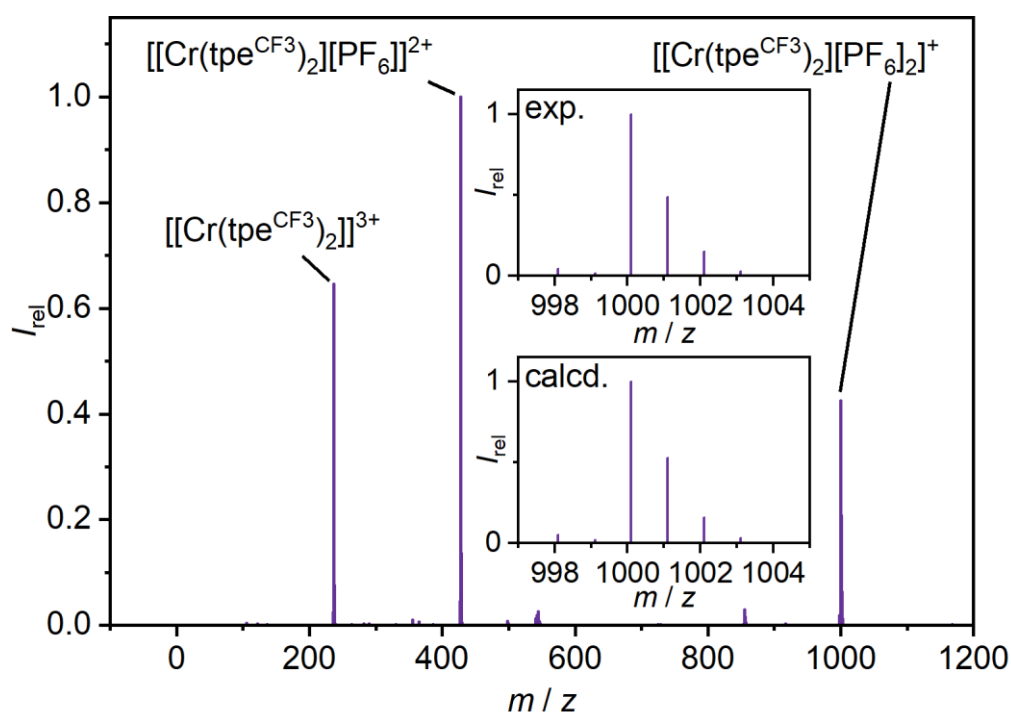


Figure S16. ESI⁺ mass spectrum of *cis*- $[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_3$ in MeCN. Insets show experimental and calculated isotope patterns of the $\{[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_2\}^+$ peak, respectively.

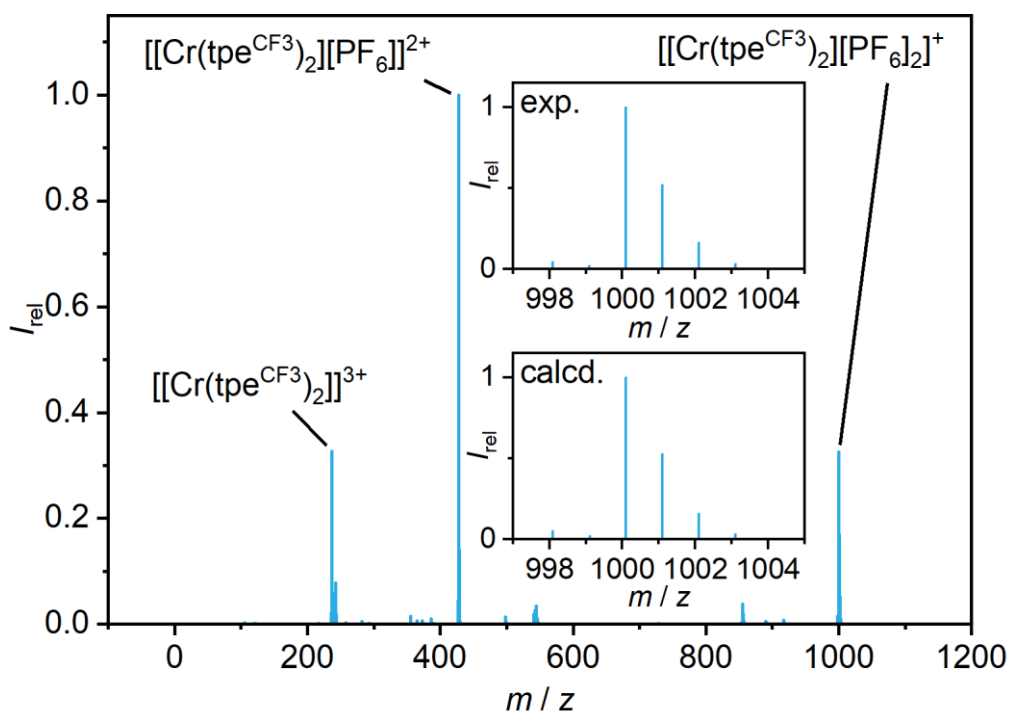


Figure S17. ESI⁺ mass spectrum of *trans*-[Cr(tpe^{CF3})₂][PF₆]₃ in MeCN. Insets show experimental and calculated isotope patterns of the {[Cr(tpe^{CF3})₂][PF₆]₂}⁺ peak, respectively.

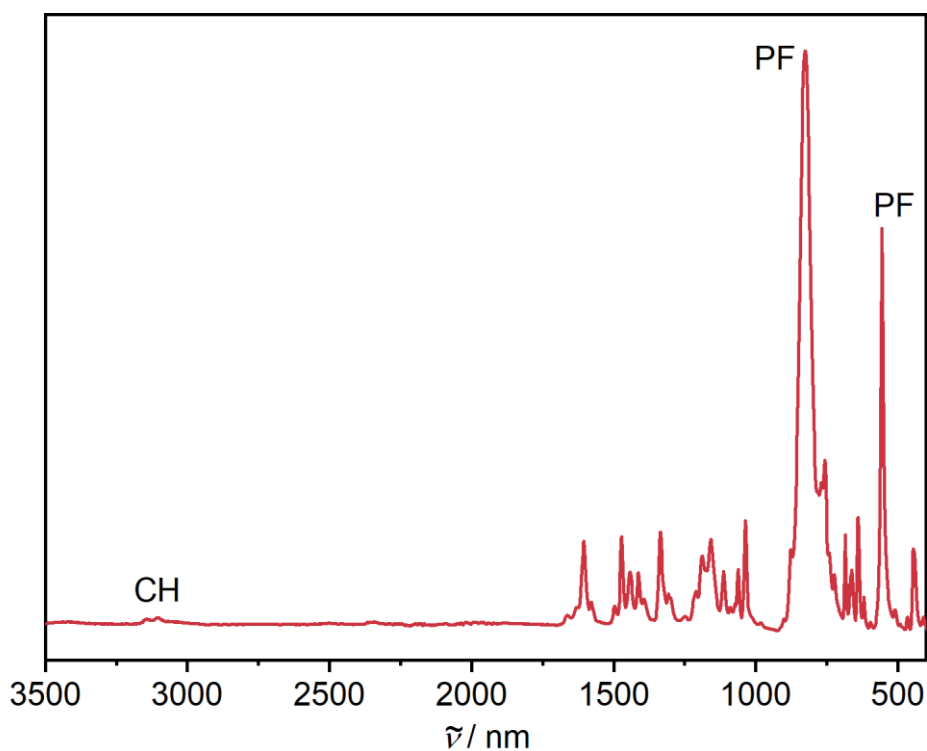


Figure S18. ATR-IR spectrum of [Cr(tpe)(tpe^{CF3})]PF₆]₃. Some of the characteristic bands have been assigned.^[78]

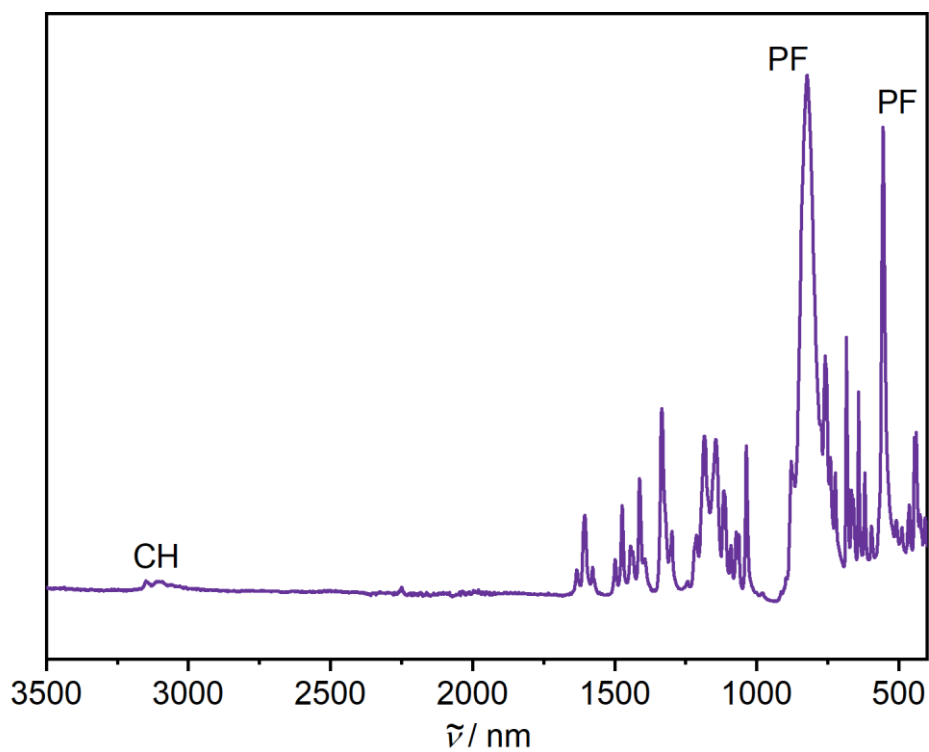


Figure S19. ATR-IR spectrum of *cis*-[Cr(tpe^{CF3})₂][PF₆]₃. Some of the characteristic bands have been assigned.^[78]

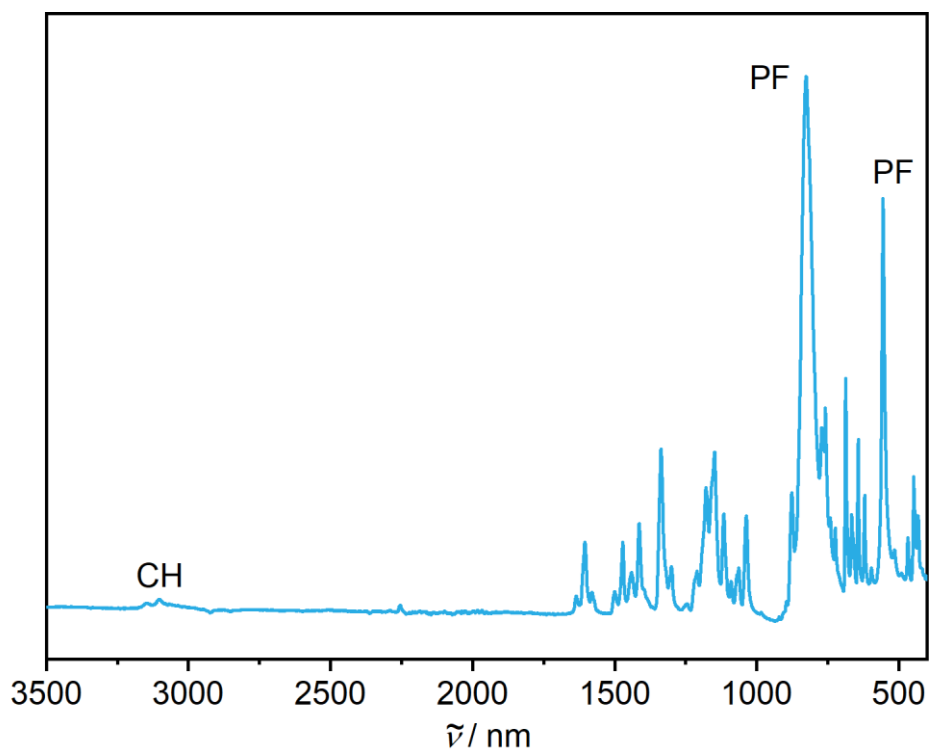


Figure S20. ATR-IR spectrum of *trans*-[Cr(tpe^{CF3})₂][PF₆]₃. Some of the characteristic bands have been assigned.^[78]

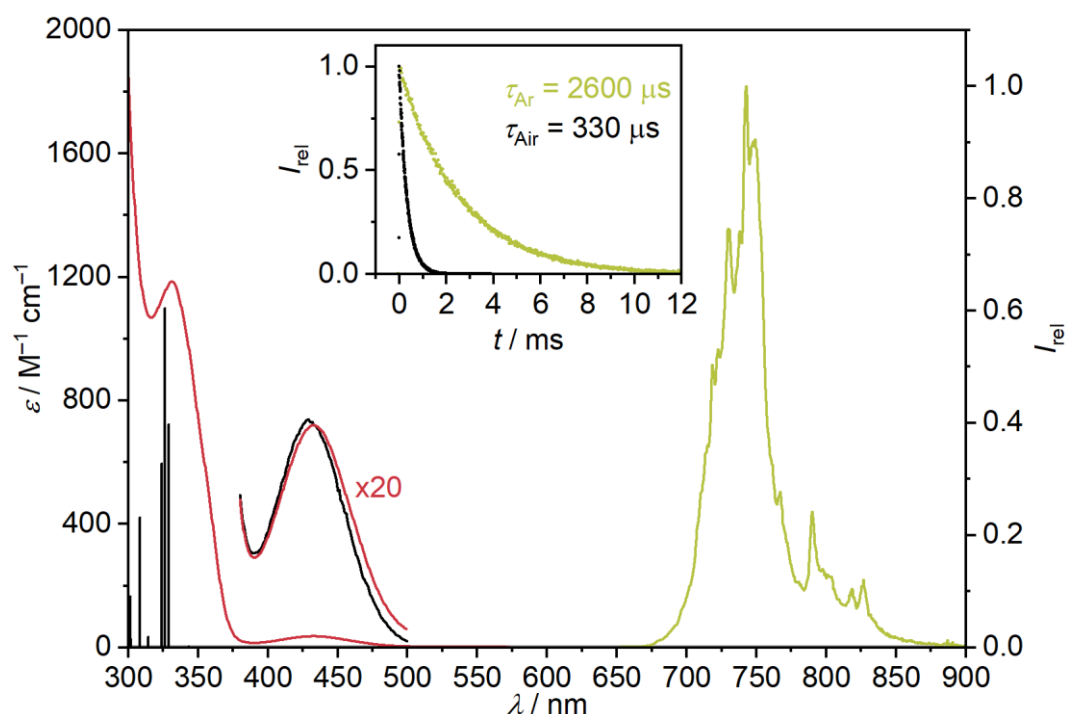


Figure S21. UV/vis absorption (red), normalized excitation ($\lambda_{\text{em}} = 742 \text{ nm}$, black) and emission spectra ($\lambda_{\text{exc}} = 435 \text{ nm}$, green) of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_3$ in MeCN. TD-DFT calculated transitions of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ shown as vertical bars (black). Inset shows emission decay curves recorded at 742 nm under argon (green) and air (black).

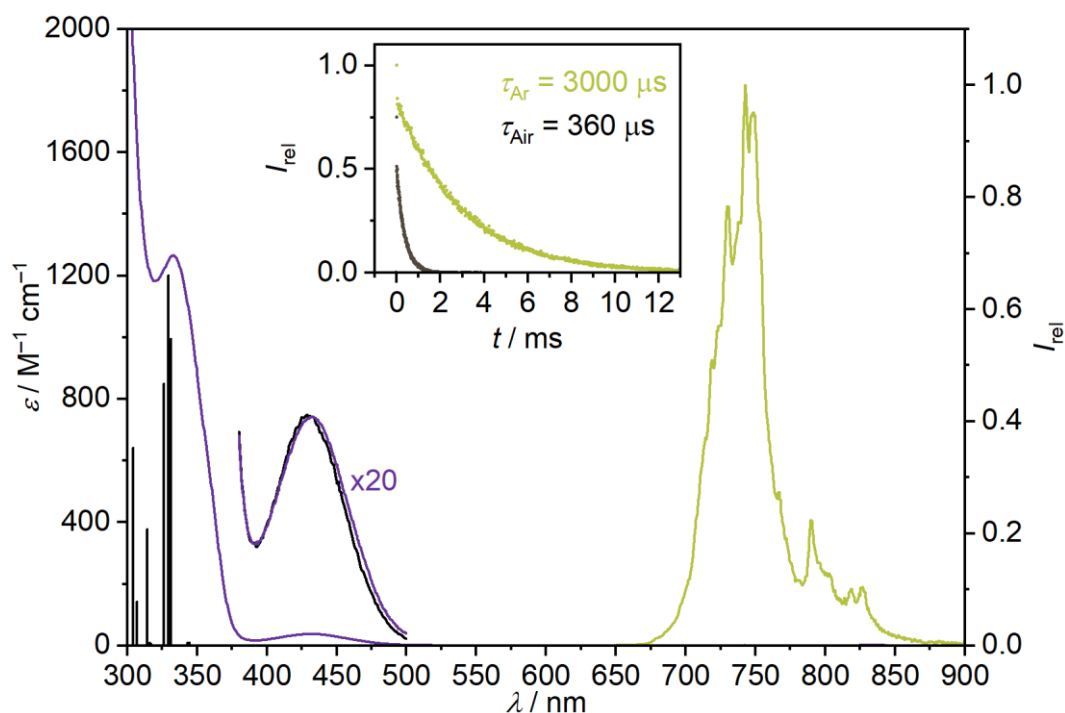


Figure S22. UV/vis absorption (purple), normalized excitation ($\lambda_{\text{em}} = 742 \text{ nm}$, black) and emission spectra ($\lambda_{\text{exc}} = 435 \text{ nm}$, green) of $\text{cis-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2][\text{PF}_6]_3$ in MeCN. TD-DFT calculated transitions of $\text{cis-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ shown as vertical bars (black). Inset shows emission decay curves recorded at 742 nm under argon (green) and air (black).

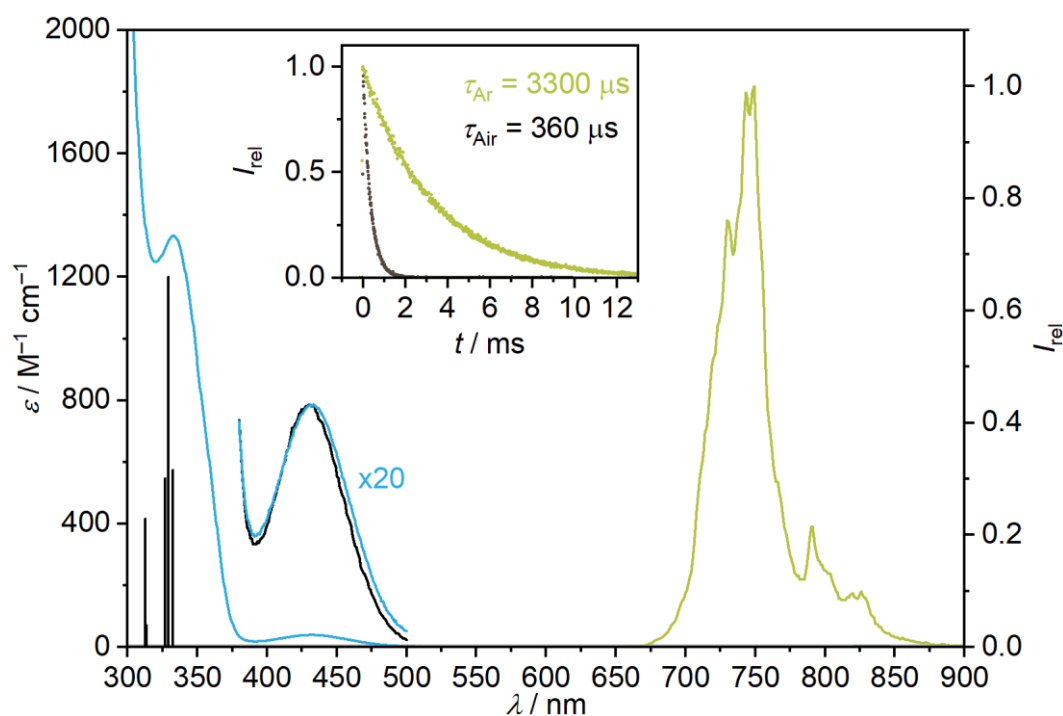


Figure S23. UV/vis absorption (blue), normalized excitation ($\lambda_{\text{em}} = 742 \text{ nm}$, black) and emission spectra ($\lambda_{\text{exc}} = 435 \text{ nm}$, green) of $\text{trans-[Cr(tpe}^{\text{CF}_3})_2][\text{PF}_6]_3$ in MeCN. TD-DFT calculated transitions of $\text{trans-[Cr(tpe}^{\text{CF}_3})_2]^{3+}$ shown as vertical bars (black). Inset shows emission decay curves recorded at 742 nm under argon (green) and air (black).

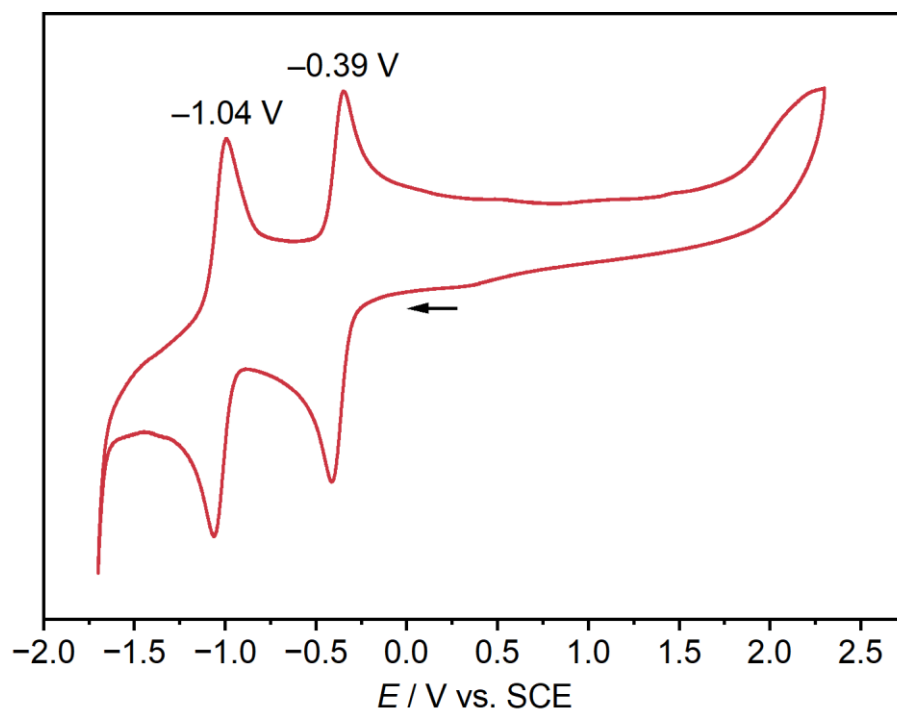


Figure S24. Cyclic voltammogram of $1 \text{ mM [Cr(tpe)(tpe}^{\text{CF}_3})][\text{PF}_6]_3$ in a 100 mM solution of $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ in MeCN.

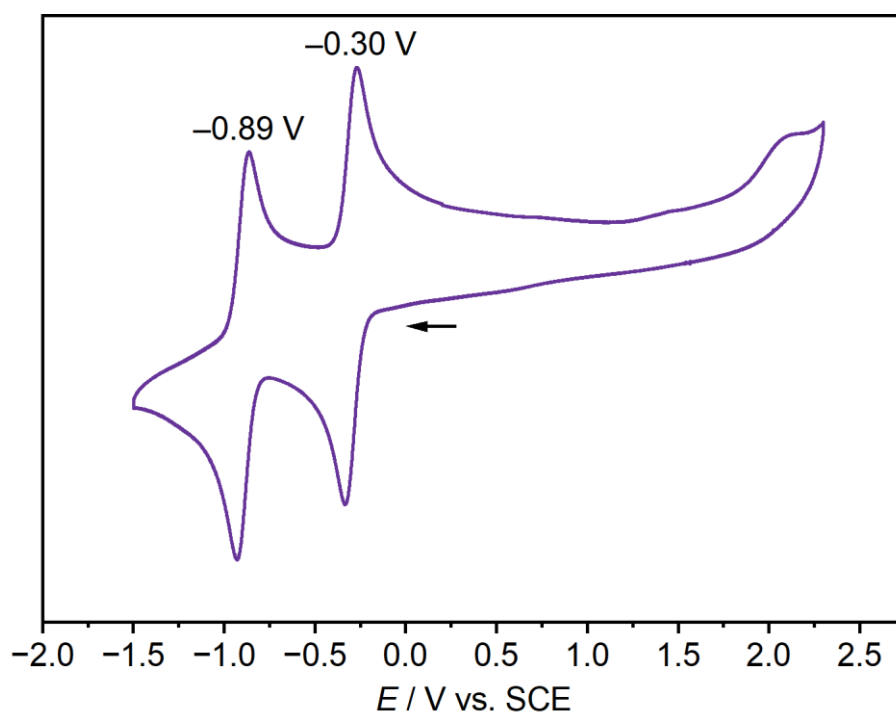


Figure S25. Cyclic voltammogram of 1 mM *cis*-[Cr(tpe^{CF3})₂][PF₆]₃ in a 100 mM solution of [*n*-Bu₄N][PF₆] in MeCN.

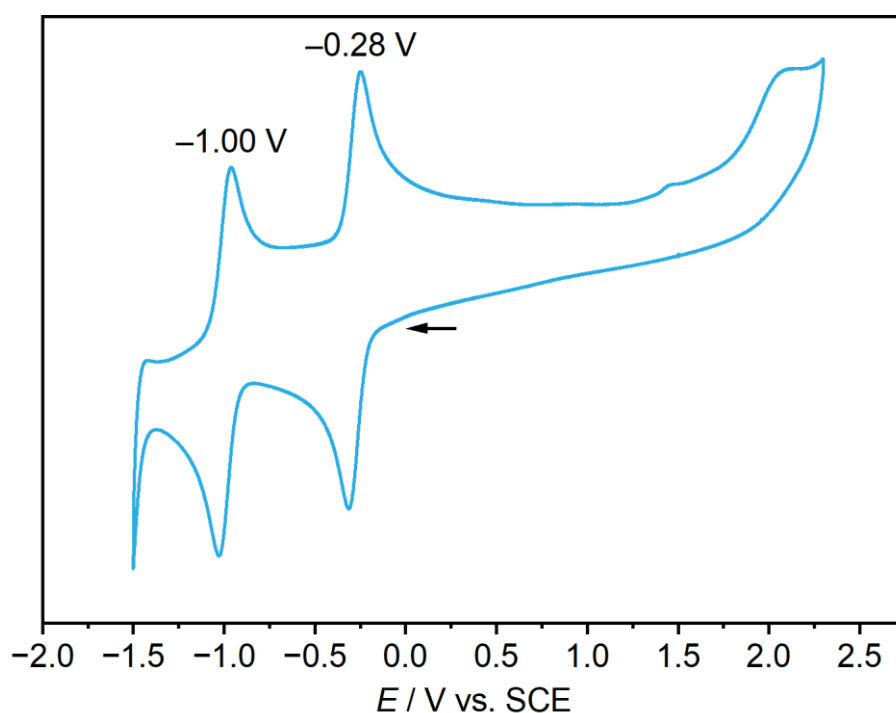


Figure S26. Cyclic voltammogram of 1 mM *trans*-[Cr(tpe^{CF3})₂][PF₆]₃ in a 100 mM solution of [*n*-Bu₄N][PF₆] in MeCN.

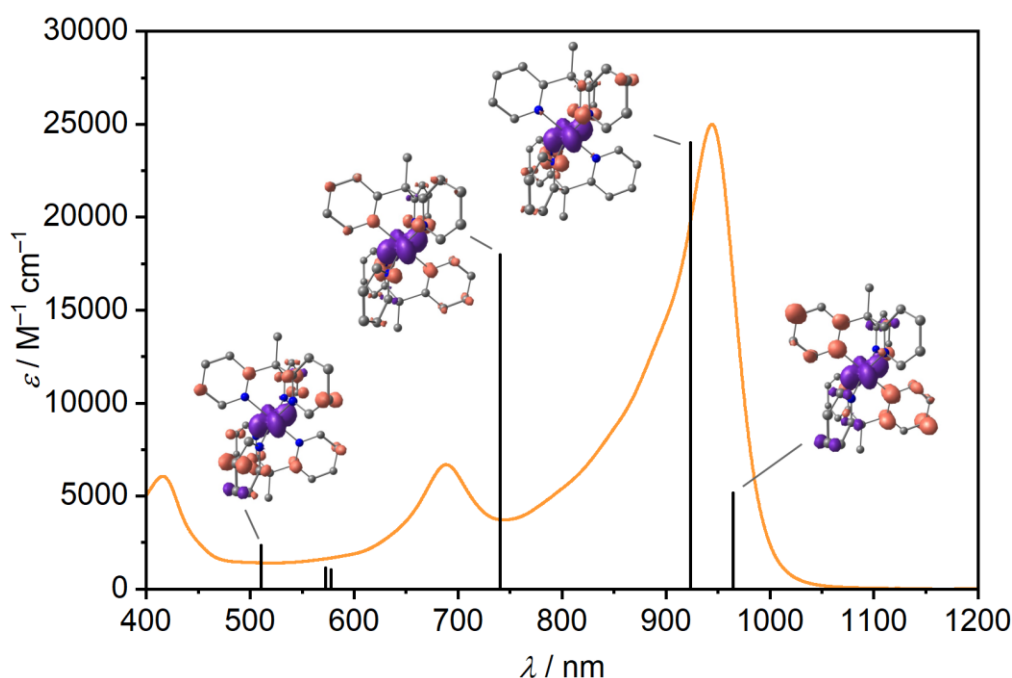


Figure S27. Vis/NIR absorption spectrum of $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_2$ (orange) prepared by reduction $[\text{Cr}(\text{tpe})_2][\text{PF}_6]_3$ with cobaltocene in MeCN. TD-DFT calculated transitions of $[\text{Cr}(\text{tpe})_2]^{2+}$ shown as vertical bars (black). Selected TD-DFT calculated electronic transitions are depicted. Orange: electron density gain, purple: electron density loss; hydrogen atoms omitted for clarity (CPCM(acetonitrile) ZORA SARC/J RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP).

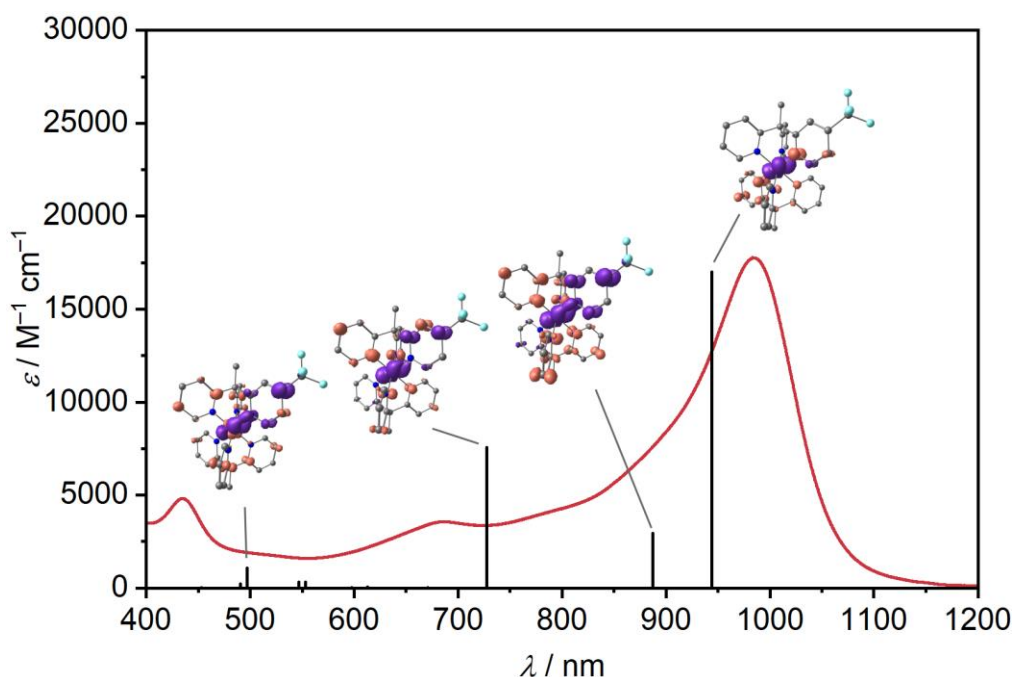


Figure S28. Vis/NIR absorption spectrum of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_2$ (red) prepared by reduction $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})][\text{PF}_6]_3$ with cobaltocene in MeCN. TD-DFT calculated transitions of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{2+}$ shown as vertical bars (black). Selected TD-DFT calculated electronic transitions are depicted. Orange/purple: electron density gain/loss; hydrogen atoms omitted for clarity (CPCM(acetonitrile) ZORA SARC/J RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP).

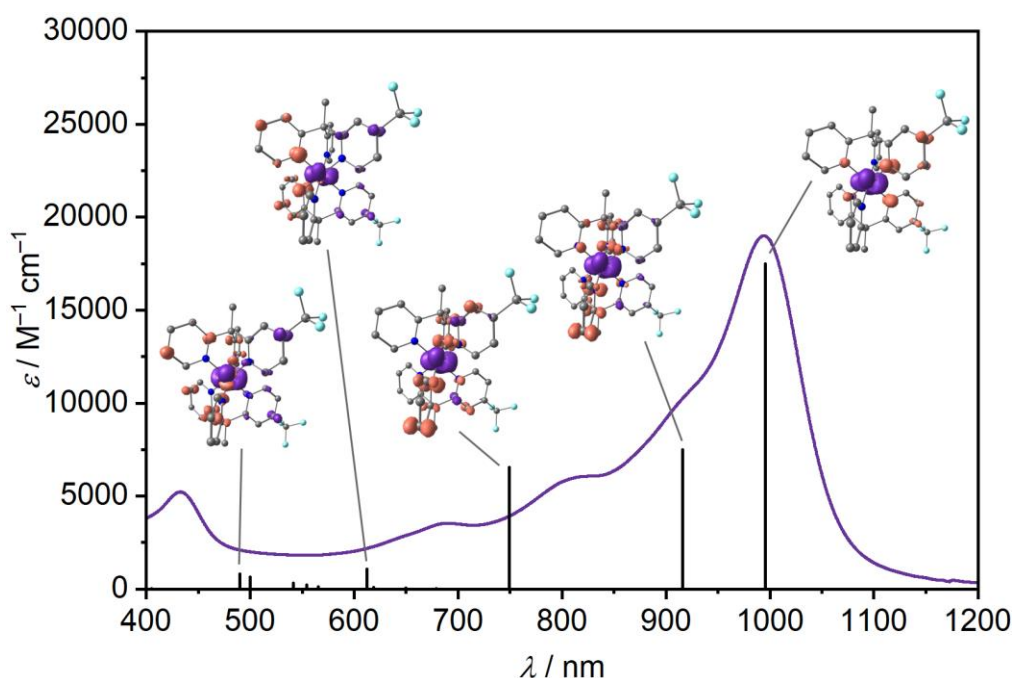


Figure S29. Vis/NIR absorption spectrum of *cis*-[Cr(tpe^{CF3})₂][PF₆]₂ (purple) prepared by reduction *cis*-[Cr(tpe^{CF3})₂][PF₆]₃ with cobaltocene in MeCN. TD-DFT calculated transitions of *cis*-[Cr(tpe^{CF3})₂]²⁺ shown as vertical bars (black). Selected TD-DFT calculated electronic transitions are depicted. Orange/purple: electron density gain/loss; hydrogen atoms omitted for clarity (CPCM(acetonitrile) ZORA SARC/J RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP).

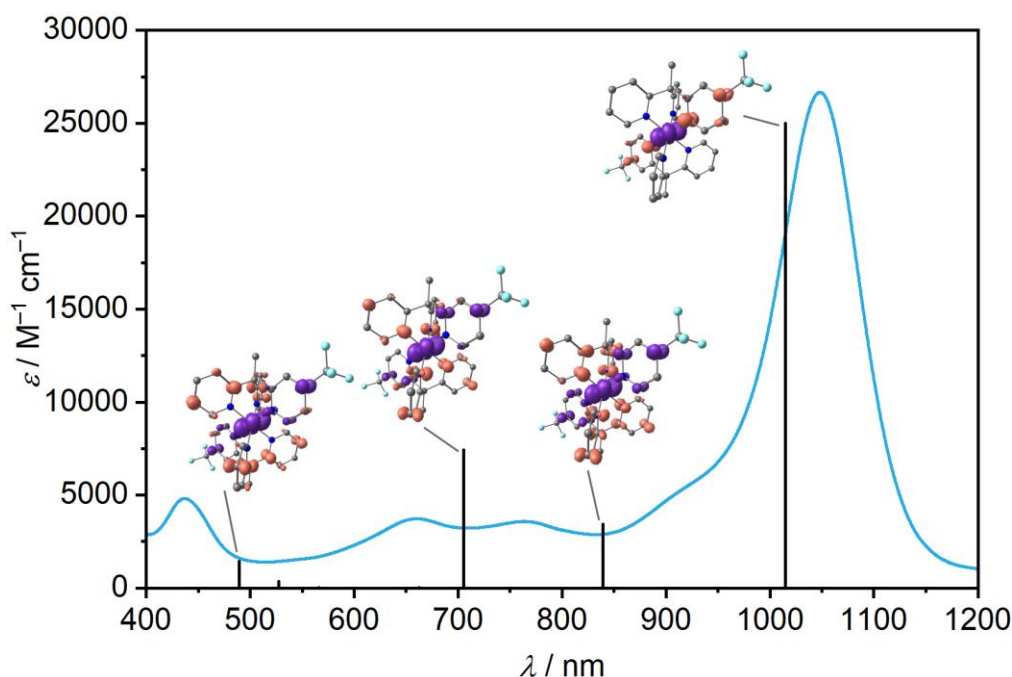


Figure S30. Vis/NIR absorption spectrum of *trans*-[Cr(tpe^{CF3})₂][PF₆]₂ (blue) prepared by reduction *trans*-[Cr(tpe^{CF3})₂][PF₆]₃ with cobaltocene in MeCN. TD-DFT calculated transitions of *trans*-[Cr(tpe^{CF3})₂]²⁺ shown as vertical bars (black). Selected TD-DFT calculated electronic transitions are depicted. Orange/purple: electron density gain/loss; hydrogen atoms omitted for clarity (CPCM(acetonitrile) ZORA SARC/J RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP).

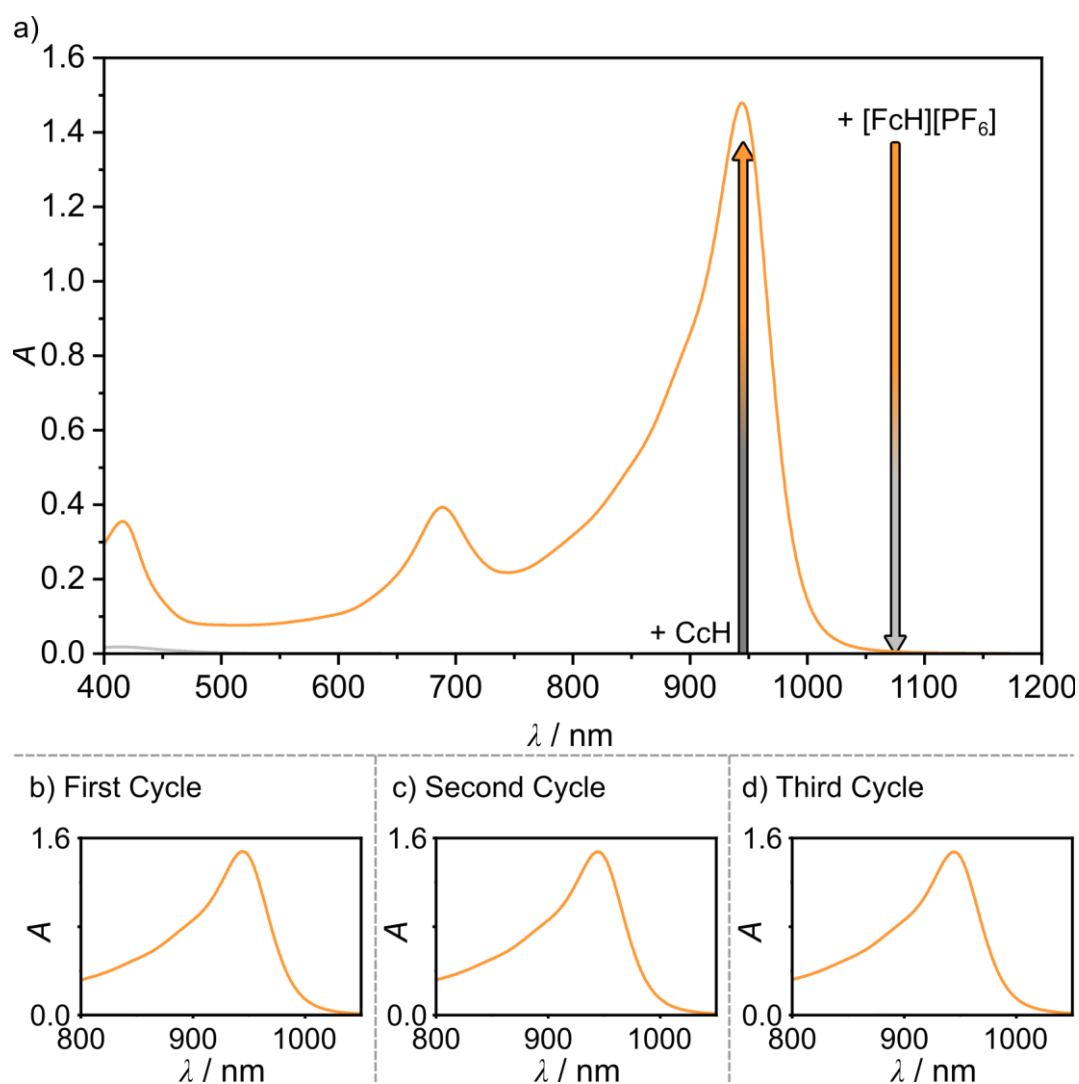


Figure S31. a) UV/vis/NIR absorption spectra of $[\text{Cr}(\text{tpe})_2]^{3+}$ (dark gray), $[\text{Cr}(\text{tpe})_2]^{2+}$ obtained by reduction of $[\text{Cr}(\text{tpe})_2]^{3+}$ with cobaltocene (CcH; orange) and $[\text{Cr}(\text{tpe})_2]^{3+}$ after reoxidation of $[\text{Cr}(\text{tpe})_2]^{2+}$ with ferrocenium hexafluorophosphate ($[\text{FcH}][\text{PF}_6]$; light gray) in MeCN. b)–d) Excerpts of NIR absorption spectra from three consecutive reduction/oxidation cycles. The $[\text{Cr}(\text{tpe})_2]^{3+}$ complex does not absorb in the NIR spectral region.

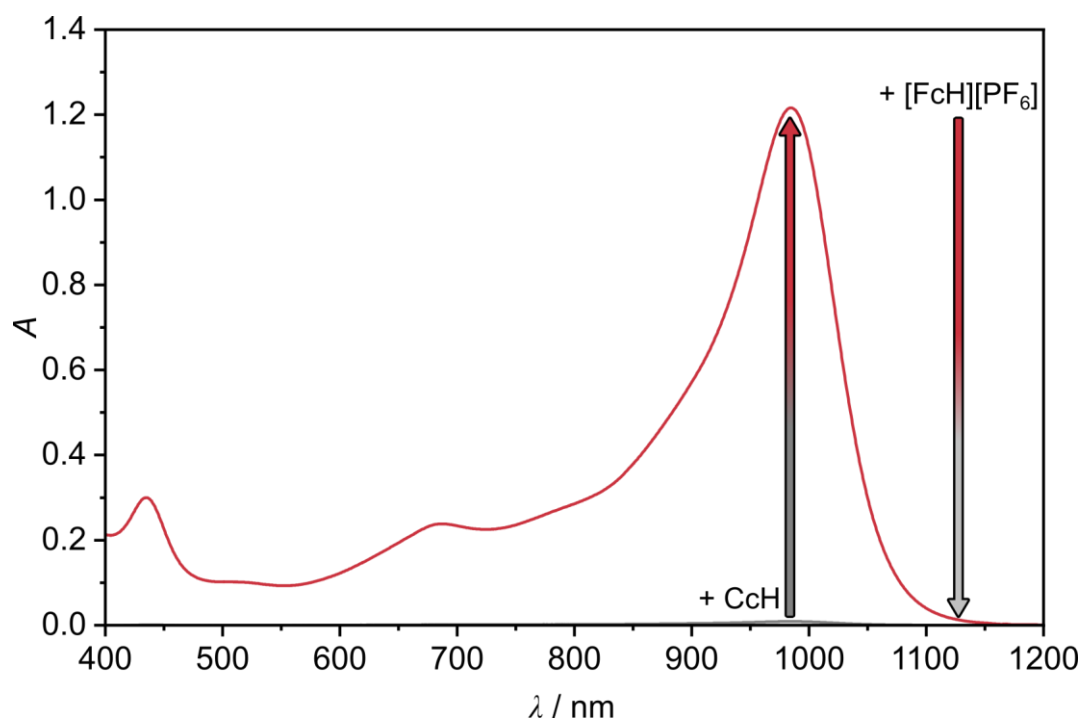


Figure S32. UV/vis/NIR absorption spectra of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ (dark gray), $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{2+}$ obtained by reduction of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ with cobaltocene (CcH; red) and $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ after reoxidation with ferrocenium hexafluorophosphate ($[\text{Fch}][\text{PF}_6]$; light gray) in MeCN.

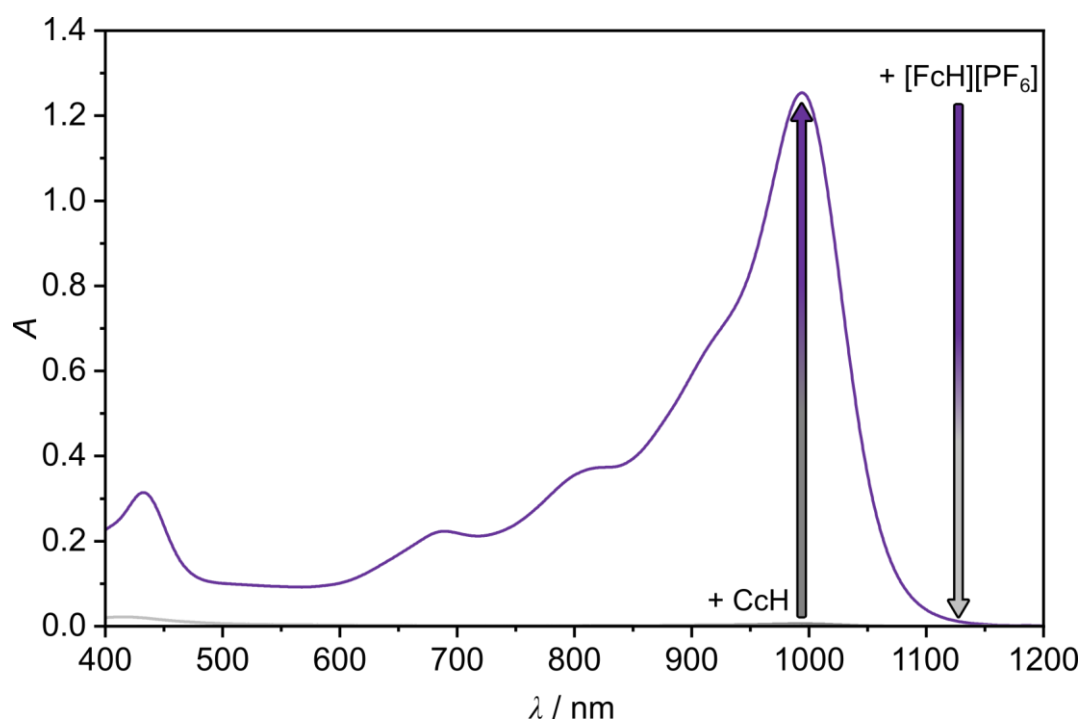


Figure S33. UV/vis/NIR absorption spectra of $\text{cis}-[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ (dark gray), $\text{cis}-[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+}$ obtained by reduction of $\text{cis}-[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ with cobaltocene (CcH; purple) and $\text{cis}-[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ after reoxidation with ferrocenium hexafluorophosphate ($[\text{Fch}][\text{PF}_6]$; light gray) in MeCN.

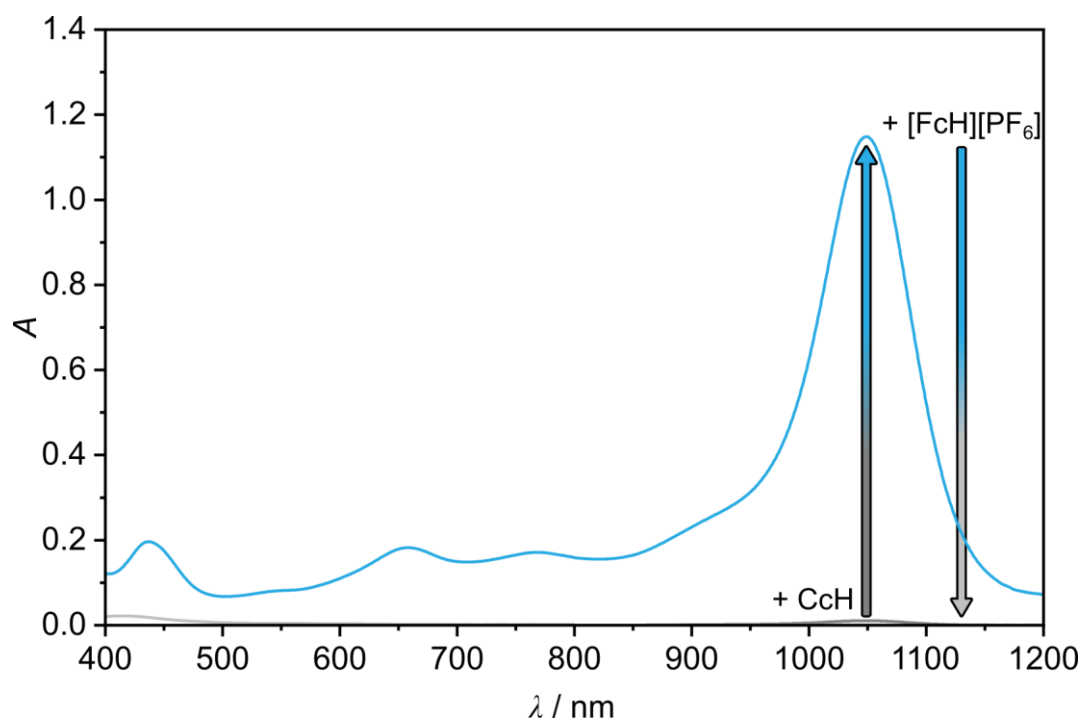


Figure S34. UV/vis/NIR absorption spectra of $trans-[Cr(tpe^{CF_3})_2]^{3+}$ (dark gray), $trans-[Cr(tpe^{CF_3})_2]^{2+}$ obtained by reduction of $trans-[Cr(tpe^{CF_3})_2]^{3+}$ with cobaltocene (CcH; blue) and $trans-[Cr(tpe^{CF_3})_2]^{3+}$ after reoxidation with ferrocenium hexafluorophosphate ([FcH][PF₆]; light gray) in MeCN.

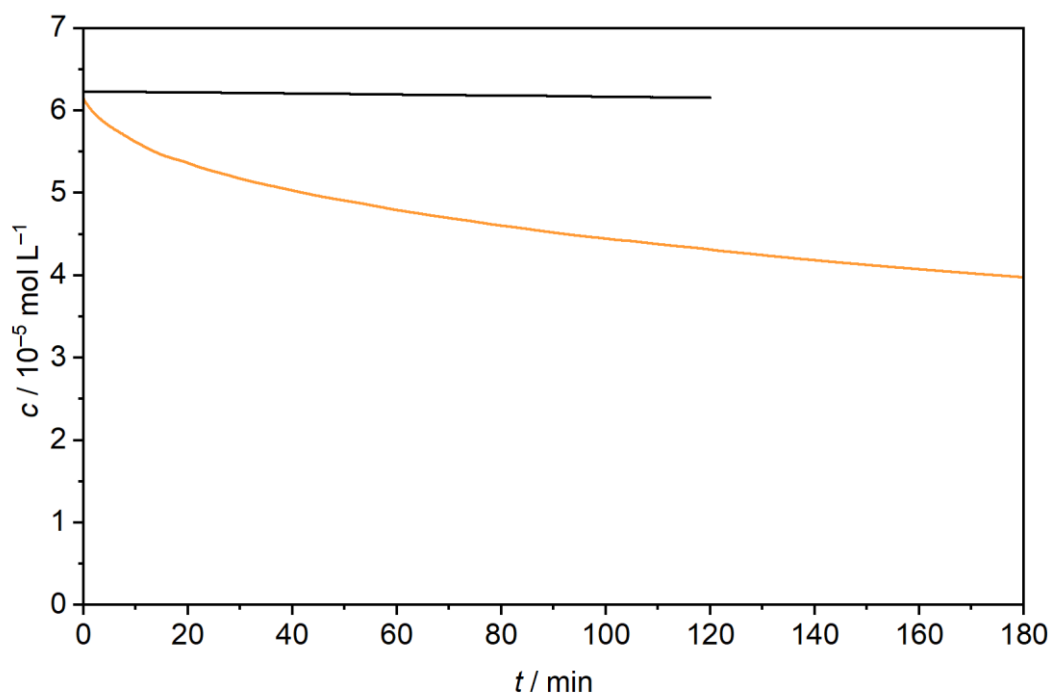


Figure S35. Decrease of the concentration of $[\text{Cr}(\text{tpe})_2]^{2+}$ (obtained by reduction of $[\text{Cr}(\text{tpe})_2]^{2+}$ with cobaltocene) in air-free (black) and air-saturated (orange) MeCN over time. The concentration was determined using the absorbance at $\lambda_{\text{abs}} = 944 \text{ nm}$.

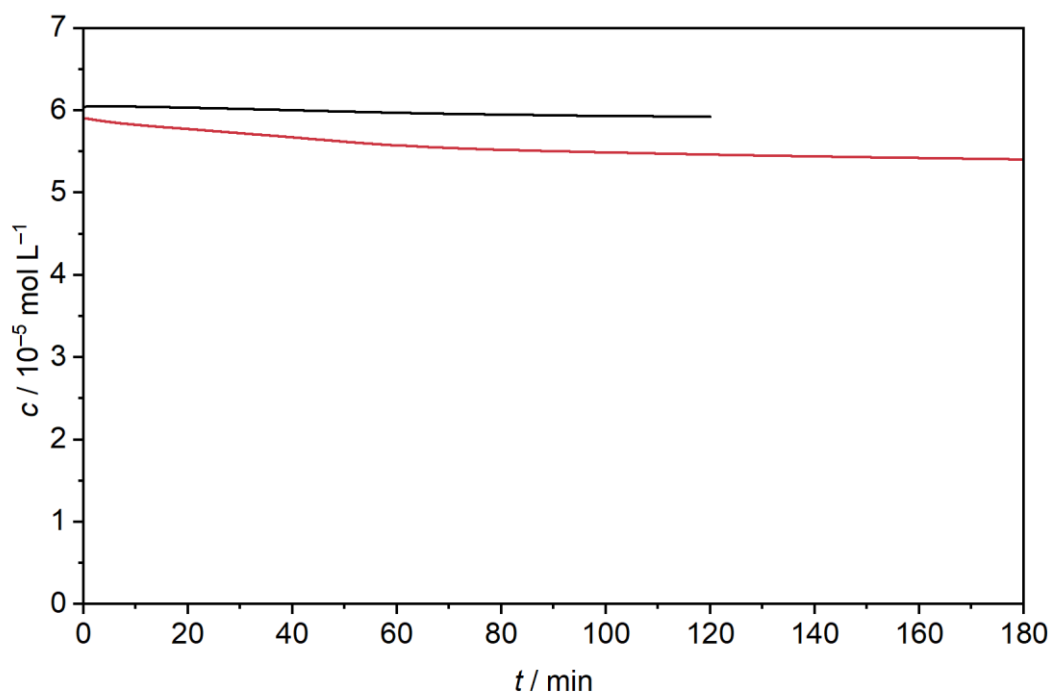


Figure S36. Decrease of the concentration of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{2+}$ (obtained by reduction of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{2+}$ with cobaltocene) in air-free (black) air-saturated (red) MeCN over time. The concentration was determined using the absorbance at $\lambda_{\text{abs}} = 985 \text{ nm}$.

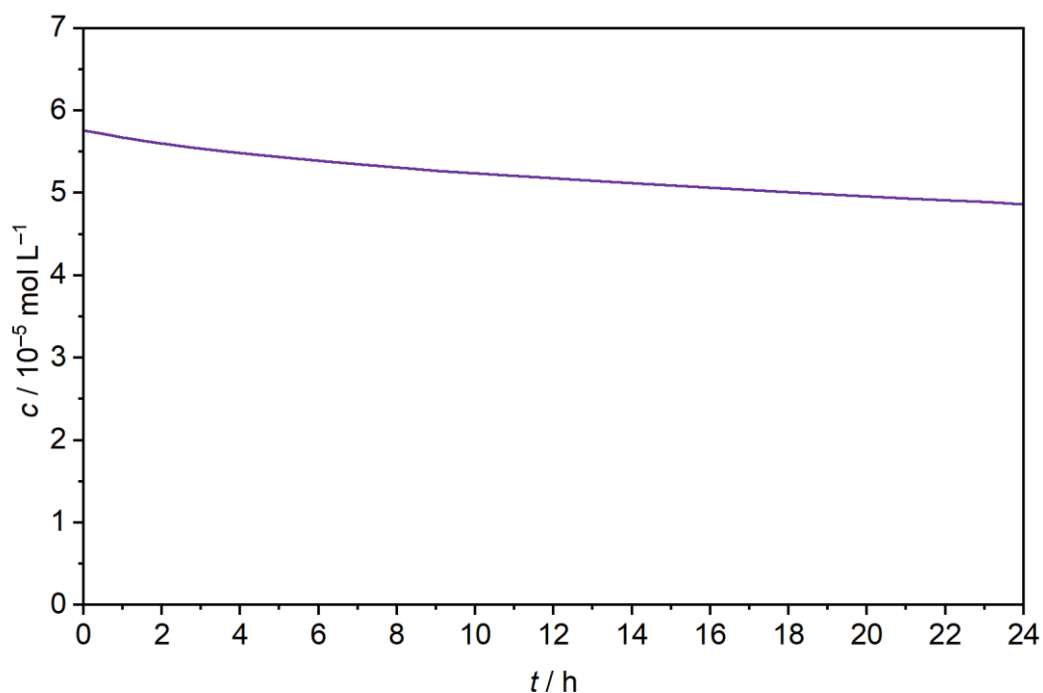


Figure S37. Decrease of the concentration of *cis*-[Cr(tpe^{CF3})₂]²⁺ (obtained by reduction of *cis*-[Cr(tpe^{CF3})₂]²⁺ with cobaltocene) in air-saturated MeCN (purple) over time. The concentration was determined using the absorbance at $\lambda_{\text{abs}} = 995$ nm. Note the different time scale with respect to Figures S35 and S36.

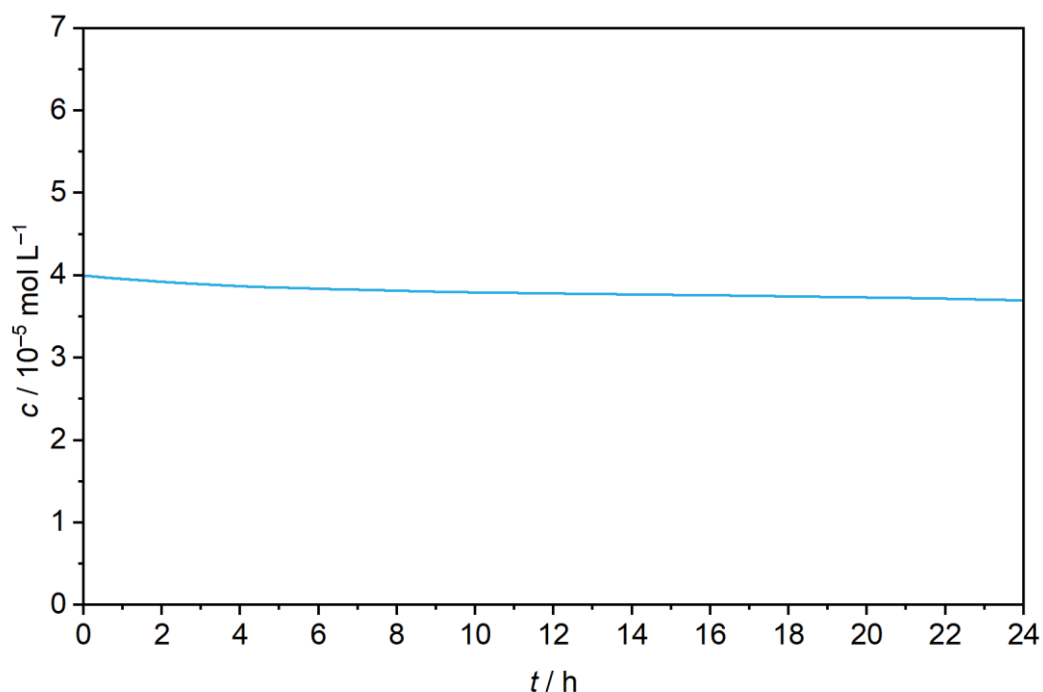


Figure S38. Decrease of the concentration of *trans*-[Cr(tpe^{CF3})₂]²⁺ (obtained by reduction of *trans*-[Cr(tpe^{CF3})₂]²⁺ with cobaltocene) in air-saturated MeCN (blue) over time. The concentration was determined using the absorbance at $\lambda_{\text{abs}} = 1048$ nm. Note the different time scale with respect to Figures S35 and S36.

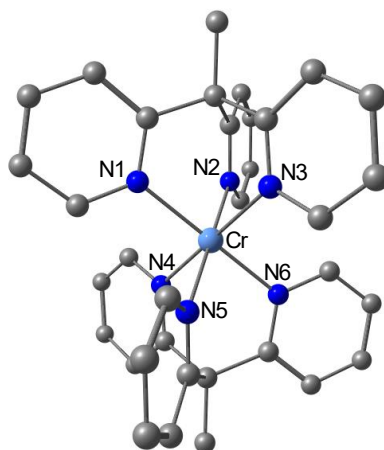


Figure S39. DFT-optimized structure of $^4[\text{Cr}(\text{tpe})_2]^{3+}$ with atom labels for Table S2.

Table S2. Bond lengths [Å] and angles [deg] of $[\text{Cr}(\text{tpe})_2]^{3+}$ in the DFT-optimized quartet and doublet states $^4[\text{Cr}]^{3+} / ^2[\text{Cr}]^{3+}$ and of $[\text{Cr}(\text{tpe})_2]^{2+}$ in the DFT-optimized triplet and quintet states $^3[\text{Cr}]^{2+} / ^5[\text{Cr}]^{2+}$. Gibbs free energies G [H] and relative energies $E_{\text{rel}} = G(^2[\text{Cr}]^{3+}) - G(^4[\text{Cr}]^{3+})$ and $E_{\text{rel}} = G(^3[\text{Cr}]^{2+}) - G(^5[\text{Cr}]^{2+})$ [eV]. Mulliken spin density at Cr.

	$^4[\text{Cr}]^{3+}$	$^2[\text{Cr}]^{3+}$	$^3[\text{Cr}]^{2+}$	$^5[\text{Cr}]^{2+}$
Cr-N1	2.056	2.050	2.030	2.117
Cr-N2	2.055	2.048	2.067	2.302
Cr-N3	2.055	2.049	2.046	2.086
Cr-N4	2.055	2.049	2.046	2.110
Cr-N5	2.055	2.048	2.067	2.333
Cr-N6	2.056	2.050	2.030	2.093
N1-Cr-N2	86.81	86.79	86.92	81.14
N1-Cr-N3	86.78	86.77	86.77	84.22
N1-Cr-N4	93.22	93.23	93.23	95.79
N1-Cr-N5	93.19	93.21	93.08	92.57
N1-Cr-N6	180.00	180.00	180.00	179.88
N2-Cr-N3	86.82	86.96	86.86	86.82
N2-Cr-N4	93.18	93.04	93.13	94.61
N2-Cr-N5	180.00	180.00	180.00	171.53
N2-Cr-N6	93.20	93.21	93.07	98.76
N3-Cr-N4	180.00	180.00	179.99	178.56
N3-Cr-N5	93.18	93.04	93.14	98.24
N3-Cr-N6	93.22	93.23	93.23	95.85
N4-Cr-N5	86.82	86.96	86.87	80.32
N4-Cr-N6	86.78	86.77	86.77	84.15
N5-Cr-N6	86.81	86.79	86.92	87.52
G / H	-2696.801	-2696.764	-2696.939	-2696.933
E_{rel} / eV	0	1.01	0	0.16
Spin density at Cr	3.22	1.13	2.51	3.96

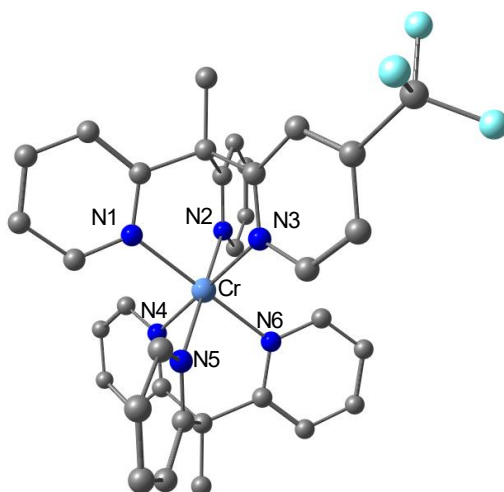


Figure S40. DFT-optimized structure of $^4[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ with atom labels for Table S3.

Table S3. Bond lengths [Å] and angles [deg] of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ in the DFT-optimized quartet and doublet states $^4[\text{Cr}]^{3+}$ / $^2[\text{Cr}]^{3+}$ and of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{2+}$ in the DFT-optimized triplet and quintet states $^3[\text{Cr}]^{2+}$ / $^5[\text{Cr}]^{2+}$. Gibbs free energies G [H] and relative energies $E_{\text{rel}} = G(^2[\text{Cr}]^{3+}) - G(^4[\text{Cr}]^{3+})$ and $E_{\text{rel}} = G(^3[\text{Cr}]^{2+}) - G(^5[\text{Cr}]^{2+})$ [eV]. Mulliken spin density at Cr.

	$^4[\text{Cr}]^{3+}$	$^2[\text{Cr}]^{3+}$	$^3[\text{Cr}]^{2+}$	$^5[\text{Cr}]^{2+}$
Cr-N1	2.056	2.049	2.058	2.098
Cr-N2	2.056	2.048	2.056	2.100
Cr-N3	2.064	2.059	1.987	2.287
Cr-N4	2.050	2.044	2.049	2.245
Cr-N5	2.055	2.048	2.061	2.075
Cr-N6	2.055	2.048	2.062	2.112
N1-Cr-N2	86.85	87.03	87.18	84.52
N1-Cr-N3	86.71	86.67	87.37	89.35
N1-Cr-N4	86.57	93.26	92.61	97.16
N1-Cr-N5	93.08	92.92	93.02	95.23
N1-Cr-N6	179.81	179.80	179.14	179.9
N2-Cr-N3	86.57	86.55	87.38	80.34
N2-Cr-N4	93.40	93.44	92.87	95.65
N2-Cr-N5	179.65	179.64	179.31	178.26
N2-Cr-N6	93.22	93.04	93.11	95.54
N3-Cr-N4	179.93	179.93	179.75	172.03
N3-Cr-N5	93.08	93.10	93.29	97.94
N3-Cr-N6	93.12	93.15	93.45	90.75
N4-Cr-N5	86.95	86.92	86.46	86.09
N4-Cr-N6	86.94	86.92	86.56	82.75
N5-Cr-N6	86.85	87.01	86.69	84.71
G / H	-3034.330	-3034.293	-3034.473	-3034.466
E_{rel} / eV	0	1.01	0	0.19
Spin density at Cr	3.22	1.13	2.64	3.87

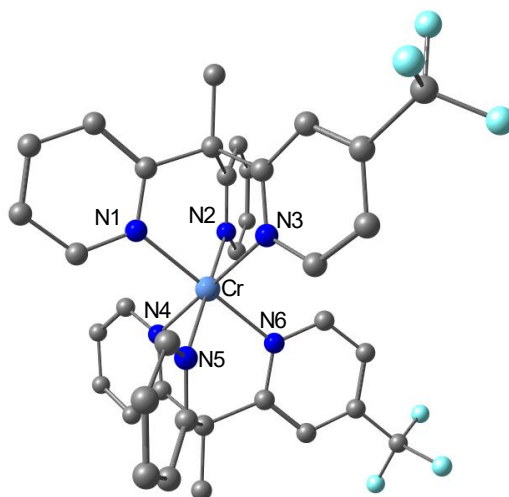


Figure S41. DFT-optimized structure of $cis\text{-}^4[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ with atom labels for Table S4.

Table S4. Bond lengths [Å] and angles [deg] of $cis\text{-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ in the DFT-optimized quartet and doublet states $^4[\text{Cr}]^{3+} / ^2[\text{Cr}]^{3+}$ and of $cis\text{-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+}$ in the DFT-optimized triplet and quintet states $^3[\text{Cr}]^{2+} / ^5[\text{Cr}]^{2+}$. Gibbs free energies G [H] and relative energies $E_{\text{rel}} = G(^2[\text{Cr}]^{3+}) - G(^4[\text{Cr}]^{3+})$ and $E_{\text{rel}} = G(^3[\text{Cr}]^{2+}) - G(^5[\text{Cr}]^{2+})$ [eV]. Mulliken spin density at Cr.

	$^4[\text{Cr}]^{3+}$	$^2[\text{Cr}]^{3+}$	$^3[\text{Cr}]^{2+}$	$^5[\text{Cr}]^{2+}$
Cr-N1	2.049	2.042	2.048	2.262
Cr-N2	2.056	2.048	2.070	2.079
Cr-N3	2.064	2.059	2.023	2.125
Cr-N4	2.051	2.046	2.048	2.090
Cr-N5	2.054	2.047	2.068	2.105
Cr-N6	2.063	2.056	2.022	2.312
N1-Cr-N2	86.96	87.15	86.75	86.12
N1-Cr-N3	86.81	86.79	86.78	82.07
N1-Cr-N4	93.34	93.37	92.80	98.94
N1-Cr-N5	93.33	93.17	93.11	95.88
N1-Cr-N6	179.85	179.83	179.46	171.73
N2-Cr-N3	86.67	86.63	87.08	84.26
N2-Cr-N4	93.17	93.22	92.98	95.51
N2-Cr-N5	179.65	179.62	179.78	177.96
N2-Cr-N6	93.07	92.88	93.06	97.71
N3-Cr-N4	179.77	179.78	179.57	178.95
N3-Cr-N5	93.15	93.18	93.09	95.67
N3-Cr-N6	93.04	93.05	93.71	90.99
N4-Cr-N5	87.01	86.97	86.85	84.52
N4-Cr-N6	86.81	86.79	86.71	88.02
N5-Cr-N6	86.63	86.80	87.08	80.25
G / Eh	-3371.858	-3371.821	-3372.005	-3371.996
E_{rel} / eV	0	1.01	0	0.24
Spindensity at Cr	3.22	1.13	2.61	3.91

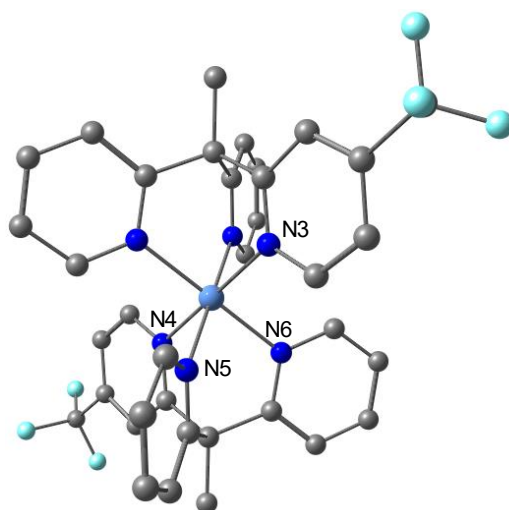


Figure S42. DFT-optimized structure of $trans\text{-}^4[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ with atom labels for Table S5.

Table S5. Bond lengths [Å] and angles [deg] of $trans\text{-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{3+}$ in the DFT-optimized quartet and doublet states $^4[\text{Cr}_2]^{3+} / ^2[\text{Cr}]^{3+}$ and of $trans\text{-}[\text{Cr}(\text{tpe}^{\text{CF}_3})_2]^{2+}$ in the DFT-optimized triplet and quintet states $^3[\text{Cr}]^{2+} / ^5[\text{Cr}]^{2+}$. Gibbs free energies G [H] and relative energies $E_{\text{rel}} = G(^2[\text{Cr}]^{3+}) - G(^4[\text{Cr}]^{3+})$ and $E_{\text{rel}} = G(^3[\text{Cr}]^{2+}) - G(^5[\text{Cr}]^{2+})$ [eV]. Mulliken spin density at Cr.

	$^4[\text{Cr}]^{3+}$	$^2[\text{Cr}]^{3+}$	$^3[\text{Cr}]^{2+}$	$^5[\text{Cr}]^{2+}$
Cr-N1	2.055	2.048	2.060	2.080
Cr-N2	2.055	2.047	2.061	2.114
Cr-N3	2.059	2.054	2.018	2.277
Cr-N4	2.060	2.055	2.018	2.287
Cr-N5	2.055	2.048	2.061	2.086
Cr-N6	2.055	2.048	2.059	2.108
N1-Cr-N2	86.83	87.00	86.83	84.52
N1-Cr-N3	86.86	86.84	86.90	87.59
N1-Cr-N4	93.32	93.33	93.07	98.10
N1-Cr-N5	93.06	92.89	93.11	95.36
N1-Cr-N6	179.92	179.95	179.94	178.58
N2-Cr-N3	86.73	86.69	86.87	81.18
N2-Cr-N4	93.48	93.52	93.28	92.20
N2-Cr-N5	179.79	179.72	179.84	179.40
N2-Cr-N6	93.19	93.02	93.22	95.58
N3-Cr-N4	179.93	179.73	179.84	170.86
N3-Cr-N5	93.02	93.05	92.98	98.22
N3-Cr-N6	93.07	93.11	93.13	93.83
N4-Cr-N5	86.77	86.74	86.86	88.40
N4-Cr-N6	86.75	86.72	86.91	80.49
N5-Cr-N6	86.92	87.09	86.83	84.55
G / Eh	-3371.860	-3371.8203	-3372.005	-3371.998
E_{rel} / eV	0	1.07	0	0.19
Spindensity at Cr	3.22	1.13	2.62	3.90

Table S6. Energies and depictions of the orbitals used in the active space of the CASSCF(7,12)-SC-NEVPT2 calculation of $[\text{Cr}(\text{tpe})_2]^{3+}$ (contour value of 0.03 a.u.; hydrogen atoms omitted for clarity).

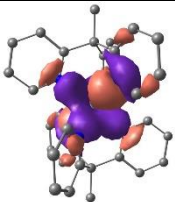
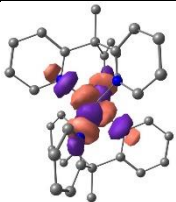
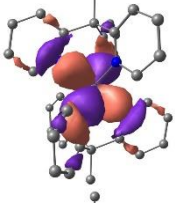
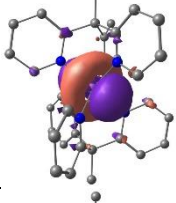
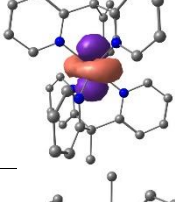
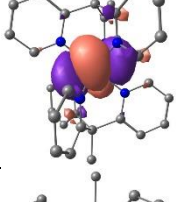
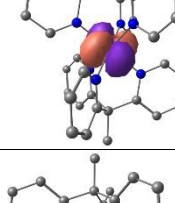
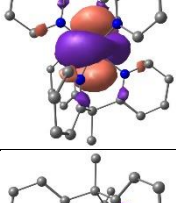
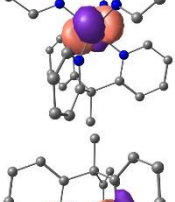
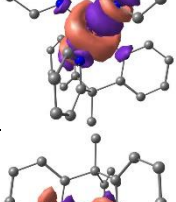
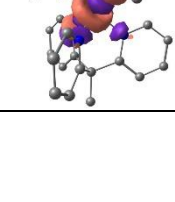
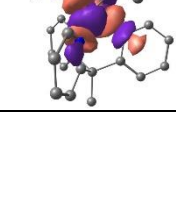
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148	-0.1346		154	0.9551	
149	-0.1181		155	1.0248	
150	-0.1159		156	1.6681	
151	0.0832		157	1.6689	

Table S7. Energies and depictions of the orbitals used in the active space of the CASSCF(7,12)-SC-NEVPT2 calculation of $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF}_3})]^{3+}$ (contour value of 0.03 a.u.; hydrogen atoms omitted for clarity).

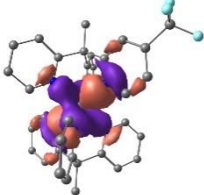
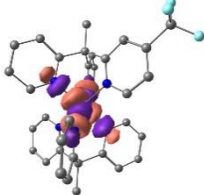
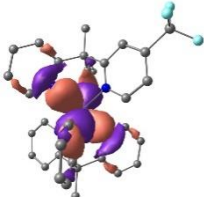
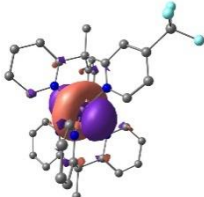
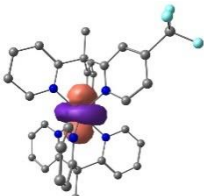
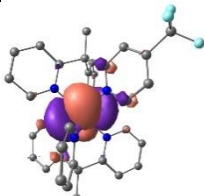
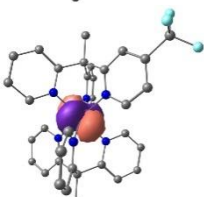
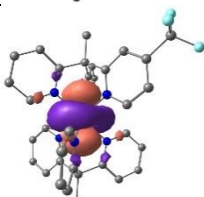
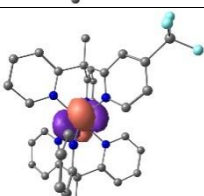
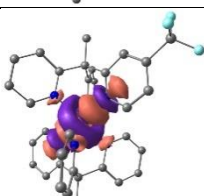
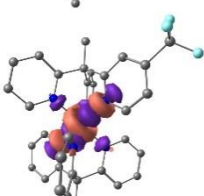
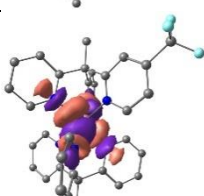
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163	−0.5964		169	0.9589	
164	−0.1381		170	0.9447	
165	−0.1240		171	1.0271	
166	−0.1172		172	1.6628	
167	0.0767		173	1.6679	

Table S8. Energies and depictions of the orbitals used in the active space of the CASSCF(7,12)-SC-NEVPT2 calculation of *cis*-[Cr(tpe^{CF3})₂]³⁺ (contour value of 0.03 a.u.; hydrogen atoms omitted for clarity).

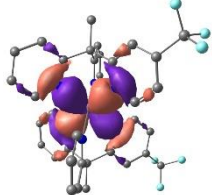
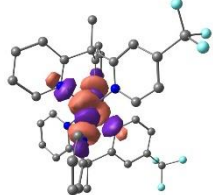
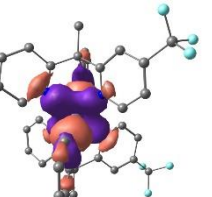
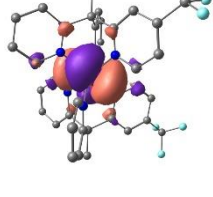
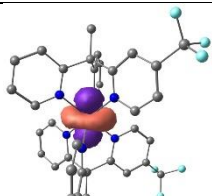
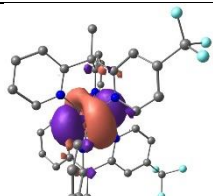
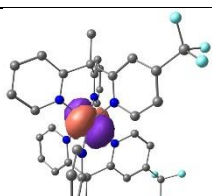
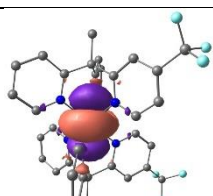
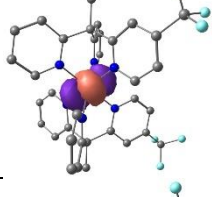
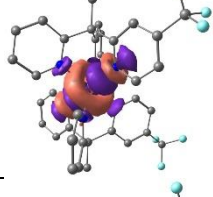
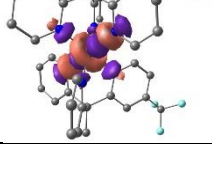
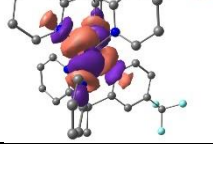
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180	−0.1420		186	0.9497	
181	−0.1259		187	1.0205	
182	−0.1225		188	1.6603	
183	0.0748		189	1.6636	

Table S9. Energies and depictions of the orbitals used in the active space of the CASSCF(7,12)-SC-NEVPT2 calculation of *trans*-[Cr(tpe^{CF3})₂]³⁺ (contour value of 0.03 a.u.; hydrogen atoms omitted for clarity).

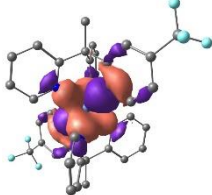
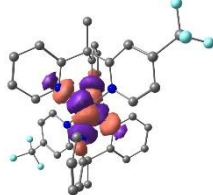
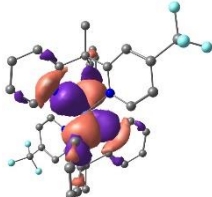
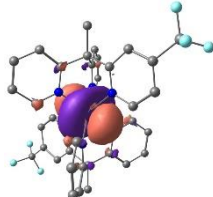
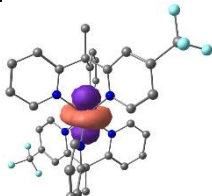
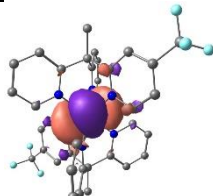
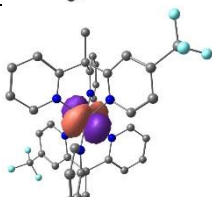
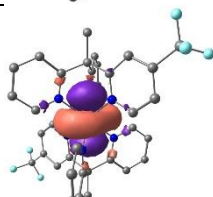
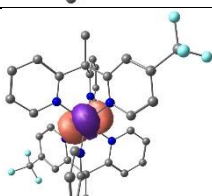
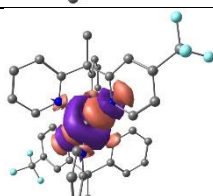
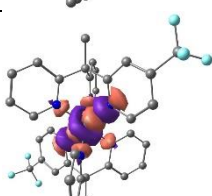
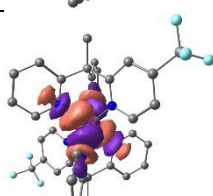
#	<i>E</i> / H	orbital	#	<i>E</i> / H	orbital
178	−0.6042		184	0.0839	
179	−0.5986		185	0.9555	
180	−0.1419		186	0.9360	
181	−0.1294		187	1.0269	
182	−0.1193		188	1.6566	
183	0.0703		189	1.6671	

Table S10. CASSCF(7,12)-SC-NEVPT2 results of $[\text{Cr}(\text{tpe})_2]^{3+}$ (orange) and $[\text{Cr}(\text{tpe})(\text{tpe}^{\text{CF3}})]^{3+}$ (red); energies in cm^{-1} relative to the $^4\text{A}_2$ ground state; energies of doublet states scaled by 0.89^[44,49] (bold values indicate the lowest state of each multiplicity). Light gray: doublet character, dark gray: quartet character.

Term Symbol	E / cm^{-1}	E / cm^{-1} (scaled with 0.89)	Term Symbol	E / cm^{-1}	E / cm^{-1} (scaled with 0.89)
$^2\text{T}_1(1)$	15225	13550	$^2\text{T}_1(1)$	15219	13545
$^2\text{E}(1)$	15231	13556	$^2\text{E}(1)$	15230	13555
$^2\text{T}_1(2)$	15640	13920	$^2\text{T}_1(2)$	15618	13900
$^2\text{T}_1(3)$	15644	13923	$^2\text{T}_1(3)$	15660	13937
$^2\text{E}(2)$	16571	14748	$^2\text{E}(2)$	16578	14754
$^2\text{T}_2(1)$	22729	20229	$^2\text{T}_2(1)$	22735	20234
$^4\text{T}_2(1)$	24250		$^4\text{T}_2(1)$	24242	
$^2\text{T}_2(2)$	24851	22117	$^2\text{T}_2(2)$	24805	22076
$^2\text{T}_2(3)$	24858	22124	$^2\text{T}_2(3)$	24906	22166
$^4\text{T}_2(2)$	24999		$^4\text{T}_2(2)$	24947	
$^4\text{T}_2(3)$	25001		$^4\text{T}_2(3)$	25030	
$^4\text{T}_1(1)$	30104		$^4\text{T}_1(1)$	30106	
$^4\text{T}_1(2)$	32530		$^4\text{T}_1(2)$	32413	
$^4\text{T}_1(3)$	32554		$^4\text{T}_1(3)$	32690	
$^2\text{A}_1$	37253	33155	$^2\text{A}_1$	37261	33162
$^2\text{A}_2$	38105	33913	$^2\text{A}_2$	38064	33877
$^4\text{T}_1(1)$	52119		$^4\text{T}_1(1)$	52130	
$^4\text{T}_1(2)$	52466		$^4\text{T}_1(2)$	52393	
$^4\text{T}_1(3)$	52473		$^4\text{T}_1(3)$	52520	

Table S11. CASSCF(7,12)-SC-NEVPT2 results of *cis*-[Cr(tpe^{CF3})₂]³⁺ (purple) and *trans*-[Cr(tpe^{CF3})₂]³⁺ (blue); energies in cm⁻¹ relative to the ⁴A₂ ground state; of doublet states scaled by 0.89^[44,49] (bold values indicate the lowest state of each multiplicity). Light gray: doublet character, dark gray: quartet character.

Term Symbol	<i>E</i> / cm ⁻¹	<i>E</i> / cm ⁻¹ (scaled with 0.89)	Term Symbol	<i>E</i> / cm ⁻¹	<i>E</i> / cm ⁻¹ (scaled with 0.89)
²T₁(1)	15235	13559	²T₁(1)	15228	13553
² E(1)	15247	13570	² T ₁ (2)	15239	13563
² T ₁ (2)	15620	13902	² E(1)	15597	13881
² T ₁ (3)	15671	13947	² T ₁ (3)	15678	13953
² E(2)	16582	14758	² E(2)	16581	14757
² T ₂ (1)	22737	20236	² T ₂ (1)	22747	20245
⁴T₂(1)	24239		⁴T₂(1)	24200	
² T ₂ (2)	24798	22070	² T ₂ (2)	24740	22019
² T ₂ (3)	24898	22160	⁴ T ₂ (2)	24844	
⁴ T ₂ (2)	24956		² T ₂ (3)	24948	22204
⁴ T ₂ (3)	25022		⁴ T ₂ (3)	25077	
⁴ T ₁ (1)	30105		⁴ T ₁ (1)	30059	
⁴ T ₁ (2)	32387		⁴ T ₁ (2)	32269	
⁴ T ₁ (3)	32700		⁴ T ₁ (3)	32836	
² A ₁	37259	33161	² A ₁	25077	33144
² A ₂	38076	33888	² A ₂	37960	33784
⁴ T ₁ (1)	52121		⁴ T ₁ (1)	52132	
⁴ T ₁ (2)	52343		⁴ T ₁ (2)	52267	
⁴ T ₁ (3)	52497		⁴ T ₁ (3)	52533	

References

- [71] STOE & Cie, X-Area, STOE & Cie GmbH: Darmstadt, Germany.
- [72] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33–38.
- [73] A. L. Spek, *Acta Crystallogr. Sect. D* **2009**, *65*, 148–155.
- [74] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.
- [75] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
- [76] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- [77] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
- [78] P. J. Larkin, *Infrared and Raman Spectroscopy*, Elsevier Inc., 2018, 2nd ed..
- [79] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
- [80] F. Neese, F. Wennmohs, U. Becker, C. Riplinger, *J. Chem. Phys.* **2020**, *152*, 224108.
- [81] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2022**, *12*, e1606.
- [82] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [83] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200–206.
- [84] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2009**, *356*, 98–109.
- [85] R. Izsák, F. Neese, *J. Chem. Phys.* **2011**, *135*, 144105.
- [86] D. A. Pantazis, X.-Y. Chen, C. R. Landis, F. Neese, *J. Chem. Theory Comput.* **2008**, *4*, 908–919.
- [87] S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117–129.
- [88] V. Barone, M. Cossi, *J. Phys. Chem.* **1998**, *102*, 1995–2001.
- [89] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.
- [90] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.
- [91] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [92] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [93] B. O. Roos, P. R. Taylor, P. E. Siegbahn, *Chem. Phys.* **1980**, *48*, 157–173.
- [94] P. E. M. Siegbahn, J. Almlöf, A. Heiberg, B. O. Roos, *J. Chem. Phys.* **1981**, *74*, 2384–2396.
- [95] F. Weigend, M. Kattannek, R. Ahlrichs, *J. Chem. Phys.* **2009**, *130*, 164106.
- [96] S. Kossmann, F. Neese, *Chem. Phys. Lett.* **2009**, *481*, 240–243.
- [97] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, J.-P. Malrieu, *J. Chem. Phys.* **2001**, *114*, 10252–10264.
- [98] C. Angeli, R. Cimiraglia, J.-P. Malrieu, *J. Chem. Phys.* **2002**, *117*, 9138–9153.
- [99] K. Pierloot, *Int. J. Quantum Chem.* **2011**, *111*, 3291–3301.

6.5 Supporting Information: Thermally Activated and Non-activated Excited State Decay of $[\text{Cr}(\text{dgpy})_2]^{3+}$

Supporting Information

Thermally Activated and Non-activated Excited State Decay of [Cr(dgpy)₂]³⁺

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[REDACTED]

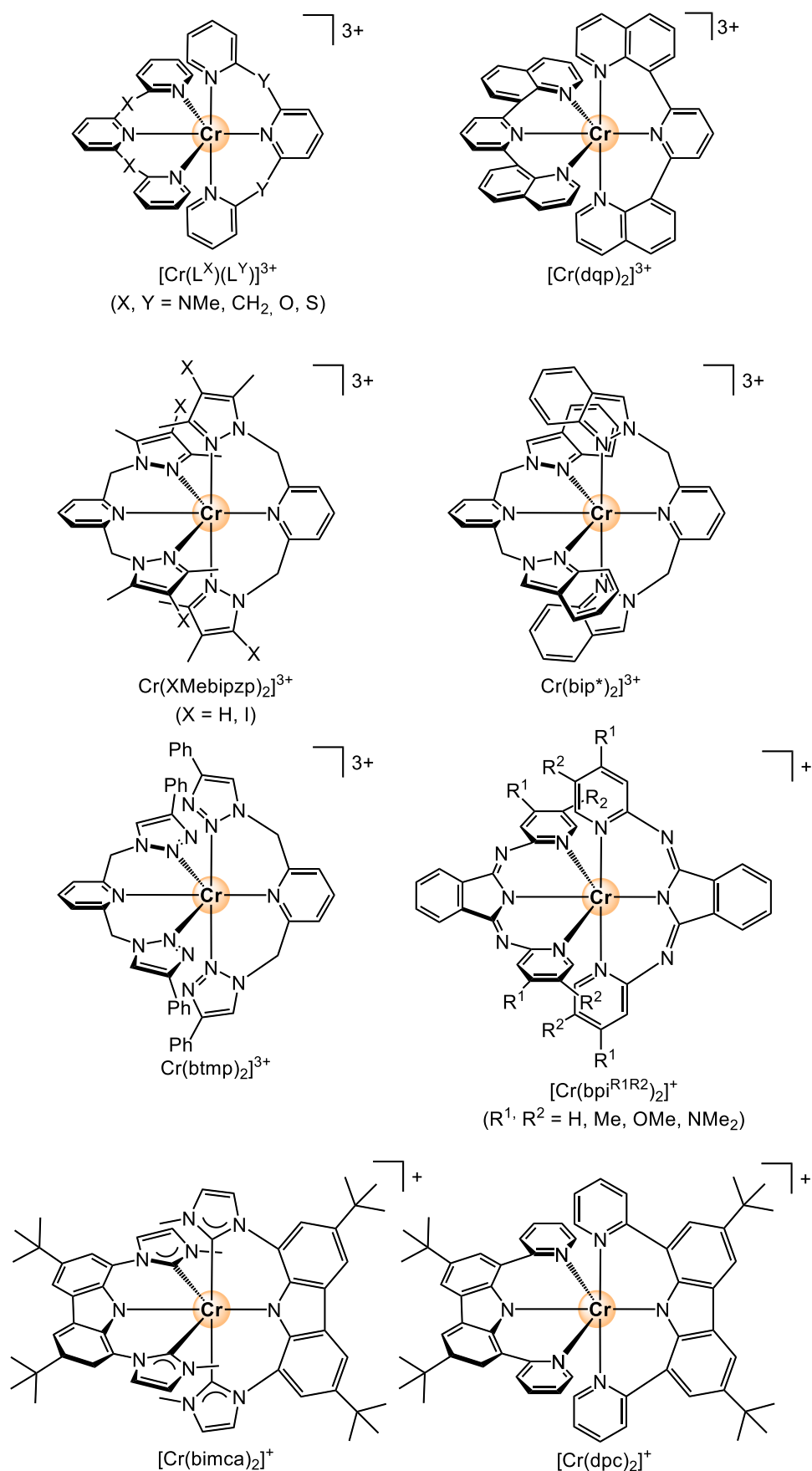
[REDACTED]

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Chart S1. a) Pseudo-octahedral chromium(III) complexes with strong-field ligands, but highly variable PL quantum yields.



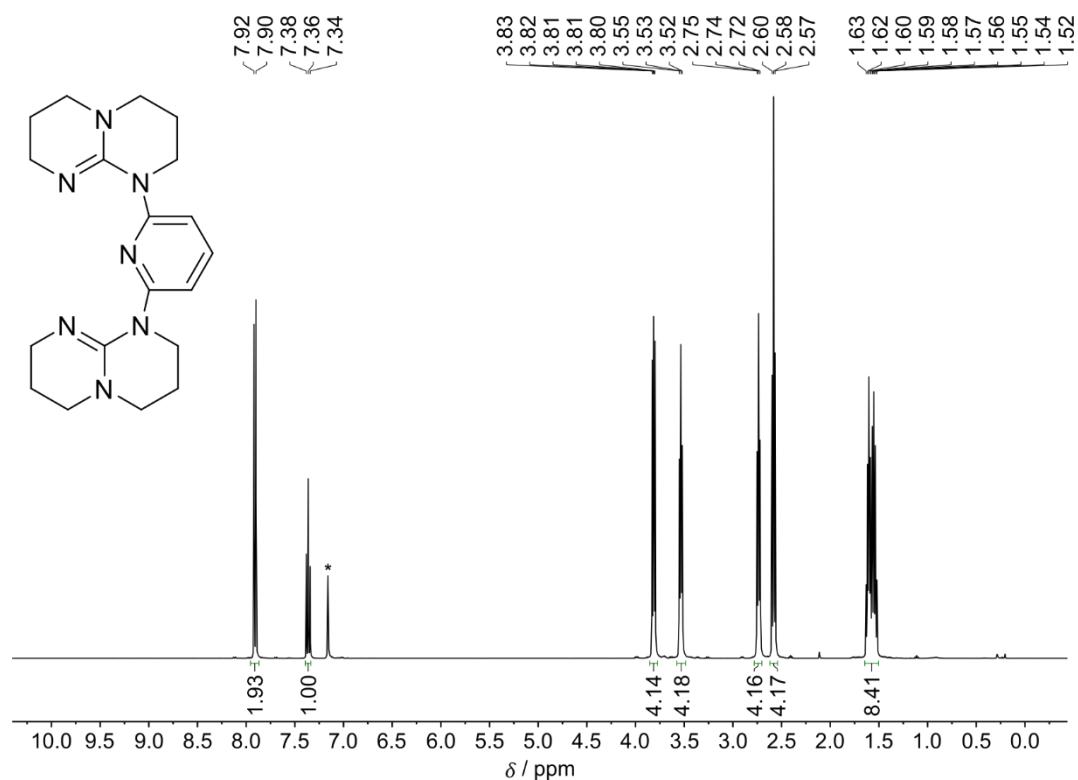


Figure S1. ^1H NMR spectrum of dried dgpy in C_6D_6 . The asterisk * denotes benzene solvent resonance. The spectrum confirms the absence of water and guanidine protonation.



Figure S2. Photograph of crystals of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3 \cdot 1.5 \text{ DMF}$.

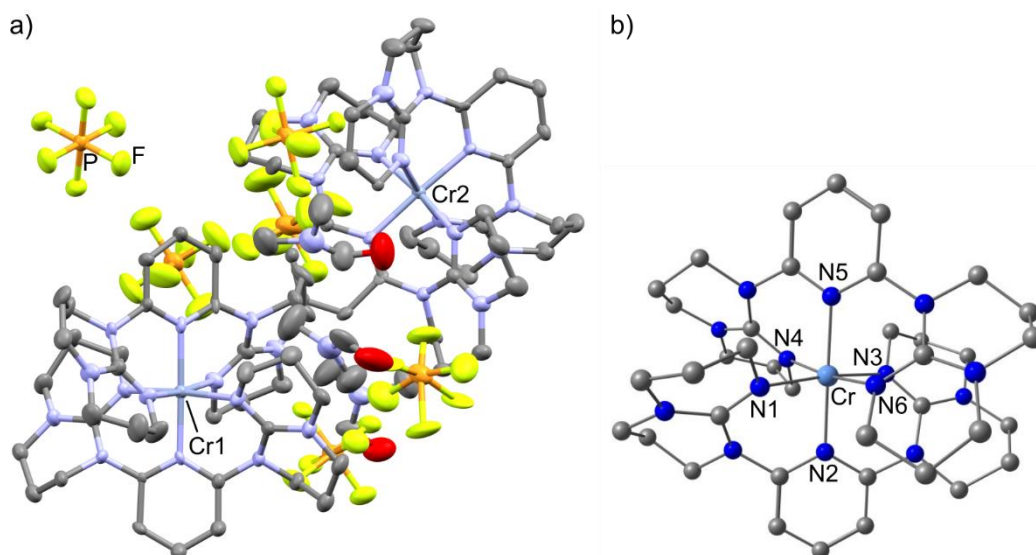


Figure S3. a) Molecular structure of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3 \cdot 1.5 \text{ DMF}$ with two independent cations in the unit cell. Thermal ellipsoids set to 50 % probability. b) DFT-calculated structure of $[\text{Cr}(\text{dgpy})_2]^{3+}$. The numbering of atoms corresponds to that used in Table S1. Hydrogen atoms were removed for clarity.

Table S1. Bond lengths [Å] and angles [deg] of $[\text{Cr}(\text{dgpy})_2]^{3+}$ obtained from DFT calculations in the optimized $^4\text{A}_2$ ground state, the optimized lowest-energy ^2MC state and the optimized lowest-energy ^4MC state ($^4\text{T}_2(1)$).

	$^4\text{A}_2$	^2MC	^4MC
Cr–N1	2.040	2.035	2.054
Cr–N2	2.045	2.039	2.177
Cr–N3	2.041	2.031	2.036
Cr–N4	2.042	2.042	2.107
Cr–N5	2.042	2.038	2.341
Cr–N6	2.038	2.019	1.976
N1–Cr–N2	87.4	87.4	86.4
N1–Cr–N3	173.8	174.0	168.4
N1–Cr–N4	92.6	92.1	90.5
N1–Cr–N5	93.4	93.4	96.7
N1–Cr–N6	86.7	86.7	89.5
N2–Cr–N3	86.4	86.8	82.4
N2–Cr–N4	93.3	92.9	98.3
N2–Cr–N5	179.3	179.1	174.0
N2–Cr–N6	94.1	94.1	104.5
N3–Cr–N4	87.0	86.7	88.0
N3–Cr–N5	92.8	92.4	94.2
N3–Cr–N6	94.6	95.2	96.4
N4–Cr–N5	86.7	86.7	76.6
N4–Cr–N6	172.6	172.8	157.2
N5–Cr–N6	86.0	86.3	80.8
Cr–N2–C _{para}	179.4	179.4	160.2
Cr–N5–C _{para}	179.5	179.2	161.5

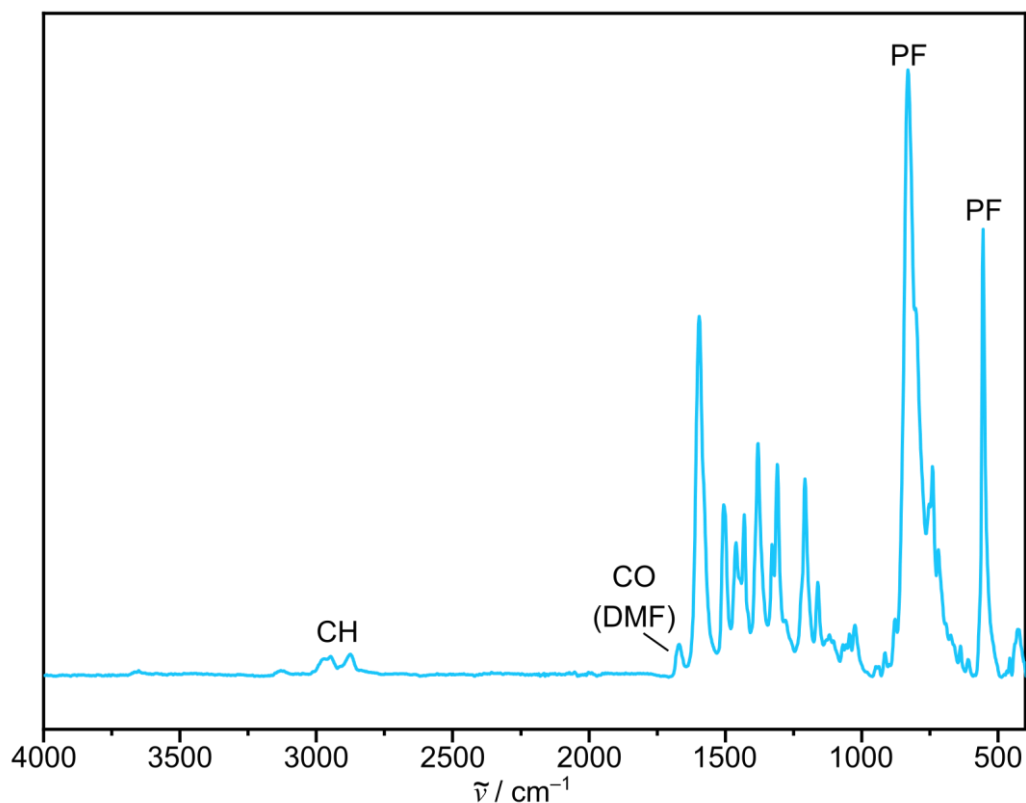


Figure S4. ATR-IR spectrum of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$. Some of the characteristic bands have been assigned.¹

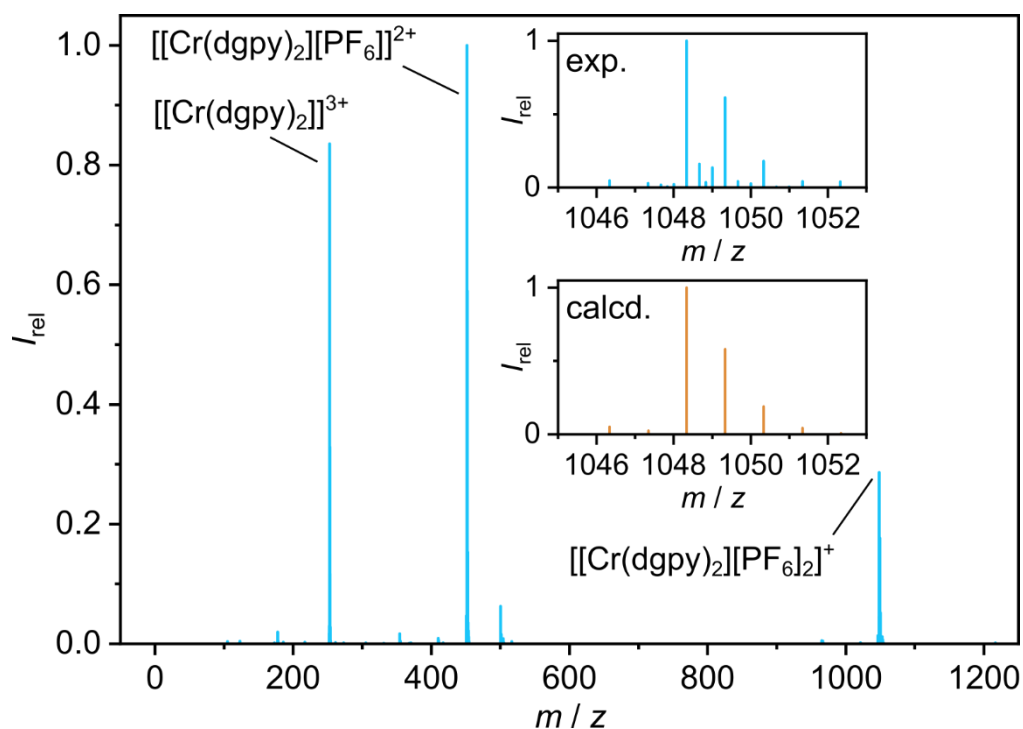


Figure S5. ESI⁺ mass spectrum of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$ in MeCN with comparison of experimental and calculated ($\text{C}_{38}\text{H}_{54}\text{N}_{14}\text{F}_{12}\text{P}_2\text{Cr}$) isotope patterns of the $[[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_2]^+$ peak. The most intense peaks have been assigned.

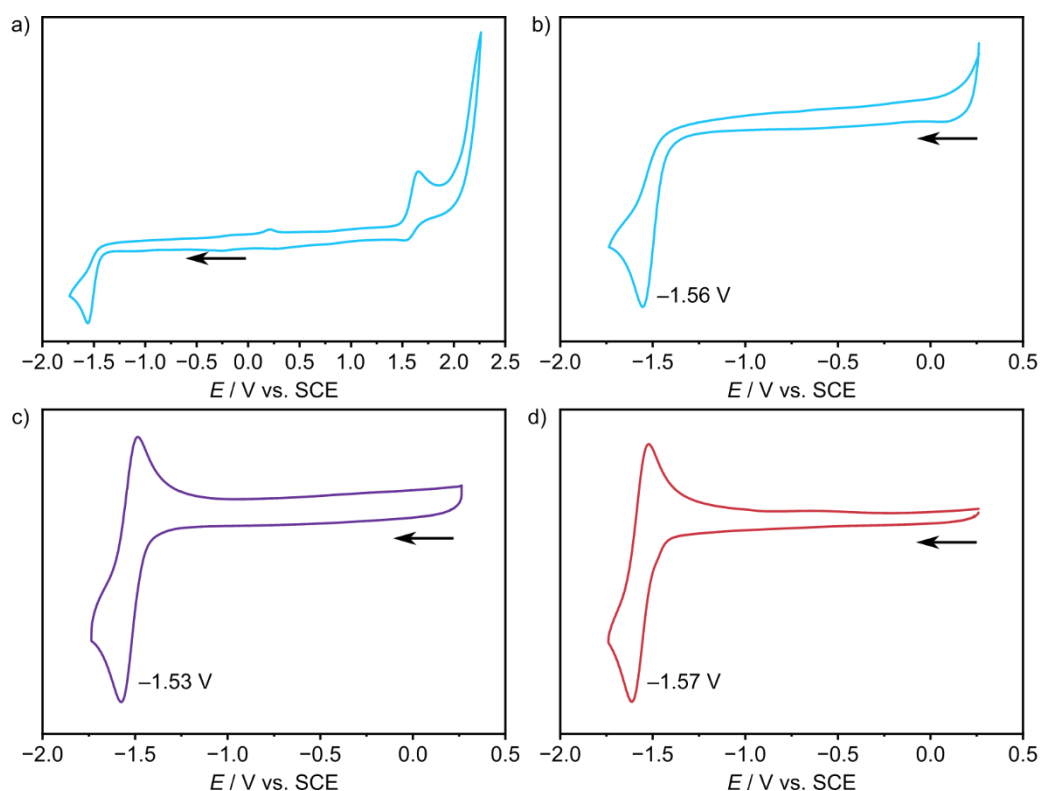


Figure S6. a/b) Cyclic voltammograms of 1 mM $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$ in a 100 mM solution of $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ in MeCN. The peak maximum has been labeled. c) Cyclic voltammogram of 1 mM $[\text{Cr}(\text{dgpy})_2][\text{OTf}]_3$ in a 100 mM solution of $[\text{n-Bu}_4\text{N}][\text{ClO}_4]$ in MeCN. $E_{1/2}$ has been labeled. d) Cyclic voltammogram of 1 mM $[\text{Cr}(\text{dgpy})_2][\text{OTf}]_3$ in a 100 mM solution of $[\text{n-Bu}_4\text{N}][\text{ClO}_4]$ in DMF. $E_{1/2}$ has been labeled.

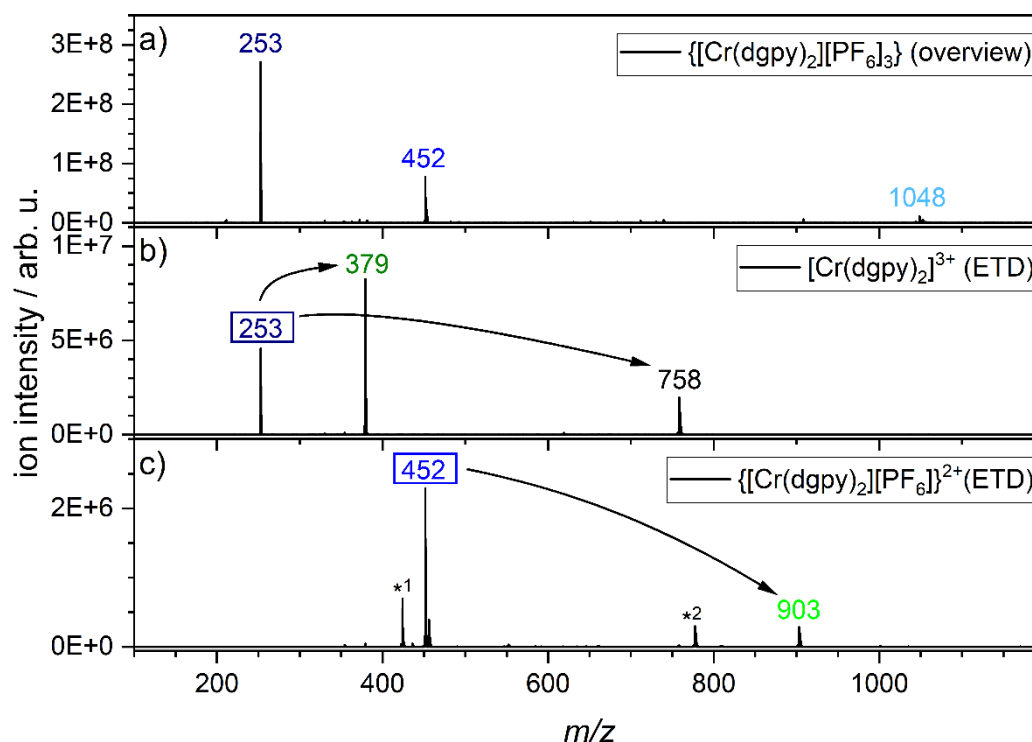


Figure S7. a) Overview mass spectrum of a solution of $[Cr(dgpy)_2][PF_6]_3$ in MeCN. Resulting spectra of the ETD processes of b) $[Cr(dgpy)_2]^{3+}$ and c) $\{[Cr(dgpy)_2][PF_6]_2\}^{2+}$. The arrows show one-electron reduction steps. The asterisks denote $\{[Cr(dgpy)]F\}^+$ (*1) and $\{[Cr(dgpy)_2]F\}^+$ (*2).

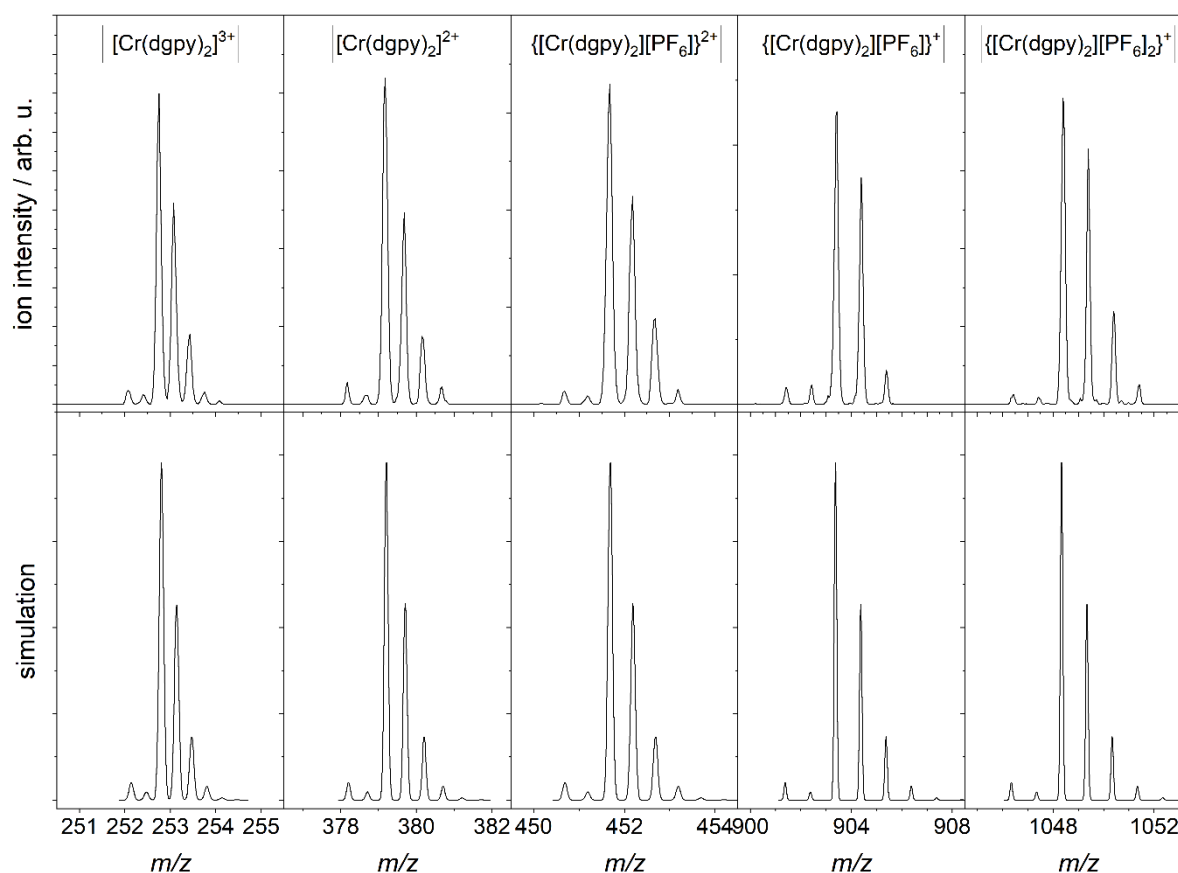


Figure S8. Mass spectra of the isolated species obtained from a solution of $[Cr(dgpy)_2][PF_6]_3$ in MeCN in combination with ETD (top) and the respective simulated isotope patterns (bottom).

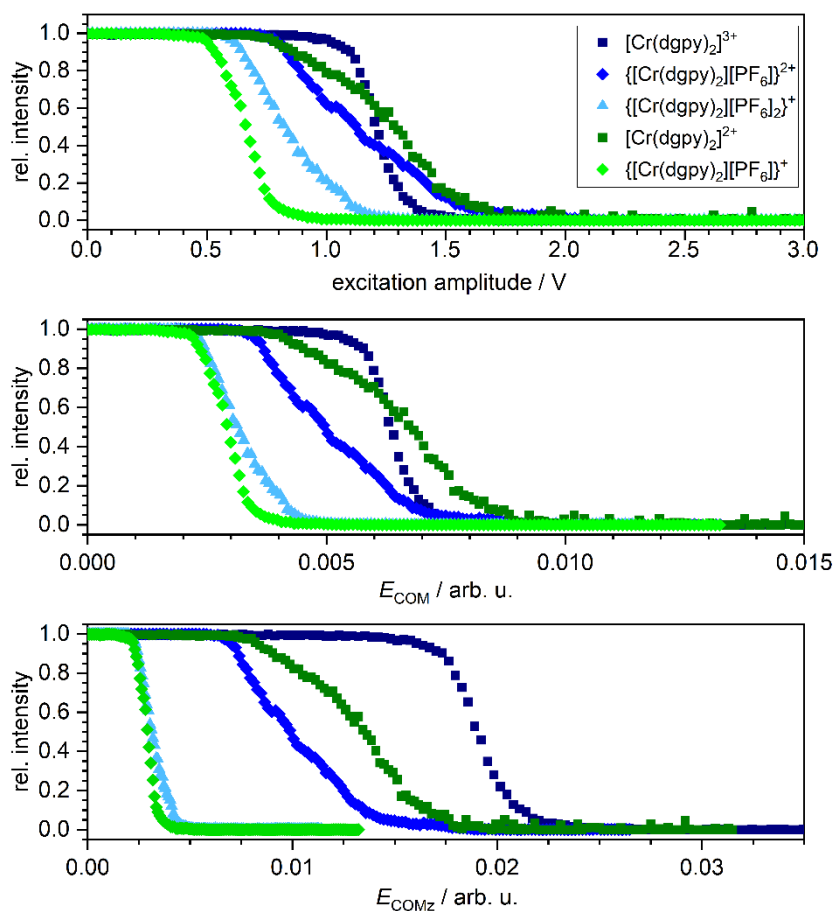


Figure S9. CID break down curves for the five investigated chromium species with different calculated energy axes. a) the RF amplitude given by the software, b) mass corrected E_{COM} values to account for the different masses of the complex and c) mass and charge corrected values E_{COMz} to account for the different charge states. Only the decrease of the parent ion is plotted against the mass and charge corrected E_{COMz} values (see method section).

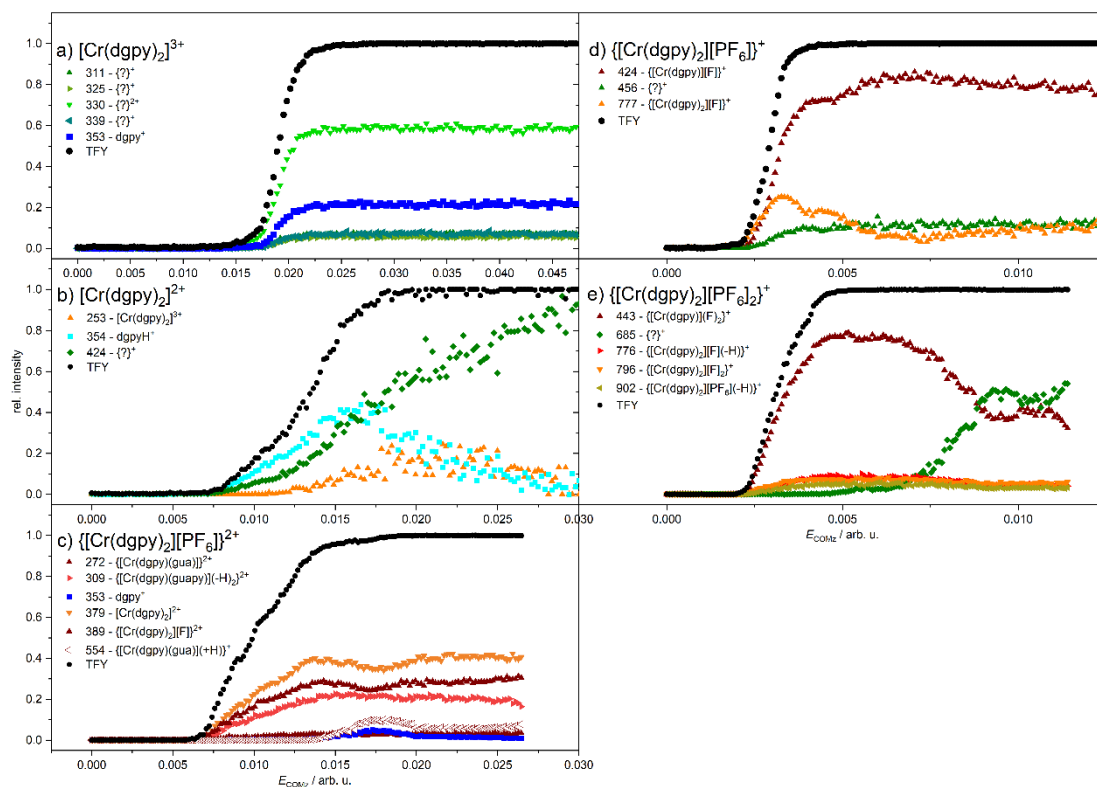


Figure S10. Comparison of the CID appearance curves against the respective E_{COMz} values of the chromium species as labeled. Fragmentation channels are only assigned when reasonable molecular structures could be found.

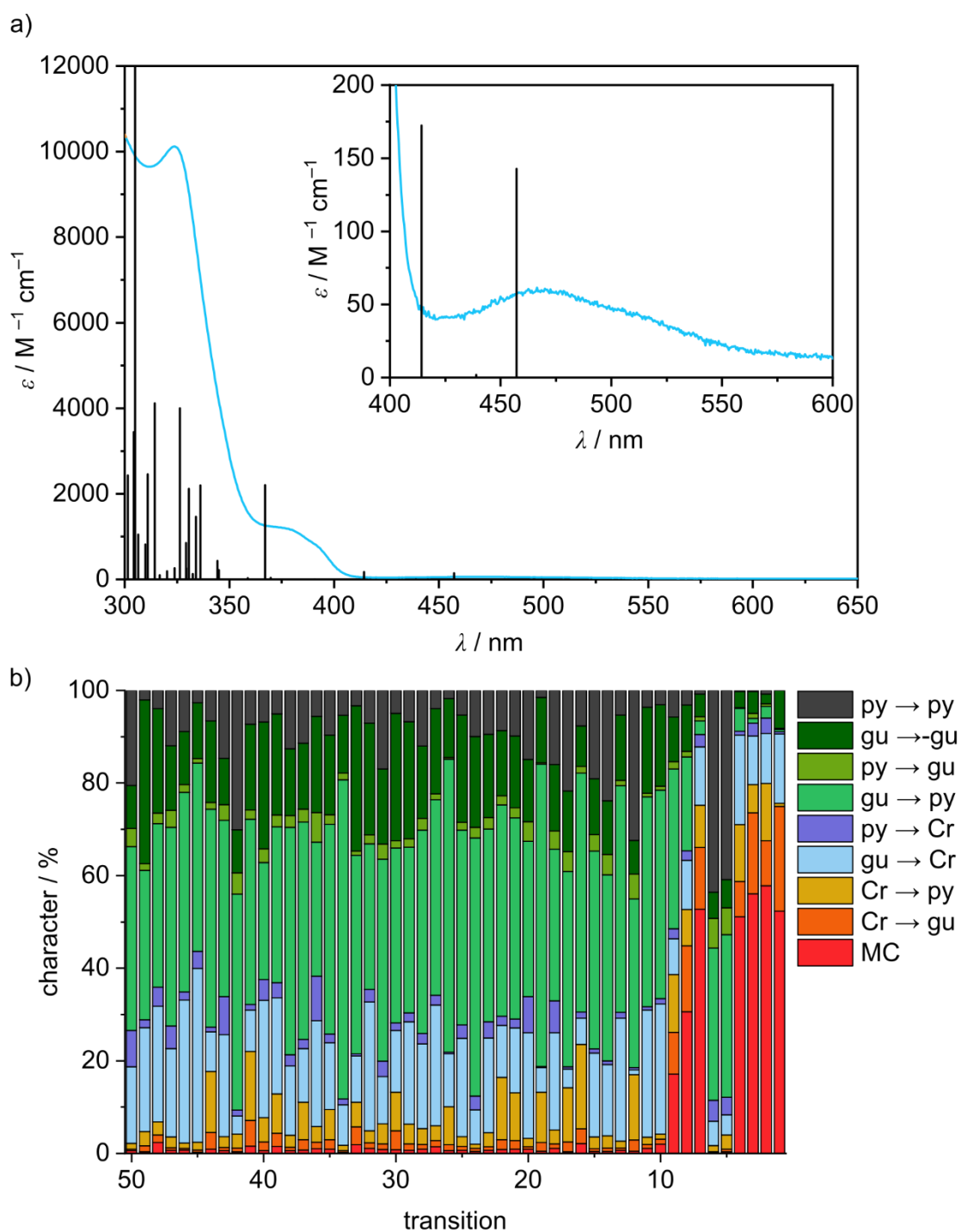
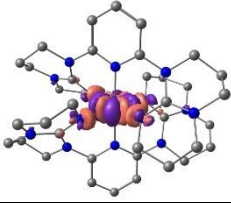
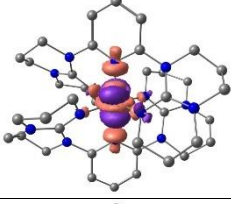
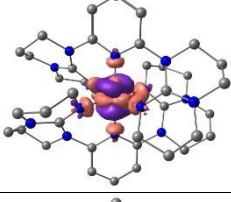
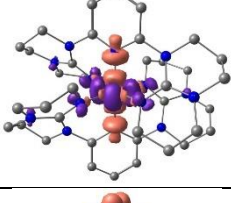
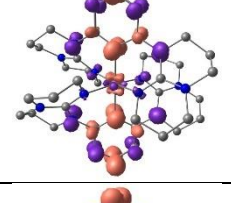
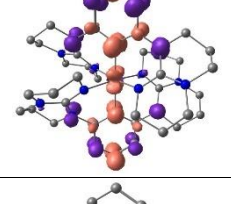
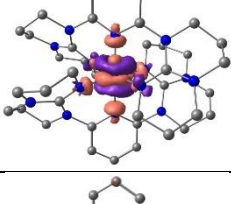
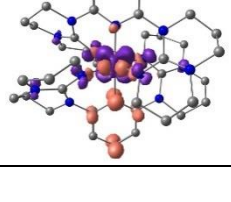
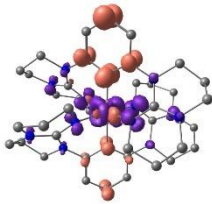
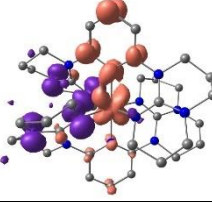
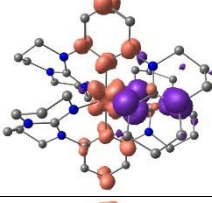
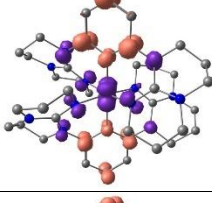
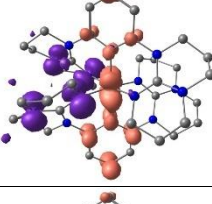
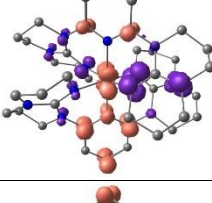
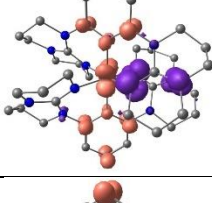
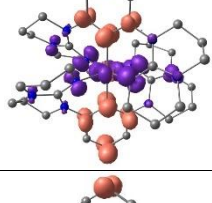
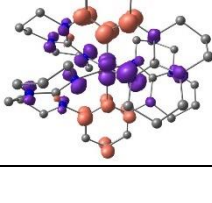
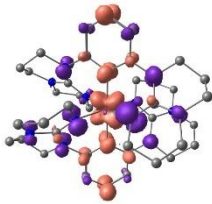
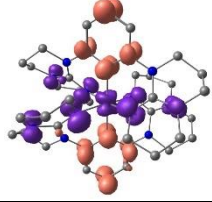
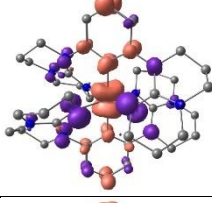
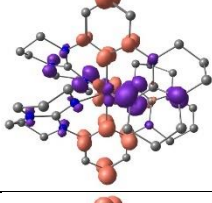
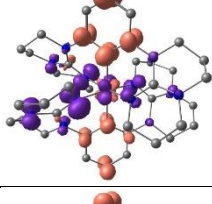
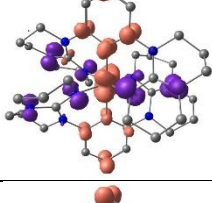
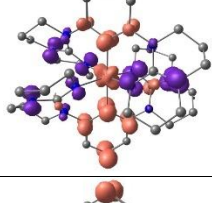
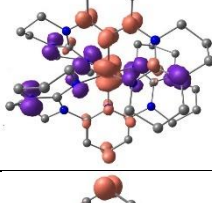
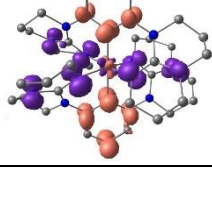


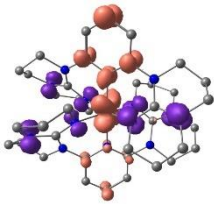
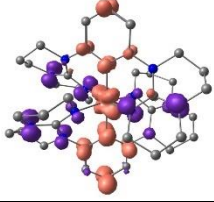
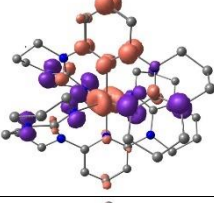
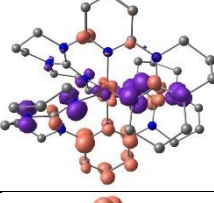
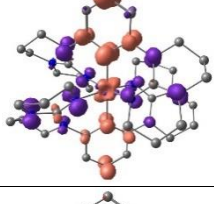
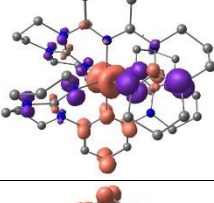
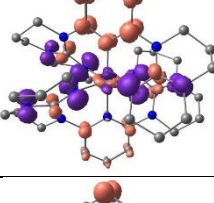
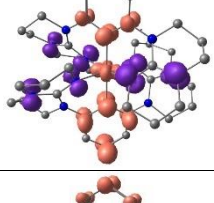
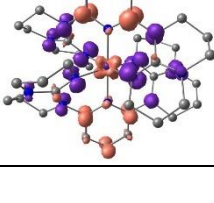
Figure S11. a) UV/vis absorption spectrum of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$ in MeCN (blue). TD-DFT calculated transitions shown as vertical lines (black). b) Charge transfer number analysis of the 50 lowest energy spin-allowed transitions using the TheoDore software package.^{1,2}

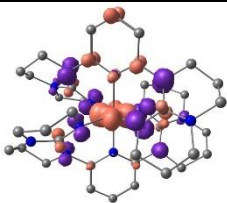
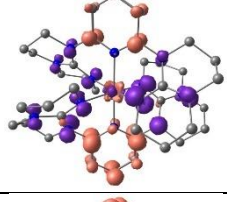
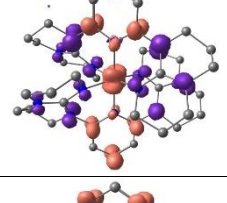
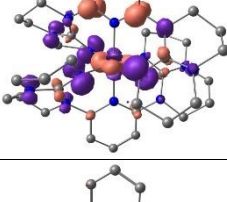
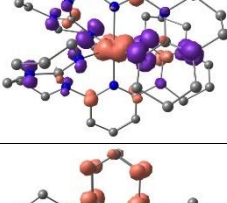
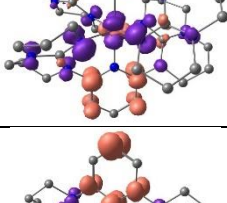
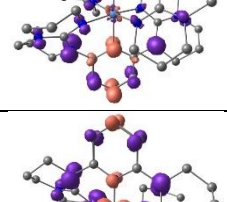
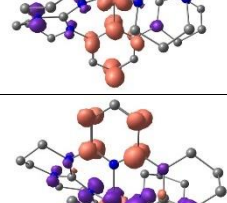
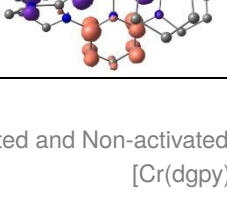
Table S2. TDDFT-calculated electronic transitions of $[\text{Cr}(\text{dgpy})_2]^{3+}$. Orange: electron density gain, purple: electron density loss; hydrogen atoms omitted for clarity (CPCM(acetonitrile) ZORA SARC/J RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP).

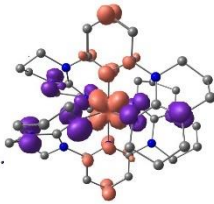
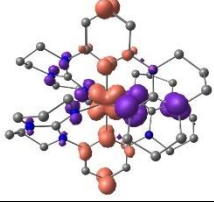
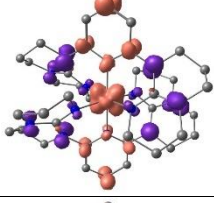
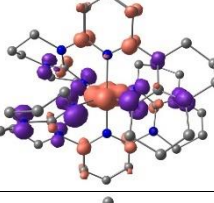
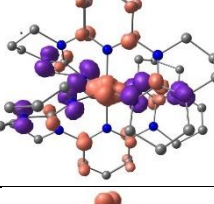
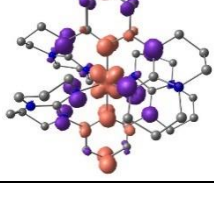
#	λ / nm	f	TDDFT difference density (isosurface value 0.003 a.u.)
1	457.2	7.14×10^{-4}	
2	439.0	9.73×10^{-6}	
3	414.3	8.62×10^{-4}	
4	390.8	7.66×10^{-6}	
5	369.7	1.53×10^{-4}	
6	367.0	0.01099	
7	358.7	1.22×10^{-4}	
8	345.0	0.00109	

9	344.3	0.00216	
10	336.1	0.01098	
11	334.0	0.00732	
12	332.5	6.21×10^{-4}	
13	330.6	0.01059	
14	329.5	0.00132	
15	329.3	0.00425	
16	326.4	0.02	
17	323.8	0.00131	

18	320.2	9.58×10^{-4}	
19	316.7	4.80×10^{-4}	
20	314.3	0.02058	
21	311.0	0.01229	
22	309.9	0.00408	
23	306.4	0.00522	
24	305.0	0.07363	
25	304.3	0.01722	
26	301.5	0.01215	

27	298.0	0.01081	
28	297.6	0.02873	
29	296.5	0.01494	
30	296.0	0.01239	
31	295.1	0.08182	
32	293.5	0.0143	
33	289.1	0.01106	
34	287.5	0.00225	
35	286.3	0.03436	

36	284.7	3.47×10^{-4}	
37	283.5	0.01567	
38	282.6	9.70×10^{-4}	
39	278.4	0.01384	
40	277.2	0.00314	
41	276.0	0.00157	
42	275.4	0.00129	
43	274.3	4.68×10^{-4}	
44	273.1	0.00244	

45	272.2	0.00158	
46	270.8	0.00349	
47	270.4	0.03952	
48	270.1	0.12339	
49	268.5	0.00305	
50	267.7	0.01959	

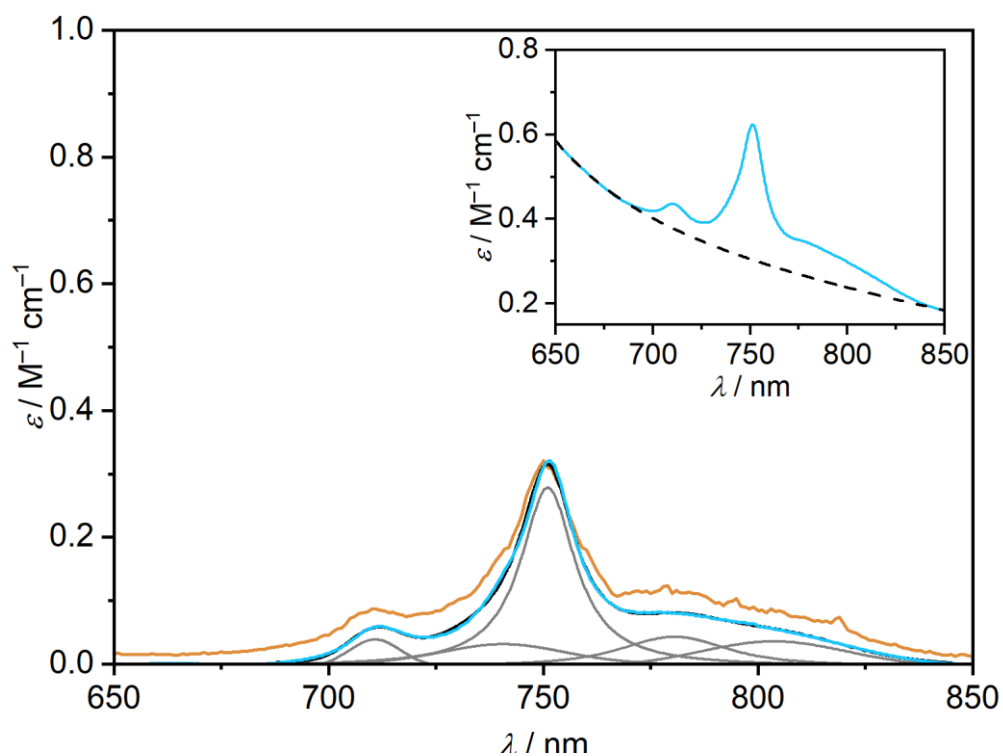


Figure S12. Baseline corrected vis/NIR absorption (blue) spectrum with sum fit (black) consisting of five Voigt functions (grey) and excitation spectrum ($\lambda_{\text{em}} = 875$ nm, orange) of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$ in MeCN. Inset: vis/NIR absorption spectrum of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$ (blue) with biexponential fit (black, dashed) describing the tail of the spin-allowed transitions as baseline correction.

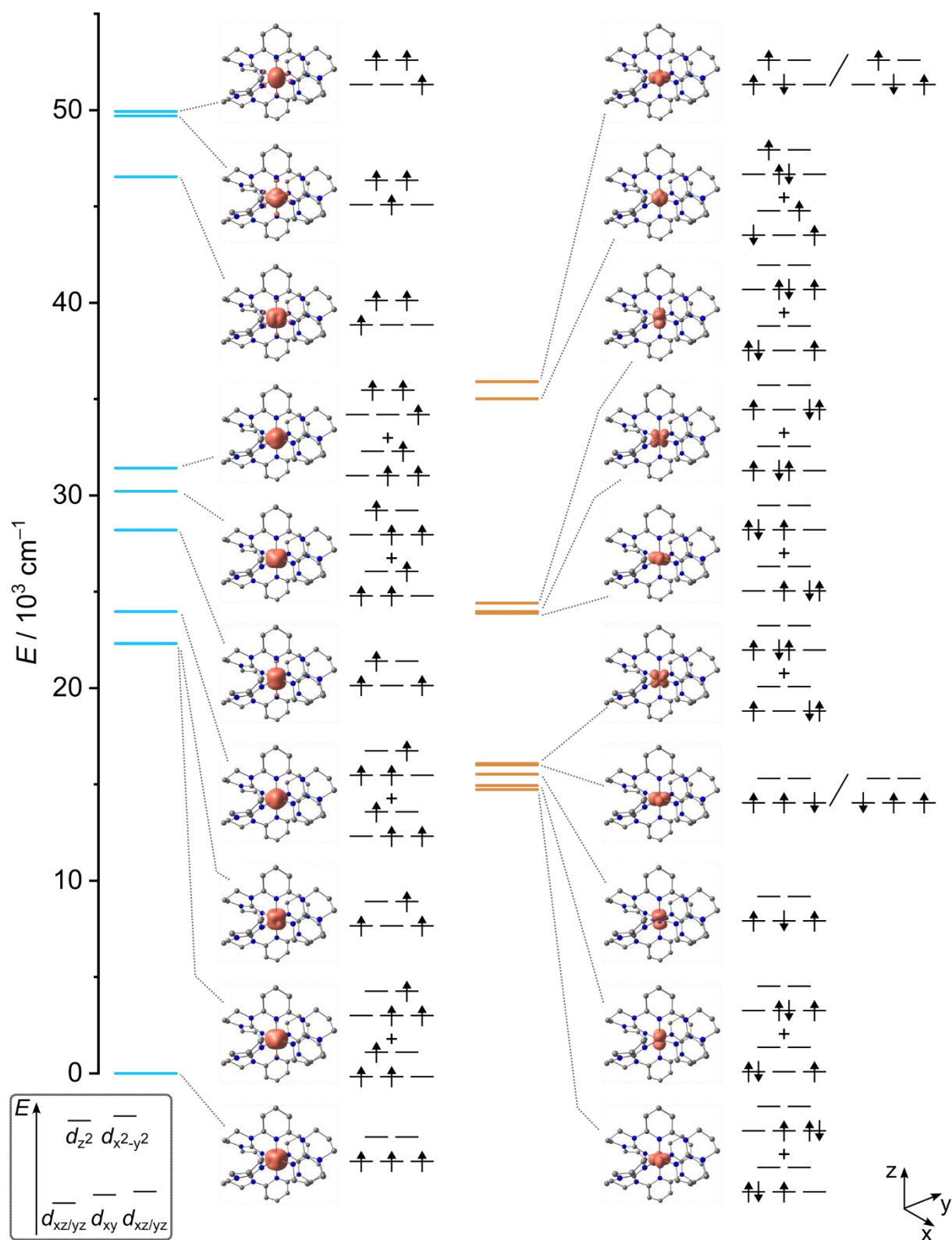


Figure S13. Energy levels of quartet (blue) and doublet (orange) states of $[\text{Cr}(\text{dgpy})_2]^{3+}$, determined by CASSCF(7,12)-SC-NEVPT2 calculations (hydrogen atoms omitted for clarity). A coordinate system referring to the displayed structures and d orbital labels with their relative energies from the NEVPT2 calculations are included. Due to significant mixing, the d_{xz} and d_{yz} orbitals are labelled as $d_{xz/yz}$. Note that the orbital energies in the main figure do not reflect the symmetry lowering in order to avoid confusion, so that these levels merely serve to indicate the electron population.

Table S3. Energies and depictions of the orbitals used in the active space of the CASSCF(7,12)-SC-NEVPT2 calculation of $[\text{Cr}(\text{dgpy})_2]^{3+}$ (contour value of 0.03 a.u.; hydrogen atoms omitted for clarity).

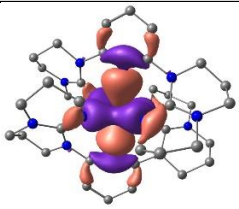
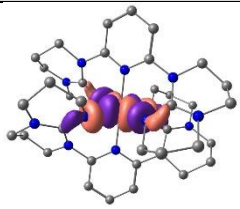
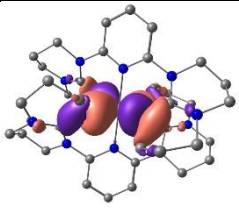
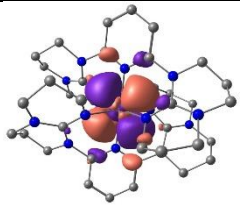
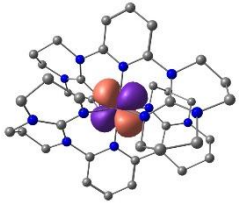
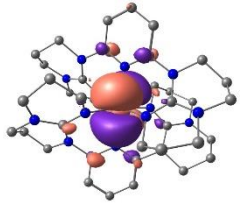
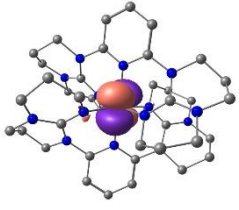
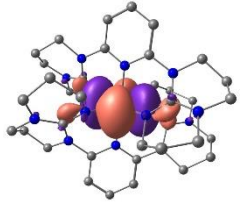
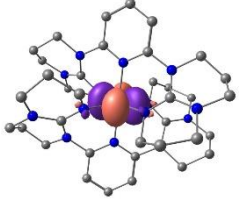
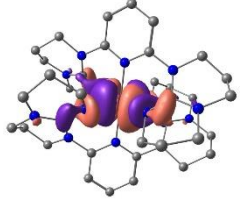
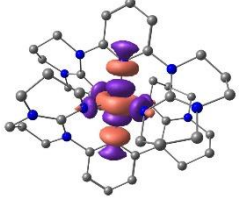
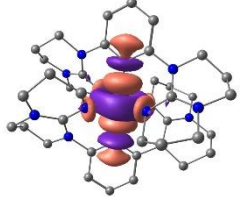
#	E / H	orbital	#	E / H	orbital
197	-0.5621		203	0.1761	
198	-0.5440		204	1.0338	
199	-0.1036		205	1.0509	
200	-0.0929		206	1.1155	
201	-0.0877		207	1.6130	
202	0.1753		208	1.6952	

Table S4. CASSCF(7,12)-NEVPT results of $[\text{Cr}(\text{dgy})_2]^{3+}$; energies in cm^{-1} relative to the $^4\text{A}_2$ ground state (bold values indicate the lowest state of each multiplicity). Blue = quartet character, orange = doublet character. Doublet energies are scaled with 0.86 to better fit to the experiment in the third column.

Term symbol	E / cm^{-1}	E / cm^{-1} (scaled with 0.86)
$^2\text{T}_1(1)$	14733.8	12671.1
$^2\text{T}_1(2)$	14934.0	12843.2
$^2\text{E}(1)$	15529.8	13355.6
$^2\text{E}(2)$	16006.2	13765.3
$^2\text{T}_1(3)$	16080.0	13828.8
$^4\text{T}_2(1)$	22302.8	
$^4\text{T}_2(2)$	22318.3	
$^2\text{T}_2(1)$	23882.6	20539.0
$^2\text{T}_2(2)$	23962.9	20608.1
$^4\text{T}_2(3)$	23972.1	
$^2\text{T}_2(3)$	24401.3	20985.1
$^4\text{T}_1(1)$	28197.9	
$^4\text{T}_1(2)$	30219.1	
$^4\text{T}_1(3)$	31411.1	
$^2\text{A}_1$	35007.9	30106.8
$^2\text{A}_2$	35904.2	30877.6
$^4\text{T}_1(1)$	46532.2	
$^4\text{T}_1(2)$	49698.2	
$^4\text{T}_1(3)$	49923.1	

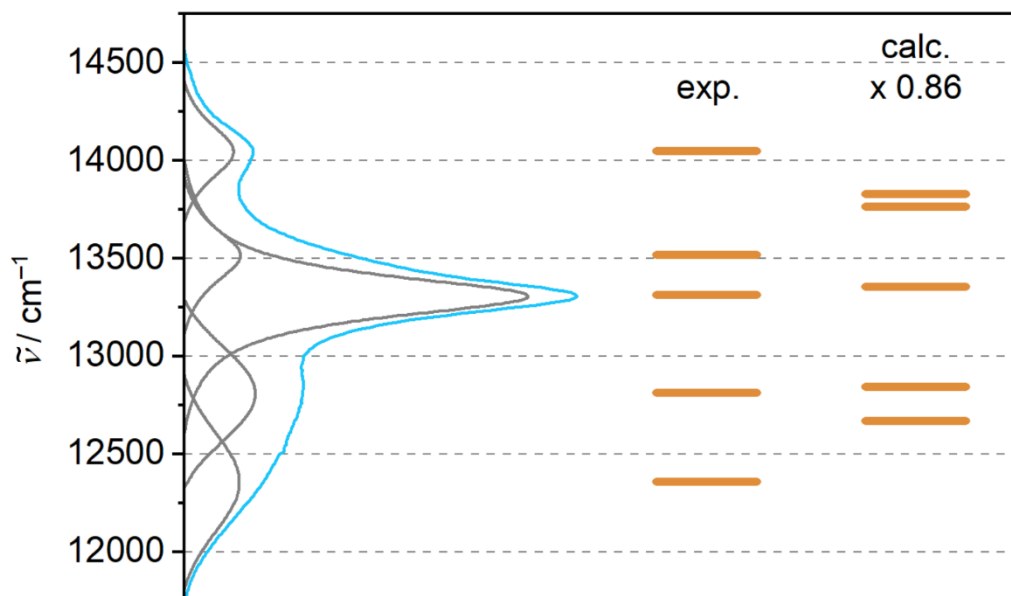


Figure S14. Comparison of experimental (from deconvoluted spin-flip absorption bands; exp.) and CASSCF(7,12)-SC/NEVPT2 calculated doublet energies (calc.). The calculated values were scaled with a factor of 0.86.

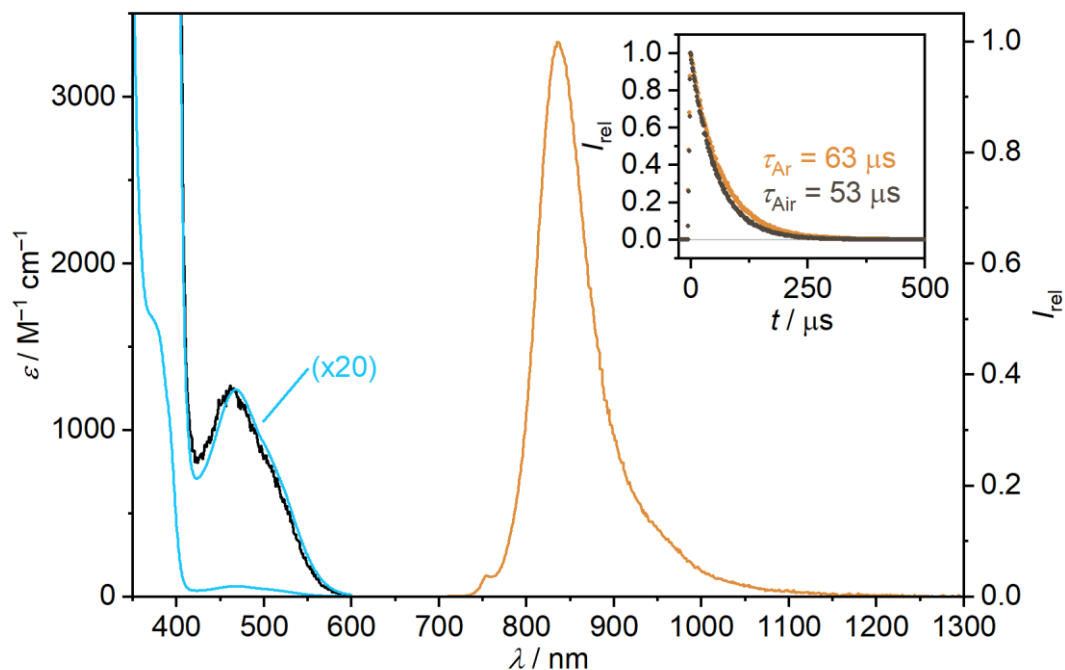


Figure S15. Absorption (blue), normalized excitation ($\lambda_{em} = 836$ nm, black) and emission ($\lambda_{exc} = 468$ nm, orange) spectra of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$ in MeCN. Inset: emission decay traces recorded at 836 nm under argon (orange) and air (brown) after $\lambda_{exc} = 451$ nm.

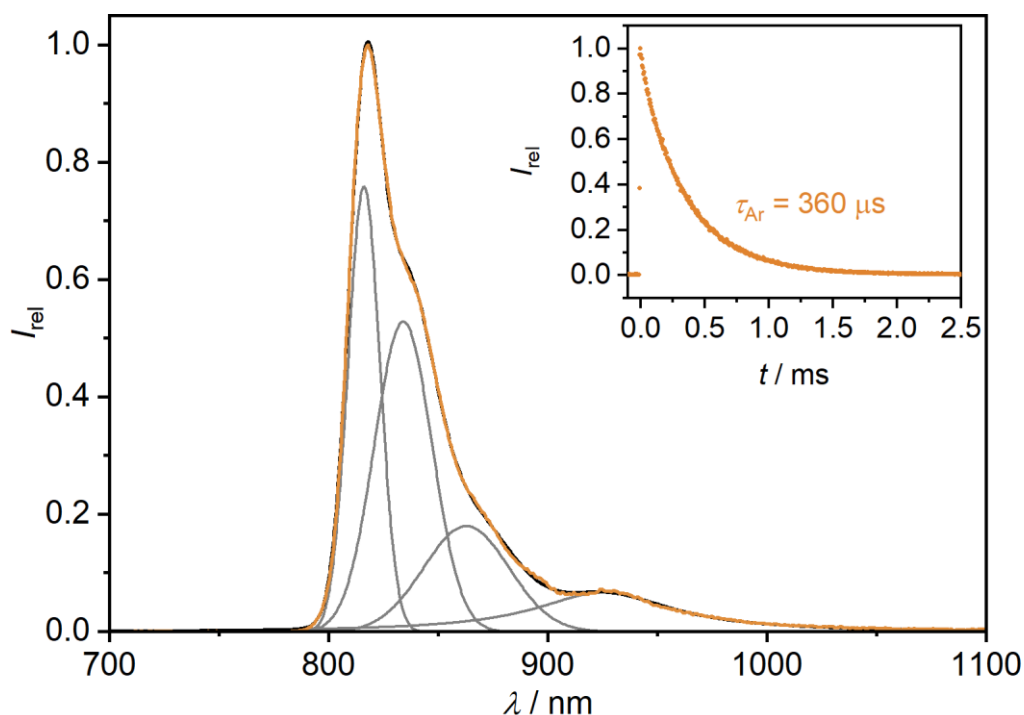


Figure S16. Normalized emission ($\lambda_{exc} = 450$ nm) spectrum of $[\text{Cr}(\text{dgpy})_2][\text{PF}_6]_3$ in n -PrCN at 77 K with sum fit (black) consisting of four Voigt functions (grey). Inset: emission decay trace recorded at 836 nm under argon.

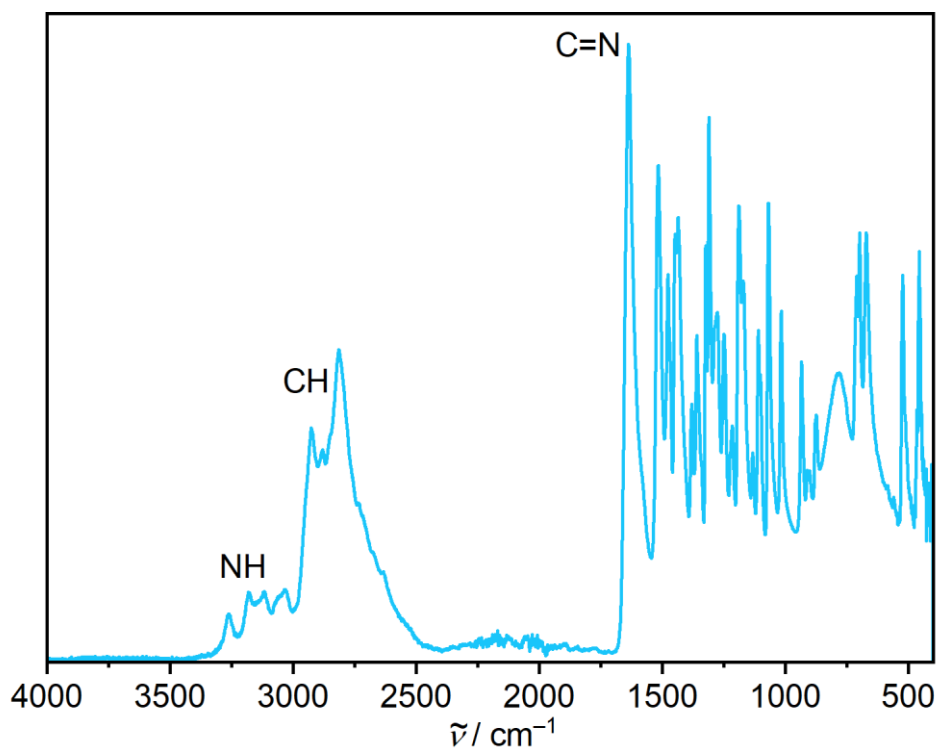


Figure S17. ATR-IR spectrum of 1,5,7-triazabicyclo[4.4.0]dec-5-ene. Some of the characteristic bands have been assigned.^{3,4}

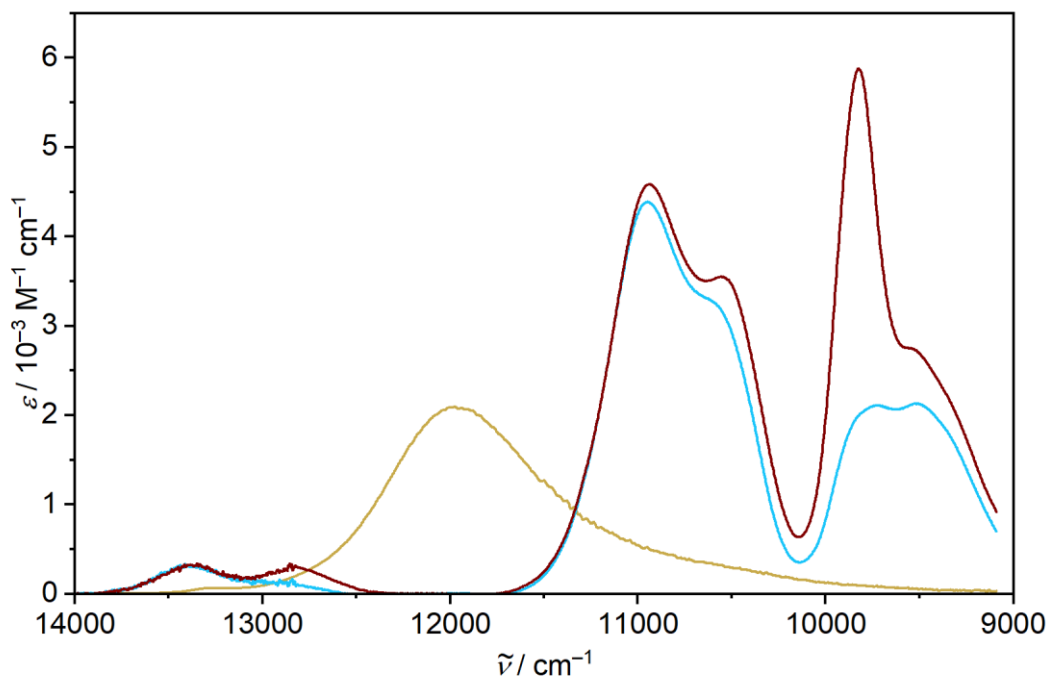


Figure S18. NIR absorption spectrum of non-deuterated (brown) and *N*-deuterated (blue) 1,5,7-triazabicyclo[4.4.0]dec-5-ene in CD₂Cl₂ overlaid with the emission spectrum (normalized to a unit area) of [Cr(dgpy)₂]³⁺ in MeCN at 293 K (orange).

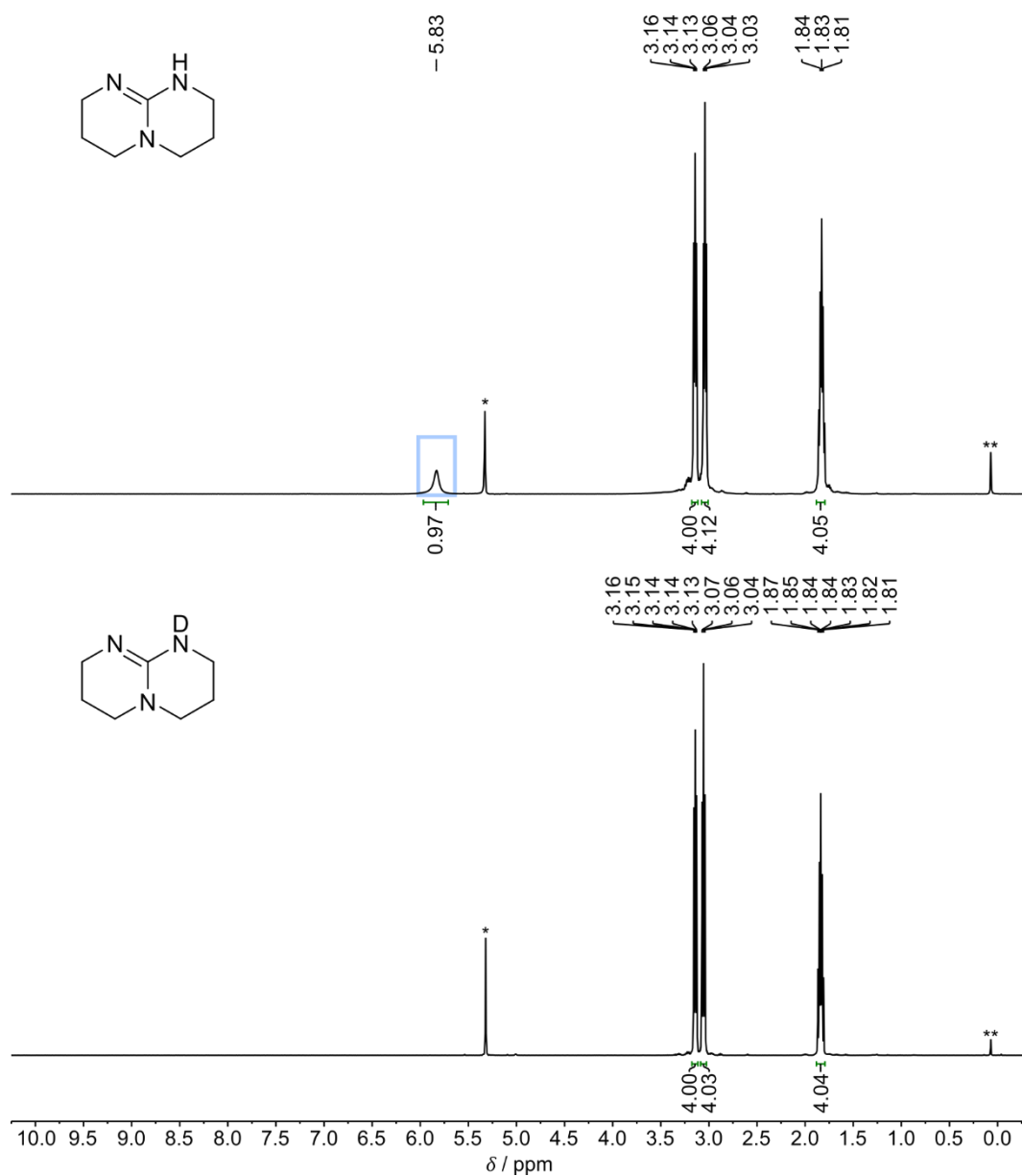


Figure S19. ^1H NMR spectra of 1,5,7-triazabicyclo[4.4.0]dec-5-ene in CD_2Cl_2 before and after *N*-deuteration. The N-H proton resonance of the non-deuterated molecule is highlighted in blue. The asterisk * denotes dichloromethane solvent resonance. The double asterisk ** denotes silicone grease resonance.

References

- (1) Mai, S.; Plasser, F.; Dorn, J.; Fumanal, M.; Daniel, C.; González, L. Quantitative wave function analysis for excited states of transition metal complexes. *Coord. Chem. Rev.* **2018**, *361*, 74–97. DOI: 10.1016/j.ccr.2018.01.019.
- (2) Plasser, F. TheoDORE: A toolbox for a detailed and automated analysis of electronic excited state computations. *J. Chem. Phys.* **2020**, *152*, 84108. DOI: 10.1063/1.5143076.
- (3) Larkin, P. J. *Infrared and Raman Spectroscopy*; Elsevier Inc., 2018. 2nd. ed., DOI: 10.1016/C2015-0-00806-1.
- (4) Brzezinski, B.; Schroeder, G.; Rybachenko, V. I.; Kozhevina, L. I.; Kovalenko, V. V. Study of 1,5,7-triazabicyclo[4,4,0]dec-5-ene protonation by vibrational spectroscopic methods. *J. Mol. Struct.* **2000**, *516*, 123–130. DOI: 10.1016/S0022-2860(99)00129-5.

Acknowledgements

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Curriculum Vitae

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Further Experiences

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