

Chromium(III) Complexes

Emission Energy Tuning and Functionalization

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Abstract

Light is the foundation of life. Inspired by photosynthesis, modern technological applications aim to convert light energy into chemical energy. The past decade gave rise to a group of highly emissive chromium(III) complexes, called molecular rubies. They are promising earth-abundant alternatives for typically employed expensive and rare-earth transition metals. Additionally, as spin-flip emitters, molecular rubies can not only replace, but also complement the characteristics of the presently used charge transfer emitters and offer unique opportunities for applications.

The research presented in this work pursues two main goals. In the first project objective, the structure of a prototypical molecular ruby is optimized for expanding its scope of application by functionalization of the ligand scaffold. The central theme of the second objective of this thesis revolves around the luminescence properties of cyclometalated chromium(III) complexes to shed light on the nephelauxetic effect that governs the excited state energy in these systems.

The first part of the thesis presents a study on the protection of chromium(III) complexes from oxygen quenching using bulky ligands. Sterically demanding ligands to shield the chromium(III) center are introduced, aiming to enhance photoluminescence quantum yields and lifetimes under aerobic conditions to expand their applicability in these areas. The study provides extensive experimental and computational data on the synthesis, characterization, and optical properties of the novel molecular rubies. The results demonstrate the efficacy of this approach in reducing oxygen sensitivity and improving luminescence properties.

Further expanding on the theme, the second section focuses on the synthesis of functionalized ligands to attach molecular rubies to materials and substrates. A synthesis was developed that allows for introduction of various functional groups in a late stage of the route. With an azide functionality to enable attachment to materials *via* click reactions, $\text{ddpd}^{\text{CH}_2\text{N}_3}$, and the corresponding homo- and heteroleptic chromium(III) complexes were aimed at. In a copper catalyzed cycloaddition, heteroleptic complex $[\text{Cr}(\text{ddpd})(\text{ddpd}^{\text{CH}_2\text{N}_3})]^{3+}$ was attached to artificial DNA, an alkyne functionalized oligonucleotide. Longing for DNA uncaging, the photodissociation mechanism of the molecular ruby $[\text{Cr}(\text{ddpd})_2]^{3+}$ was investigated by irradiation experiments as proof of concept. The spectroscopic data provided from this study offers a deeper understanding of the behavior of these complexes, which is crucial for their potential application in RNA interference as photolabile protecting groups.

In the second objective of this thesis, three cyclometalated chromium(III) complexes are investigated. The findings contribute significantly to the understanding of the nephelauxetic effect and the associated luminescence energy tuning in chromium(III) emitters. Their optical properties were investigated and interpreted using structural data from X-ray crystallography and support from extensive quantum chemical calculations. In the first study on this topic, *fac*-Cr(ppy)₃, the chromium(III) analog of the green phosphorescent Ir(ppy)₃ was examined. This study elucidates the effect of cyclometalation on the spin-flip emission. It reveals that the complex exhibits emission above 900 nm in solution at room temperature. This discovery marks a significant advancement for complexes of earth-abundant transition metals showing emission in the NIR region. The complex's structure, emission spectra, and quantum yield measurements are thoroughly explored. Building on these initial results, different ligand scaffolds were explored, namely cyclometalated amine and phosphane complexes. In contrast to the sharp red phosphorescence of the former ($\lambda_{\text{em}} = 765$ nm), the phosphane complex shows a rather broad and solvent dependent emission profile in the NIR region ($\lambda_{\text{em}} = 865$ nm). For the phosphane complex, a solvent-dependent equilibrium between the six-coordinate facial complex and a five-coordinate species was discovered using ³¹P-NMR spectroscopy. As the complexes show a strong temperature-dependent luminescence, details on non-radiative decay pathways are discussed.

An important result of the combined research is the establishment of a nephelauxetic series, which provides a comparative analysis of ligand covalency effects on the emission energies of chromium(III) complexes. Overall, the studies offer valuable insights into the ligand field parameters and their relationship with the spin-flip emission characteristics of the complexes for the future design of chromium(III)-based chromophores.

This research demonstrates that through strategic design of the ligand scaffold it is possible to achieve desirable photophysical properties such as increased NIR luminescence, longer excited state lifetimes, and higher photoluminescence quantum yields, even under challenging conditions such as the presence of oxygen. This thesis also emphasize the tunability of the spin-flip emission energy through ligand design in the first coordination sphere of the metal center. The advances made in the synthesis and characterization of these complexes, as well as the fundamental insights gained into their behavior, lay a solid foundation for future research in the field of photophysical and inorganic chemistry.

Kurzzusammenfassung

Licht ist Leben. Inspiriert von der Photosynthese zielen moderne technologische Anwendungen darauf ab Lichtenergie in chemische Energie umzuwandeln. Im letzten Jahrzehnt wurde eine Gruppe stark emittierender Chrom(III)-Komplexe, sogenannte molekulare Rubine, entwickelt. Sie gelten als vielversprechende Alternativen für üblicherweise verwendete teure und seltene Übergangsmetalle. Molekulare Rubine können als Spin-Flip-Emitter die Eigenschaften der gegenwärtig verwendeten Ladungstransfer-Emitter nicht nur ersetzen, sondern auch ergänzen und bieten einzigartige Möglichkeiten für Anwendungen.

Diese Arbeit verfolgt zwei Hauptziele. Im ersten Themenbündel wird die Struktur eines molekularen Rubins optimiert, um dessen Anwendungsbereich durch gezielte Funktionalisierung des Ligandgerüsts zu erweitern. Das zentrale Thema des zweiten Teils dieser Arbeit dreht sich um die Lumineszenzeigenschaften von zyklometallierten Chrom(III)-Komplexen, um den nephelauxetischen Effekt zu beleuchten, welcher die Energie ihrer angeregten Zustände bestimmt.

Im ersten Teil der Dissertation wird eine Studie über den Schutz von Chrom(III)-Komplexen vor Sauerstofflöschung durch sperrige Liganden vorgestellt. Mit dem Ziel, die Photolumineszenzquantenausbeute und -lebensdauer unter aeroben Bedingungen zu verbessern und so ihre Anwendbarkeit auf diese Bereiche zu erweitern, werden sterisch anspruchsvolle Liganden eingeführt, um das Chrom(III)-Zentrum abzuschirmen. Die Studie liefert umfangreiche experimentelle und rechnerische Daten zur Synthese, Charakterisierung und zu den optischen Eigenschaften der neuen molekularen Rubine. Die Ergebnisse zeigen die Wirksamkeit dieser Herangehensweise zur Verringerung der Sauerstoffempfindlichkeit und der Verbesserung der Lumineszenzeigenschaften.

Im zweiten Abschnitt wird das Thema weiter vertieft und befasst sich mit der Synthese von funktionalisierten Liganden, mit denen molekulare Rubine an Materialien und Substrate gebunden werden können. Der Ligand wird in einem mehrstufigen Verfahren synthetisiert, das die Einführung verschiedener funktioneller Gruppen zu einem späten Zeitpunkt der Syntheseroute erlaubt. Um Anbindung an Materialien über Click-Reaktionen zu ermöglichen, wurden $\text{ddpd}^{\text{CH}_2\text{N}_3}$ und die entsprechenden homo- und heteroleptischen Chrom(III)-Komplexe mit Azid-Funktionalisierung angestrebt. Über eine kupferkatalysierte Cycloaddition wurde der heteroleptische Komplex $[\text{Cr}(\text{ddpd})(\text{ddpd}^{\text{CH}_2\text{N}_3})]^{3+}$ an künstliche DNA, ein alkinfunktionalisiertes Oligonukleotid, gebunden. Mit dem Ziel der DNA Freisetzung, wurde als Nachweis des Konzepts der Photodissoziationsmechanismus des molekularen Rubins

$[\text{Cr}(\text{ddpd})_2]^{3+}$ durch Bestrahlungsexperimente untersucht. Die in dieser Studie gewonnenen spektroskopischen Daten ermöglichen ein tieferes Verständnis des Verhaltens dieser Komplexe, was für ihre potenzielle Anwendung bei der RNA-Interferenz als photolabile Schutzgruppen entscheidend ist.

Für das zweite Ziel der Arbeit, werden drei zyklometallierte Chrom(III)-Komplexe untersucht. Die Ergebnisse tragen wesentlich zum Verständnis des nephelauxetischen Effekts und der damit verbundenen Verschiebung der Lumineszenzenergie in Chrom(III)-Emitttern bei. Die optischen Eigenschaften der Komplexe wurden untersucht und mit Hilfe von Strukturdaten aus der Röntgenkristallographie und Unterstützung durch quantenchemische Berechnungen interpretiert. In einer ersten Studie zu diesem Thema wurde *fac*-Cr(ppy)₃, das Chrom(III)-Analogon des grün phosphoreszierenden Ir(ppy)₃ untersucht. In dieser Studie wird die Auswirkung der Zyklometallierung auf die Spin-Flip-Emission aufgeklärt. *fac*-Cr(ppy)₃ zeigt in Lösung bei Raumtemperatur eine Emission bei über 900 nm. Diese Entdeckung stellt einen bedeutenden Fortschritt für NIR-Emitter aus Komplexen mit häufigen Übergangsmetallen dar. Die Struktur des Komplexes und seine Emissionseigenschaften werden eingehend untersucht. Auf diesen ersten Ergebnissen aufbauend, wurden weitere Ligandgerüste untersucht, dies sind zyklometallierte Amin- und Phosphankomplexe. Im Gegensatz zur scharfen roten Phosphoreszenz des Ersteren ($\lambda_{\text{em}} = 765 \text{ nm}$) zeigt der Phosphankomplex ein breites und lösungsmittelabhängiges Emissionsprofil im NIR-Bereich ($\lambda_{\text{em}} = 865 \text{ nm}$). Für den Phosphankomplex wurde mit Hilfe der ³¹P-NMR-Spektroskopie ein lösungsmittelabhängiges Gleichgewicht zwischen dem sechsfach koordinierten Komplex und einer fünffach koordinierten Spezies entdeckt. Da die Emission der Komplexe stark temperaturabhängig ist, werden nicht-strahlenden Relaxationspfade diskutiert. Ein wichtiges Ergebnis der vereinten Forschung ist die Ermittlung einer nephelauxetischen Reihe, die eine vergleichende Analyse der Auswirkungen der Kovalenz der Metall-Ligandbindung auf die Emissionsenergien von Chrom(III)-Komplexen ermöglicht. Insgesamt bieten die Studien wertvolle Einblicke in die Ligandenfeldparameter und ihre Beziehung zu den Spin-Flip-Emissionseigenschaften der Komplexe für das zukünftige Design von Chrom(III)-basierten Chromophoren.

Diese Forschungsarbeit zeigt, dass es durch strategisches Design im Ligandengerüst möglich ist, wünschenswerte photophysikalische Eigenschaften wie erhöhte NIR-Lumineszenz, längere Lumineszenzlebenszeiten und höhere -quantenausbeuten zu erreichen, selbst unter herausfordernden Bedingungen wie der Anwesenheit von Sauerstoff. In dieser Arbeit wird auch die Verschiebung der Spin-Flip-Emissionsenergie durch Ligandendesign in der ersten Koordinationssphäre des Metallzentrums betont. Die Fortschritte bei der Synthese und Charakterisierung dieser Komplexe, sowie die grundlegenden Erkenntnisse über ihr Verhalten bilden eine solide Grundlage für die künftige Forschung und Entwicklung auf dem Gebiet der photophysikalischen und anorganischen Chemie.

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List of Abbreviations

A acceptor

acac[−] acetylacetonate

bISC back-intersystem crossing

bpi[−] 1,3-bis(pyridin-2-ylimino)isoindolin-2-ide

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

bpy 2,2'-bipyridine

CASSCF Complete Active Space Self-Consistent Field

CSU cooperative sensitization upconversion

CT charge-transfer

CuAAC copper catalyzed azide alkyne cycloaddition

cw continous wave

D donor

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

DFT density functional theory

DNA deoxyribonucleic acid

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

en ethylenediamine

EnT energy transfer

ES excited state

ESA excited state absorption

ESI electrospray ionization

ET electron transfer

ETU energy transfer upconversion
F fluorescence
FLUPS fluorescence upconversion spectroscopy
FRET Förster resonance energy transfer
GS ground state
HPLC high-performance liquid chromatography
H₂tpda 2,6-bis(2-pyridylamino)pyridine
IC internal conversion
ILCT intraligand-charge-transfer
ISC intersystem crossing
IR infrared
KHMDS potassium bis(trimethylsilyl)amide
LC ligand-centered
LED light emitting diode
LF ligand field
LFS ligand field splitting
LMCT ligand-to-metal-charge-transfer
LT lifetime
MC metal-centered
Me methyl
Mes mesityl
MLCT metal-to-ligand-charge-transfer
MS mass spectrometry
NIR near-infrared
nr non-radiative
OLED organic light emitting diode
P phosphorescence
PDT photodynamic therapy

Ph phenyl

phen 1,10-phenanthroline

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

PL photoluminescence

ppy[−] deprotonated 2-phenylpyridine

PS photosensitizer

PTGS post-transcriptional gene silencing

Q quencher

QY quantum yield

r radiative

RNA ribonucleic acid

RNAi RNA interference

mRNA messenger RNA

SF spin-flip

siRNA small interfering RNA

SOC spin-orbit coupling

sTTA sensitized triplet-triplet-annihilation

SV Stern-Volmer

TA transient absorption

TADF thermally activated delayed fluorescence

^tBu *tert*-butyl

THP tetrahydropyran

TM transition metal

TMC transition metal complex

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

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

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

VR vibrational relaxation

Introduction

1.1 Seeking for Alternatives

Sustainability is omnipresent. But what does it actually mean? While it was originally defined as "meeting the needs of the present without compromising the ability of future generations to meet their own needs",^[1] today it is usually used synonymously with environmental justice. To tackle the rapidly evolving climate change and work to preserve oceans and forests, in an urgent call for actions, the United Nations established their sustainable development goals in 2015.^[2] The model is based on three pillars: social, ecological and economic factors (Fig. 1.1). To achieve these goals, society's thinking and behavior must shift from today's linear operation "take, make, waste" towards a cradle-to-cradle attitude (closed-loop circular economy), in biological and technical cycles.^[3] The concept concentrates on long term solutions for climate and resource problems by means of:

- regenerative energy supplies
- reversibility of materials' impact on the environment
- biodegradability and recycling
- reducing and eliminating garbage

Forecasts predict steadily increasing energy demands for the next years and an increasing need for optoelectronic devices.^[4,5] The duty and mission of research and science is to explore sustainable alternatives. Inspired by photosynthesis, using the almost infinite amount of energy provided by the sun to our planet, technological applications aim to convert light energy into chemical energy. Transition metal

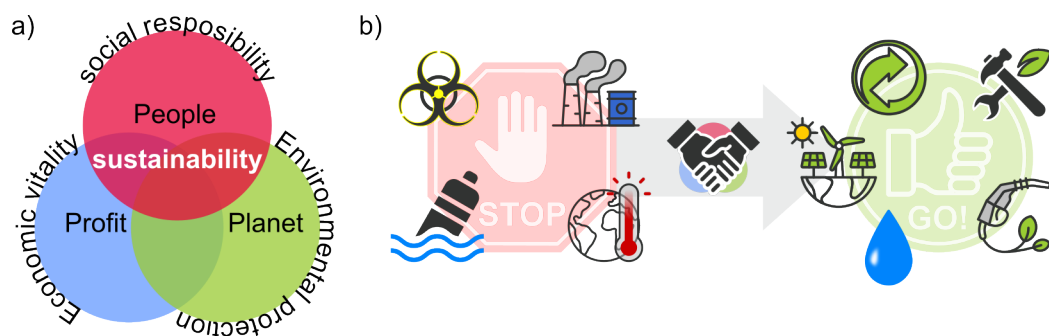


Fig. 1.1: a) Spheres of sustainability and b) goals and requirements for a circular economy.

Tab. 1.1: Abundance *A* of selected metals in earth's crust in mg/kg^[23] and their "Critical Scores" (CS).^[24]

	Fe	V	Mn	Ni	Co	Cr	Cu	W	Mo	Ru	Ir
<i>A</i>	56300	1200	950	840	250	102	60	1.25	1.2	0.001	0.001
<i>CS</i>	0.8	7.3	1.1	10.5	4.3	2.2	17.1	8.6	24.4	54.2	66.3

complexes (TMCs) have proven to be of significant value for light harvesting as well as optical devices, to name a few examples. Composed of a TM ion and a suitable ligand scaffold, TMCs exhibit extraordinary properties, true to the motto "the whole is greater than the sum of its parts". Most widely employed are rare-earth and precious metals ruthenium and iridium. Due to their favorable excited state properties they found application in numerous examples, starting from basic fundamental research over photocatalysis, dye sensitized solar cells, organic light emitting diodes (OLEDs) and to even medical therapy methods (*e.g.* photodynamic therapy, PDT).^[6–22]

While it is okay to use these metals in medical applications, such as photoinduced anticancer therapy (PACT),^[25] a severe limitation for their industrial use on a large scale is their low abundance (Tab. 1.1) and associated high costs.^[23,26,27] In 2023 the prices were at \$17500/kg for ruthenium and \$169000/kg for iridium, one of the scarcest elements on earth.^[28] Compared to that, their lighter homologues are far more abundant and cheaper by orders of magnitude (Tab. 1.1, Fe \$12/kg).^[29,30] Independent of the employed TM, mining is usually accompanied by negative impacts, including among others: high energy and water demand, air and water pollution, usage of highly toxic agents and disruption to local ecosystems. Additionally geopolitical problems arise with mining as only a few countries have access to mineral deposits.^[31] Graedel *et al.* evaluated the critically environmental implication of elements in a "Critical Score".^[24] This summary of various factors along each cradle-to-grave path, underlines the advantages of replacing precious metals by earth-abundant alternatives (Tab. 1.1).

Development of 3d TMCs has increased in the past years. Now applications include photocatalysis as well as homogeneous catalysis, bioimaging and sensing.^[32–41] Promising candidates to replace iridium complexes in OLEDs are based on copper and zinc.^[42] Some 3d TMs still need to be taught how to properly work as photoactive TMCs (*e.g.* iron).^[43] One of today's most promising candidates for many applications are chromium(III) based materials, due to their extraordinary (photo)stability.^[44–47]

This work focuses on chromium compounds, *i.e.* (pseudo)octahedral chromium(III) complexes. The first sections lay the foundation for their classification in the overall context of photoactive TMCs before diving into details about their specific properties and their promising future, based on sophisticated ligand design.

1.2 Excited State Mechanisms of TMCs

After absorption of light in the visible (VIS) or ultra violet (UV) spectral region, a molecule has many different options to release this energy. From the excited state (ES) the molecule can decay non-radiatively or with the emission of a photon (photoluminescence, PL) back to its ground state (GS). The focus of research on photoactive TMCs has undergone a paradigm shift in the last few years, after having been focussed on emitters based on 4d and 5d TMCs for decades.^[30,33–35,37,39,40,42,48] Generally, the ES of a TMC can be of metal-centered (MC), ligand-centered (LC) or charge-transfer (CT) nature. While LC transitions take place between $\pi - \pi^*$ or $n - \pi^*$ orbitals within the ligand scaffold and MC transitions only involve the d-orbitals of the TM ion, CT transitions can be seen as intramolecular redox processes between TM ion and ligand, or between two ligands L and L'.

The following sections cover the different decay mechanisms of excited TMCs and place chromium(III) complexes in the context of other photoactive TMCs while elaborating their (dis)advantages and highlighting their opportunities in applications.

1.2.1 Luminescence

Luminescence in a TMC usually occurs from a spin-forbidden ES via phosphorescence (P) in the visible (VIS, 380–750 nm) or near infrared spectrum (NIR > 750–1700 nm). In principle, spin-allowed fluorescence (F) is also possible. However, in TMCs spin-orbit coupling (SOC) often facilitates (fast) intersystem crossing (ISC), leaving the complex in a longer-lived ES of a different multiplicity than the GS.^[49] The main origins of TMC luminescence, specifically covered here, are emission pathways from metal-to-ligand-charge-transfer (MLCT) and spin-flip (SF) ESs. Ligand-to-metal-charge-transfer (LMCT) will not be discussed in detail. Prototypical examples for MLCT emitters are pseudooctahedral d^6 low-spin complexes like $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine). SF emission can be found in pseudooctahedral d^2 , d^3 , d^4 and d^8 complexes.

One common requirement for both types of emission is a strong ligand field (LF), induced by a high intrinsic ligand field splitting (LFS) of the TM ion or by σ donating and π accepting character of the ligand. The intrinsic LFS emerges from the primogenic effect. In 3d TMCs the d orbitals are rather contracted, resulting in smaller orbital overlap with ligand orbitals, compared to heavier homologues of 4d and 5d TMCs.^[50] Hence, the LFS increases down a group in the periodic table of elements. It additionally grows with increasing oxidation number of a TM ion due to the resulting stronger coulombic attraction between ligand and metal ion. According to their electronic properties of σ and π , electron donating or accepting character,

the spectrochemical series of ligands was first proposed in 1938.^[51] It is still valid, but nowadays, the situation is more complex, as most often multidentate ligands, utilizing the chelating effect, are employed.^[33]

Key properties, important for application of photoactive TMCs, in OLEDs, bimolecular catalysis, or biological applications are their ES lifetime (LT) and PL quantum yield (QY). Besides PL, described by the radiative rate constants $k_{r,i}$ ($i = F, P$), a combination of non-radiative pathways is always present in TMCs. These are described by the sum of non-radiative rate constants $k_{nr,i}$ (see section 1.2.2). Together, their reciprocal value corresponds to the ES LT τ (eq. 1.1). The PL QY describes the efficiency of luminescence, mathematically defined as the ratio of emitted photons ($\sum k_{r,i}$) to absorbed photons $\sum k_{r,i} + \sum k_{nr,i}$. Looking explicitly at the phosphorescence from an ES with multiplicity differing from the GS, the phosphorescence QY Φ_P can be calculated using eq. 1.2.

$$\tau = \frac{1}{\sum k_{r,i} + \sum k_{nr,i}} \quad (1.1)$$

$$\Phi_P = \Phi_{ISC} \cdot k_P \cdot \tau = \Phi_{ISC} \cdot \frac{k_P}{k_P + k_F + \sum k_{nr,i}} \quad (1.2)$$

Charge Transfer Emission

One of the most prominent examples of a CT emitter is $[\text{Ru}(\text{bpy})_3]^{2+}$, showing red emission ($\lambda_{\text{em}} \approx 620 \text{ nm}$) with an ES lifetime (τ) in the nanosecond range.^[52–54] With its $4d^6$ low-spin electron configuration in the ^1GS and a low-energy π^* orbital of bpy, photo-excitation will initially lead to a $^1\text{MLCT}$ state. Because of the heavy atom effect of ruthenium and a corresponding high SOC constant,^[55] rapid transfer to the triplet manifold ($^3\text{MLCT}$) via ISC ($< 100 \text{ fs}$, $\Phi_{ISC} \approx 1$),^[56,57] is the dominant pathway, almost quantitatively suppressing fluorescence from the $^1\text{MLCT}$ state.

In MLCT states, the metal center is formally oxidized and the ligand formally reduced. This change in electron density distribution leads to an apparent geometrical distortion of the ES compared to its GS. In a one electron picture, upon charge redistribution the ES potential energy well is moved along the x -axis, representing the M–L bond length (strong coupling limit, analog to Fig. 1.2b). This results in broad solvent-dependent absorption and emission bands of CT transitions. Besides the spin-forbidden nature ($^1\text{GS} \leftarrow ^3\text{MLCT}$), CT transitions are parity allowed, exhibiting high molar absorption coefficients ($\epsilon = 10^2 - 10^6 \text{ M}^{-1} \text{ cm}^{-1}$)^[53] and high radiative rates ($k_P = 10^4 - 10^6 \text{ s}^{-1}$).^[58] Besides CT transitions, interconfigurational MC transitions can occur between the t_{2g} and e_g^* orbitals (O_h notation). The ^3MC state energy depends on the LFS Δ_O , follows the triad of 3d/4d/5d TMs (primogenic effect)^[50] and may move below the $^3\text{MLCT}$ state energy. Located in the strong coupling limit, population of the ^3MC state via internal conversion (IC) leads to efficient non-radiative decay based on potential surface crossing or may

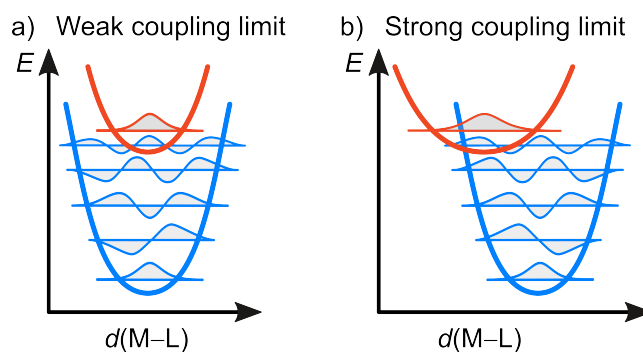


Fig. 1.2: One electron picture of a GS and ES potential energy well for a) the weak coupling limit in case of an intraconfigurational, nested ES and b) the strong coupling limit in case of an interconfigurational, distorted ES.

even result in photodissociation in extreme cases of geometrical distortions.^[59] In $[\text{Ru}(\text{bpy})_3]^{2+}$ the relaxed ^3MC state energy is in close proximity to the $^3\text{MLCT}$ state, leading to a thermal equilibrium according to the Boltzmann distribution.^[60] Theoretical calculations have shown, that multiple rate-determining states, JAHN-TELLER distorted ^3MC states, are at play, influencing temperature-dependent pathways.^[61] Still, the PL QY at room temperature is high with $\Phi_p = 9.5\%$.^[62]

In TMCs with the most abundant TM in earth's crust, iron, the non-radiative cascade *via* dark ^3MC and low lying ^5MC states is very prominent.^[43] $[\text{Fe}(\text{bpy})_3]^{2+}$, for example, readily populates the ^5MC state (2 x ISC within 50 fs), which then decays non-radiatively to the GS within 650 ps.^[63,64] In only a very little number of examples, luminescence from iron(II)^[65] or iron(III)^[66] complexes was achieved.

Another very well known $^3\text{MLCT}$ emitter from the group of 4d and 5d TMCs is *fac*- $\text{Ir}(\text{ppy})_3$ (ppy^- = deprotonated 2-phenylpyridine). Its potential, concerning photophysical properties and role as photocatalyst, was already recognized in a first investigation in 1985.^[67] Up till now, green emitting *fac*- $\text{Ir}(\text{ppy})_3$ is very popular and widely employed in photocatalysis ($\tau = 1.9\ \mu\text{s}$, $\Phi_p = 40\%$). Many derivatives of the phenylpyridine ligand have been designed to tune the emission maxima over a wide spectral range.^[68] Additionally, *fac*- $\text{Ir}(\text{ppy})_3$ and its derivatives are intensely investigated and utilized in OLEDs, biological applications such as imaging and phototherapeutics.^[6,9,68,69]

Besides famous examples of 4d and 5d TMCs, such as $[\text{Ru}(\text{bpy})_3]^{2+}$ and $\text{Ir}(\text{ppy})_3$, in recent years isolectronic 3d TMCs of chromium(0) and manganese(I) have been developed. With strong field isocyanide ligands (π acceptor), their MC states were energetically lifted above the $^3\text{MLCT}$ states.^[37] The homoleptic tris(diisocyanide) and bis(triisocyanide) complexes of chromium(0) and manganese(I) show unprecedented characteristics of $3d^6$ TMCs with Φ_p up to 1 % and ES LTs of 2–47 μs .^[70–73]

A common strategy to prevent the issues associated with (dark) MC states is using TM ions with completely empty (*e.g.* zirconium(IV) complexes) or filled d-shells (*e.g.*

copper(I) or zinc(II) complexes).^[37,40] Copper(I) complexes with their d^{10} electron-configuration, however, bring along another problem: Their tetrahedral geometry undergoes flattening distortion to square-pyramidal geometry after photo-excitation into the MLCT state, and non-radiative decay to the GS. Prominent luminescent examples are copper(I) complexes with 2,9-disubstituted 1,10-phenanthroline ligands that prevent flattening distortion and nucleophilic accessibility.^[39,74] Another educational example in which the JAHN-TELLER distortion is sterically hindered, are halido (X) bis(triphenylphosphane) copper(I) complexes $\text{CuX}(\text{PPh}_3)_2\text{L}$ with a varying *N*-donor ligand L.^[75] They show phosphorescence from the $^3\text{MLCT}$ state at low temperatures (77 K) and thermally activated delayed fluorescence (TADF) from the singlet manifold at room temperature, both with almost unity PL QY.

Spin-flip Emission

Whereas experienced as parasitic for CT emission, MC ESs can be highly emissive under certain circumstances. In intraconfigurational (SF) ESs the GS electron configuration is preserved. They are undistorted (weak coupling limit, Fig. 1.2) and emission bands from these nested states are usually very sharp.^[48,76,77] SF states can be found in (pseudo)octahedral complexes with TM ions of d^2 , d^3 , d^4 and d^8 electron configuration. In a first consideration of SF emitters, CT states are ignored as they are often higher in energy than the intraconfigurational MC states. Just like for CT emitters, sufficient population of the SF states for high phosphorescence intensities is only achieved after efficient ISC. Photophysical properties of these complexes are explained by means of ligand field theory, using TANABE-SUGANO (TS) diagrams of the corresponding electron configuration and coordination geometry (e.g. Fig. 1.6 for d^3 in O_h symmetry).^[78–80] As SF states are essentially independent from the LFS Δ_O , TM ions need to be embedded in strong LFs so that the SF states turn out to be the energetically lowest ESs. States of other multiplicity need to be lifted in energy by means of strong field ligands. This strategy was intensely exploited and successfully implemented in the past years, leading to highly emissive chromium(III) complexes. Based on the instructive examples of the prominent molecular rubies, a detailed elaboration on designing SF emitters will follow in section 1.3.2.

Being basically independent of Δ_O , the screw to tune SF state energies are the RACAH parameters *B* and *C*, describing interelectronic repulsion. Recently, focus of research on SF emission shifted towards the design of ligands to tune the emission energy.^[81] This topic being a main focus of this work, will be discussed in more detail in section 1.4.

In an octahedral geometry, SF transitions are not only spin-forbidden but also prohibited by LAPORTE's rule^[82] and their transition dipole moments are quite low (small ϵ). Based on these prerequisites, and assuming non-radiative rates are low (see section 1.2.2), radiative rates in SF emitters are small ($20 - 200 \text{ s}^{-1}$).^[77] The in

turn resulting long ES LTs up to the millisecond range make SF emitters suitable for a variety of applications, i.e. optical sensing or photocatalysis. Even if non-radiative processes are slow, they always compete and have to be kept in mind when designing new and updating established molecular systems. In section 1.2.2, undesired non-radiative processes and how to overcome them, as well as ways to exploit them, will be discussed.

As mentioned, CT states are ignored in a first consideration of SF emitters. Simple visualization of ES properties and mechanisms by use of TS diagrams is not sufficient in all cases. Having a similar electron configuration (e.g. d^3), the oxidation states are different in each TM ion. This gives rise to low-energy CT states in some cases (e.g. MLCT in vanadium(II), LMCT in manganese(IV) complexes).^[83,84] Also, TS diagrams are only strictly valid for perfect octahedral symmetry in the ground and excited states, limiting its quantitative validity in pseudooctahedral coordination geometries and with strong ES distortions.

Based on the situation of close lying CT states, SF emission from other combinations than d^3 electron configuration and +III oxidation state are more difficult to obtain. Only a handful of (room temperature) pseudooctahedral SF emitters other than chromium(III) complexes are known so far, among them a molybdenum(III) complex with the lowest spin-flip emission energy reported until today.^[77,85]

With a d^2 configuration (3GS), $[V(ddpd)_2]^{3+}$ ($ddpd = N,N'$ -dimethyl- N,N' -dipyridin-2-yl-pyridine-2,6-diamine) was the first emissive vanadium(III) complex at room temperature.^[86] Emission arises in the NIR-II region with a PL QY of $\Phi_P = 0.00018\%$. The phosphorescence shows three peaks at 982, 1088 and 1109 nm, as a result of a split 3T_1 GS. Fluorescence from a 3LMCT state occurs simultaneously, peaking at 396 nm occurs with a PL QY of $\Phi_F = 2.1\%$. With a low density of states in the singlet manifold of the ES, ISC efficiency is probably poor, facilitating the spin-allowed fluorescence.^[86]

In comparison, $mer-VCl_3(ddpd)$, with a higher ISC rate due to the heavy atom effect of chloride, only shows NIR-II SF emission ($\lambda_{em} = 1102, 1219, 1256$ nm).^[87] Increasing the phosphorescence intensity of vanadium(III) complexes remains challenging, as the small energy gap between emissive 1ES and 3GS is further reduced due to the splitting of the GS triplet manifold (energy gap law).

$[Mn(phthmeimb)]^{2+}$ ($phthmeimb = \text{phenyl}[\text{tris}(3\text{-methylimidazol-1-ylidene})]\text{borate}$) was the first emissive manganese(IV) complex, showing the emission maximum at 828 nm (solid state at 85 K).^[88,89] Very recently, NIR-II emission from a second manganese(IV) complex at room temperature was found ($\lambda_{em} = 1470$ nm), based on mixing of a 2LMCT state with the SF 2MC state.^[84]

Until now, no SF emission from pseudooctahedral complexes with low-spin d^4 configuration were reported. These systems bring along another challenge: states of three different multiplicities are relevant (3GS , 1ES and 5ES). SF emission would

only be available with very high LFSs (low-spin case, $\Delta_O > 38 B$),^[78,79] whereas population of the SF singlet states needs to follow a different route than MC excitation to avoid a non-radiative deactivation cascade via the quintet state. Additionally, *e.g.* chromium(II) complexes, are very sensitive towards oxidation and therefore challenging to handle.

In principle, SF emission from pseudooctahedral d^8 configurations, like nickel(II) complexes, is possible, but has not been achieved yet. The SF in d^8 complexes occurs in the e_g^* orbitals, with a spin-paired or unpaired microstate (1E). In the spin-paired case JAHN-TELLER distortion could lead to non-radiative decay. In many examples of nickel(II) complexes, the LFS is close to the first crossing point ($\Delta_O \approx 17 - 18 B$).^[77] In these cases the 3ES and 1ES are not sufficiently separated. Moving to even stronger ligands to access SF luminescence, such as CN^- , will however lead to preferred square planar coordination geometries as a result of extreme JAHN-TELLER distortion in the 1ES .^[90]

1.2.2 Non-radiative Decay Pathways

As already mentioned, in TMCs a variety of non-radiative decay pathways aside from luminescence and other relaxation mechanism (ISC, IC, VR = vibrational relaxation) are possible. They depend on the symmetry and distortions of the complex in the ground and ES, the LFS, the energy of the ES as well as feasible energy acceptors. Relaxation via close lying MC or CT states are covered in section 1.2.1. Some deactivation pathways are illustrated in Fig. 1.3, exemplary for chromium(III) complexes.

Depending on the intended application, relatively short (*e.g.* OLEDs) or long (*e.g.* photocatalysis) ES LTs are necessary. Therefore it is important to influence τ by addressing k_r and k_{nr} (eq. 1.1) when designing new systems.

Symmetry and Distortion

Independent of CT or SF emission, a strong LFS in combination with a high coordination symmetry is the first requirement for luminescence in pseudooctahedral complexes.^[37,48] Whereas MC states need to be lifted above the MLCT states to avoid non-radiative deactivation via surface crossing (strong coupling limit, Fig. 1.2) in CT emitters, a high LFS is necessary for intense SF emission to make bISC unfeasible (bISC = back-ISC).^[76] In a first instance, this can be achieved with strong field ligands (σ donors, π acceptors, *e.g.* pyridine), L–M–L bite angles of close to 90° to ensure large orbital overlap and a high intrinsic LFS. The latter follows the series $5d > 4d > 3d$ TM ions and grows with increasing oxidation state.^[50] With a small LFS and high bISC rates to the 4T_2 state, chromium(III)

complexes are prone to dissociation and substitution reactions (e.g. $[\text{Cr}(\text{tpy})_2]^{3+}$ or $[\text{Cr}(\text{bpy})_3]^{3+}$) (tpy = 2,2':6',2''-terpyridine).^[76,91,92] While the transitions for SF emitters are spin-forbidden (phosphorescence), LAPORTE's rule can additionally be exploited by introduction of an inversion center to reduce decay rates. For example, in centrosymmetric $[\text{Cr}(\text{CN})_6]^{3-}$ with $k_r \approx 25 \text{ s}^{-1}$, the ES LT is extremely long ($\tau = 3.45 \text{ ms}$).^[93]

If the symmetry is broken, non-radiative decay is facilitated. In MLCT emitters, geometric distortions based on charge redistribution in the ES can be reduced by delocalization effects.^[72] Distortions are generally prominent in complexes with bidentate ligands (trigonal distortions, Fig. 1.3) like bpy.^[94] To avoid surface crossing due to distortions, tridentate ligands are better suited. Besides trigonal distortion, geometry changes can be caused by twists in the flexible ligand. Rigidification of the ligand scaffold increases the ES LT from $[\text{Cr}(\text{bpy})_3]^{3+}$ to $[\text{Cr}(\text{phen})_3]^{3+}$ by a factor of almost five (phen = 1,10-phenanthroline).^[95]

Additionally, the solvent and ions in solution can affect the ES properties. The influence of solvents is less pronounced for SF emitters than for CT emitters, as CT emitters generally show solvatochromism due to the polarity of the CT ES. The effect of ions, e.g. counter ions of a charged complex or additionally added salts, can be twofold. On one hand a high ion concentration can be beneficial as they can prevent self-quenching by increasing the average distance between emitting TMCs, protect the TMCs from solvent molecules (multiphonon relaxation, see section 1.2.2) and inhibit trigonal distortion by filling pockets between ligands in a TMC.^[96–98] On the other hand, it was shown that e.g. $[\text{Cr}(\text{ddpd})_2]^{3+}$ can form contact ion pairs with some counter ions, negatively affecting the ES LT and PL QY, when the counter ion

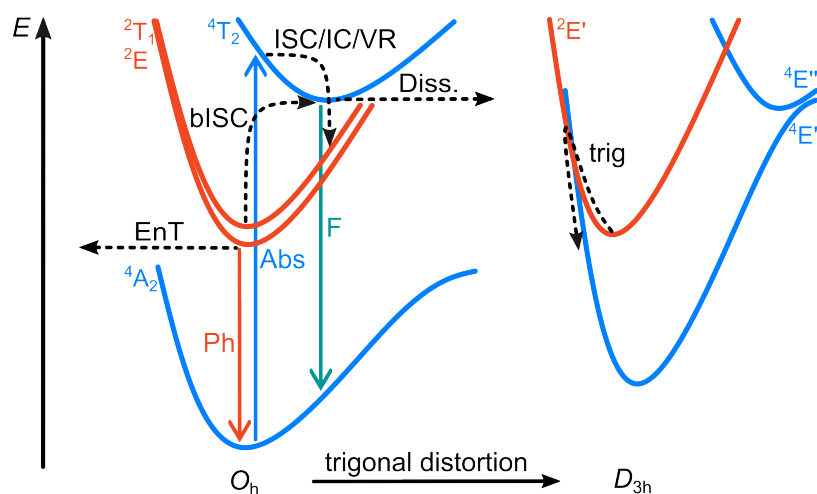


Fig. 1.3: Potential energy diagram and excited state processes of an octahedral, $\Delta_O \gg 20 B$, and trigonal prismatic chromium(III) complex. Radiative pathways solid (P: phosphorescence, F: fluorescence), non-radiative pathways dashed (EnT: energy transfer, (b)ISC: (back) intersystem crossing, IC: internal conversion, VR: vibrational relaxation, trig: surface crossing via trigonal distortion).

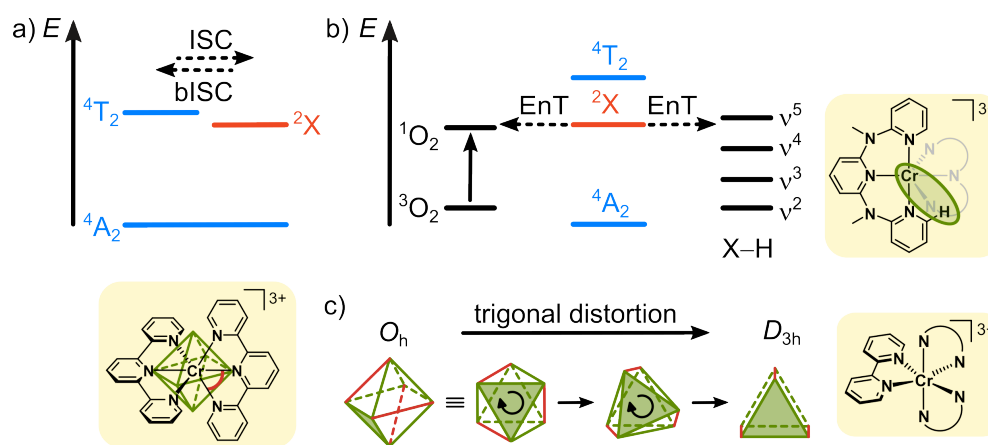


Fig. 1.4: Examples for non-radiative pathways: a) bISC due to small Δ_O , b) EnT to high energy oscillators in ligand, solvent *etc.* or accepting molecules like triplet oxygen, and c) trigonal distortion from O_h to D_{3h} symmetry leading to potential surface crossing.

introduces new C–H oscillators close to the metal center, *e.g.* $[BPh_4]^-$.^[99]

For $[Cr(H_2tpda)_2]^{3+}$, hydrogen bonding of the N–H protons to the counter ions was found (H_2tpda = 2,6-bis(2-pyridylamino)pyridine).^[100] While the emission energies are similar to the in the first coordination sphere related $[Cr(ddpd)_2]^{3+}$ complex (Tab. 1.2), the ES LTs and PL QYs are lower, demonstrating efficient quenching *via* the N–H oscillators (section 1.2.2). Additionally, the amine bridges are very acidic because of the high charge of the TM ion. Changing the pH value to basic conditions, the luminescence reversibly vanishes, probably due to non-radiative deactivation *via* low energy LMCT states or a reduced LFS, facilitating bISC. A similar effect was found for $[Cr(bpmp)_2]^{3+}$ (bpmp = 2,6-bis(2-pyridylmethyl)pyridine).^[97] The oxygen sensitivity of ES LT and PL QY in these complexes is lower compared to $[Cr(ddpd)_2]^{3+}$, probably due to a shielding effect of the close counter ions.

No clear trend was found for the influence of solvents and ions on the emission properties of chromium(III) SF emitters, yet.^[48]

Intra- and Intermolecular Quenching Mechanisms

One of the most prominent non-radiative decay pathways are intra- and intermolecular quenching mechanisms. While most of them are undesired (multi-phonon relaxation), reducing the ES LT, some intermolecular quenching mechanisms allow access to otherwise elusive ESs of substrates that are the basis for applications (energy and electron transfer, EnT and ET, respectively).^[35,41,101]

The main difference between ET and EnT are the prerequisites for their mechanism: For efficient ET the ES redox potential of the photosensitizer (PS) must be compatible with GS potential of the substrate (quencher Q). The photoinduced ET can operate in two directions, depending on the redox potentials: in a reductive or oxidative

manner. For efficient EnT the ES energy of the photosensitizer (donor, D) must be able to excite the substrate (acceptor, A). Depending on the nature of ES and GS of D and A, it can proceed *via* a FÖRSTER resonance EnT (FRET) or DEXTER exchange mechanism.^[102–104]

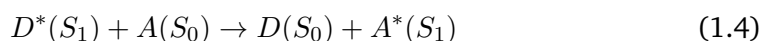
Quenching mechanisms can be investigated using STERN-VOLMER analysis.^[105] The correlation between the reduced ES LT τ or PL QY Φ and the increasing quencher concentration $[Q]$ will give the quenching constant k_q and the STERN-VOLMER constant K_{SV} (eq. 1.3).

$$\frac{\Phi_0}{\Phi} = \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] = K_{SV} [Q] \quad (1.3)$$

Depending on the preorganization of D and A or a diffusion controlled reaction, the mechanism is static or dynamic, respectively. Intramolecular quenching (static) happens on an ultrafast timescale (< 1 ns), outruling an effect on the ES LT, resulting in a reduced luminescence intensity.^[105] For a diffusion controlled mechanism, an ES LT of > 1 ns is required.^[106] To disclose if the quenching process is based on ET or EnT, the product will provide the necessary information, as the two mechanisms yield different products.^[33]

ET is described by the MARCUS theory.^[107,108] With the structural changes during the ET process (charge redistribution), the efficiency of ET is dependent on the consecutive equilibria between PS and Q and finally quantified by the cage escape yield.^[109,110]

If energy is transferred between an excited photosensitizer D^* and quencher A *via* spectral overlap J , the quenching rate k_{EnT}^F follows a distance dependence of r^{-6} according to the Förster resonance mechanism (eq. 1.5). With this requirement, FRET is possible up to distances of 10 nm between D and A.^[111] FRET is usually limited to reactions maintaining the multiplicity of D and A (eq. 1.4) because of the low molar absorption coefficients ϵ of spin-forbidden transitions and the corresponding small spectral overlap J .^[80,106]



$$k_{EnT}^F \propto J \cdot r^{-6} \quad (1.5)$$

A relevant EnT mechanism for the scope of this work is multi-phonon relaxation to energetically close lying X–H (X = C, N, O) oscillators in the ligand scaffold, solvent or other molecules (Fig. 1.4b). It is particularly dominant in the covered low energy SF emitters when their emission energy comes close to the overtone vibrational modes of X–H oscillators.^[100,112] Because X–D vibrations are of lower energy than the lighter X–H oscillations, deuteration can reduce the spectral overlap with the overtones and with this the EnT efficiency.^[113] Based on the distance dependence r^{-6} , similar to the FRET mechanism, EnT is most efficient with the

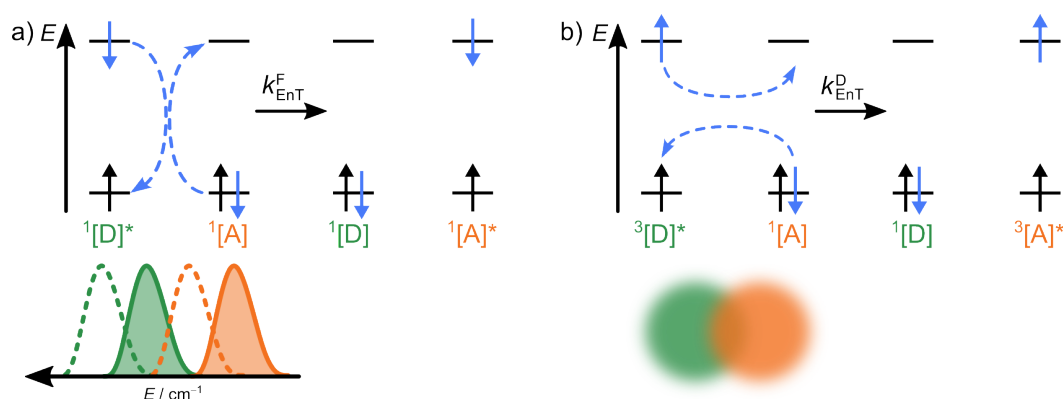
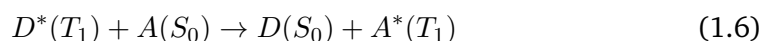


Fig. 1.5: EnT processes in a one electron description for a) FÖRSTER resonance mechanism and b) DEXTER exchange mechanism, with corresponding schematic illustration of requirement for efficient EnT.^[33]

α -C-H or bridge N-H protons in a ligand. Increased ES LTs and PL QYs were for example found in $[\text{Cr}(\text{ddpd})_2]^{3+}$, $[\text{Cr}(\text{bpmp})_2]^{3+}$, $[\text{Cr}(\text{D}_2\text{tpda})_2]^{3+}$ and *trans*- $[\text{Cr}(\text{cyclam})(\text{CN})_2]\text{ClO}_4$ after deuteration of the ligand and using deuterated solvents (cyclam = 1,4,8,11-tetraazacyclotetradecane).^[97,100,112,114]

The other very prominent EnT process is the DEXTER exchange mechanism. While FRET depends on the dipole-dipole interaction of D and A, in the DEXTER mechanism, as the name suggests, electrons between D* and A are exchanged *via* orbital overlap (double electron transfer, Fig. 1.5).^[104] To ensure orbital overlap, the distance dependence between D* and A is even more pronounced than for FRET and requires $r < 10 \text{ \AA}$. The EnT rate exponentially decreases with the distance r and is proportional to the normalized spectral overlap J' (eq. 1.7).^[101] In an exchange mechanism, spin conservation only counts for the D/A pair, while the multiplicity on D and A can change, making triplet-singlet, triplet-triplet or doublet-triplet EnT possible (eq. 1.6).



$$k_{\text{EnT}}^D \propto J' \cdot \exp\left(-\frac{2r}{L}\right) \quad (1.7)$$

DEXTER EnT is a dominant process for non-radiative deactivation in chromium(III) complexes: With a suitable ES energy, the doublet manifold (^2E , $^2\text{T}_1$) is efficiently quenched by $^3\text{O}_2$ under atmospheric conditions, forming $^1\text{O}_2$ ($E(^1\text{O}_2) = 1 \text{ eV}$). This, on one hand, leads to highly oxygen-dependent ES LTs and PL QYs of chromium(III) emitters, which is a huge drawback for their widespread applicability.^[77] On the other hand, the sensitivity of the ES towards oxygen makes this class of complexes attractive for oxygen sensing and applications exploiting $^1\text{O}_2$ formation, such as photodynamic therapy (PDT) or selective organic reactions (see section 1.3.3).^[115–119]

The degree of influence on the ES properties of chromium(III) complexes *via* EnT mechanisms was shown in a study about matrix effects on $[\text{Cr}(\text{ddpd})_2]^{3+}$.^[99] The ES LT and PL QY showed apparent changes upon counterion, solvent and other microenvironment alterations. Encapsulated in a polystyrene nanoparticle and covered with a polymer film of poly(vinyl alcohol), the luminescence of $[\text{Cr}(\text{ddpd})_2]^{3+}$ became oxygen insensitive.

Classical EnT is a downconversion process, but can be turned into an upconversion (UC) process using two photons. With mononuclear chromium(III), di- and trinuclear $[\text{Cr}]$ – $[\text{M}]$ ($\text{M} = \text{TM}$ or lanthanide) complexes and $[\text{Cr}][\text{M}]$ double salts, doublet-triplet EnT *via* TTA-UC,^[120] sequential EnT UC (ETU),^[121,122] and cooperative sensitization UC (CSU)^[123] has been realized.^[33]

1.3 Chromium(III) Complexes

1.3.1 Octahedral d^3 Complexes

The MC ES landscape of octahedral chromium(III) complexes can nicely be illustrated using the corresponding TS diagram (Fig. 1.6).^[78,79] It should be noted that in literature even for pseudo-octahedral geometries, O_h symmetry is assumed for the sake of simplicity when discussing their photophysical properties.^[33] Also, CT states, that might be energetically close, are not considered in TS diagrams. With an intrinsically stronger LFS in heavy homologues, CT states are experienced as parasitic and foster non-radiative decay. In 3d TMCs, they can be neglected in a first consideration as they usually lie higher in energy than the MC states.^[48]

With the d^3 electron configuration in an octahedral LF, $(t_{2g})^3$, the GS is of 4A_2 symmetry. The first spin-allowed transition results in the occupation of an antibonding σ orbital, $(t_{2g})^2(e_g)^1$. The 4T_2 state is JAHN-TELLER distorted. Besides decay to the GS via broad fluorescence, this state is prone to dissociation and substitution reactions (strong coupling limit, Fig. 1.2 and Fig. 1.3). Since the energy difference of the t_{2g} and e_g^* orbital sets is equivalent to the LFS Δ_O , the 4T_2 state energy rises linearly with Δ_O (eq. 1.8). Contrary, the energetically lowest doublet states of d^3 ions in octahedral geometry (2T_1 , 2E) are intraconfigurational, $(t_{2g})^3$, and nearly independent of Δ_O . Hence, their energy is mainly depending on the interelectronic interaction within the t_{2g} orbitals, represented by the RACAH parameters B and C . Their energy can be calculated using equations 1.9 and 1.10, assuming $C = 4B$.^[124] SF emission energy tuning will be elaborated in section 1.4.1.

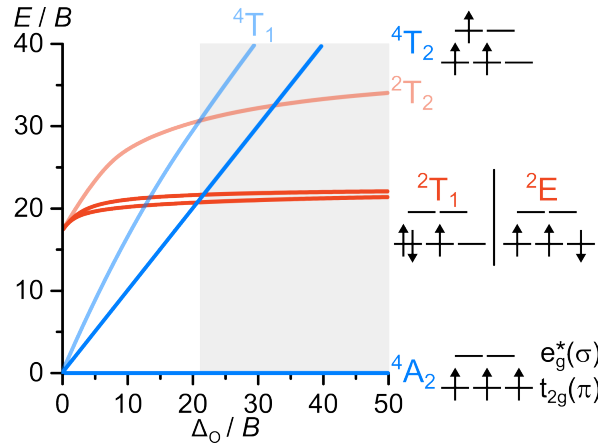


Fig. 1.6: TANABE-SUGANO diagram of an octahedral d^3 complex. Energy of MC states E and ligandfield splitting Δ_O in units of RACAH parameter B , with $C = 4B$. Grey box indicates area where Δ_O is large enough for a complex to show SF emission from doublet states.^[78,79]

$$E(4T_2) - E(4A_2) = \Delta_O \quad (1.8)$$

$$E(2T_1) - E(4A_2) \approx 9B + 3C - 24 \left(\frac{B^2}{\Delta_O} \right) \quad (1.9)$$

$$E(2E) - E(4A_2) \approx 9B + 3C - 50 \left(\frac{B^2}{\Delta_O} \right) \quad (1.10)$$

The intraconfigurational doublet states feature nearly no geometric distortion and are therefore considered nested states (weak coupling limit, Fig. 1.2). With this prerequisite, non-radiative decay via vibronic coupling is unlikely and emission from chromium(III) complexes can be remarkably sharp. Being LAPORTE- and spin-forbidden, the radiative rate back to the $4GS$ (k_P) is quite low, limiting the PL QY Φ_P . At the same time, the resulting long ES lifetime have been exploited for many types of applications.^[33,77]

For sufficient population of the SF states and the following emission to occur, a strong LF ($\Delta_O \gg 20 B$, grey box in Fig. 1.6) and efficient ISC is required. The large doublet-quartet energy gap is additionally necessary to prevent (thermally activated) back-ISC (bISC, Fig. 1.3). Based on the symmetry of the MC orbitals, a high Δ_O can be achieved with strong σ donating ligands, raising the e_g^* orbitals' energies, and/or π accepting ligands, lowering the t_{2g} orbitals' energies.

According to El-Sayed's rule, ISC in these systems should generally be quite efficient. The strong SOC is facilitated by the combination of a change in multiplicity and a change in angular orbital momentum.^[125] In fact, investigations on $Cr(acac)_3$ by transient absorption (TA) spectroscopy ($acac^-$ = acetylacetonate), supported by quantum chemical calculations, revealed insights into the ES state ordering, non-radiative processes and time constants of $\tau_{ISC} < 100$ fs and $\tau_{VC(2)} = 1.1$ ps.^[49,126,127]

Recently, fluorescence upconversion spectroscopy (FLUPS) was used to directly determine an upper value for the ISC rate in chromium(III) complexes ($\tau_{\text{ISC}} = 823$ fs), disentangled from other non-radiative processes like IC and VR.^[128]

1.3.2 Road to Molecular Rubies

Some chromium(III) complexes have been known for decades, however they were if at all only weakly luminescent. Therefore much effort was put into increasing the LFS in the past years.^[33,77]

Moving from weakly-emissive $\text{Cr}(\text{acac})_3$ with its weak field ligand acac^- and oxygen as coordinating atom, along the spectrochemical series^[51] to stronger ligands, with the purely σ donating amine in $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{en})_2]^{3+}$, phosphorescence around 670 nm was achieved (en = ethylenediamine).^[129,130] Even with one of the strongest ligands (CN^-), which puts $[\text{Cr}(\text{CN})_6]^{3-}$ to the far right of the TS diagram, the PL QY was still very low.^[129] This traces back to the extremely LAPORTE forbidden transition and corresponding low radiative decay rate k_r , ES distortions and ligand flexibility.^[93]

Employing an additional π accepting character to the nitrogen donating units utilizing polypyridine ligands like bpy in $[\text{Cr}(\text{bpy})_3]^{3+}$, the PL QY was increased by one order of magnitude (Tab. 1.2).^[95,129] Besides a large Δ_O , this strategy pursued a decrease in the system's flexibility. However, with three bidentate ligands, trigo-

Tab. 1.2: Photophysical properties of chromium(III) complexes with spin-flip band maxima λ_{em} , excited state lifetimes τ and phosphorescence quantum yields Φ (deaerated solutions at r.t., if not otherwise stated).

	Medium	$\lambda_{\text{em}} / \text{nm}$	$\tau / \mu\text{s}$	$\Phi / \%$	Ref.
Ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$)	solid state	694	4270	90	[131, 132]
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	H_2O	667	2.2	0.0055 ^a	[129]
$[\text{Cr}(\text{en})_3]^{3+}$	H_2O	670	1.85	0.0062 ^a	[129, 130]
$[\text{Cr}(\text{bpmp})_2]^{3+}$	H_2O	709	1360	12.3	[97]
$[\text{Cr}(\text{bpy})_3]^{3+}$	H_2O	727	74	0.089 ^a	[95, 129]
$[\text{Cr}(\text{dqp})_2]^{3+}$	H_2O	724/747	1270	5.2	[133]
$[\text{Cr}(\text{tpe})_2]^{3+}$	H_2O	748	2800	5.4	[96]
$[\text{Cr}(\text{tpy})_2]^{3+}$	MeCN	770	0.14	<0.001 ^b	[134, 135]
$[\text{Cr}(\text{ddpd})_2]^{3+}$	MeCN	738/775	1120	13.7	[99, 136]
$[\text{Cr}(\text{H}_2\text{tpda})_2]^{3+}$	MeCN	738/782	770	8.8	[100]
$[\text{Cr}(\text{CN})_6]^{3-}$	H_2O	820	0.14	<0.001	[129]
$\text{Cr}(\text{ppy})_3$	DCM	910	9.3	0.03	[137]
$[\text{Cr}(\text{bpi})_2]^+$	MeCN	930	10.3	0.0011	[138]
$[\text{Cr}(\text{dpc})_2]^+$	MeCN (77 K)	1067	2.0 ^c	<0.001	[139]

^a Measured in aerated solution. ^b Measured in water. ^c in $\text{H}_2\text{O}/\text{HClO}_4$.

^d Amplitude-weighted average lifetime.

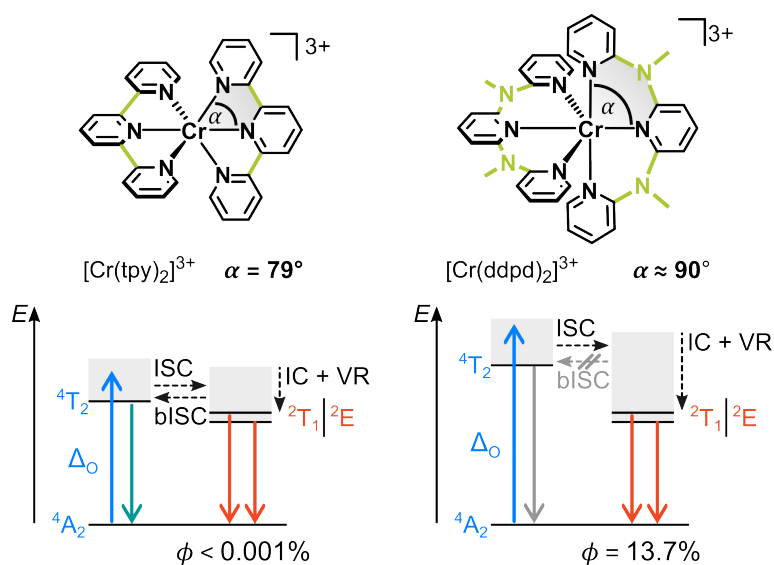


Fig. 1.7: Enhancing the PL QY by expanding the ligand bite angle, schematically shown for $[\text{Cr}(\text{tpy})_2]^{3+}$ and $[\text{Cr}(\text{ddpd})_2]^{3+}$ (blue = excitation, cyan = fluorescence, dashed = non-radiative processes, orange = phosphorescence).^[76]

nal distortion can result in potential surface crossing and enhanced non-radiative decay (Fig. 1.3).^[33,77] Rigidification of the bpy structure by preorganization of the pyridine motifs in phen lead to an increase of the PL QY, again, by one order of magnitude.^[140] Trigonal distortions and kinetic lability can be avoided with tridentate ligands like the traditional polypyridyl ligand tpy.^[92] However, the tpy ligand forms five-membered chelate rings with the chromium(III) ion, limiting the orbital overlap due to the N–Cr–N bite angle of less than 80° . This results in a decrease of Δ_{O} , facilitates bISC and finally results in a very low PL QY (Fig. 1.7). Inspired by the strongly σ donating and π accepting polypyridine motif in tridentate tpy, the ddpd ligand was designed by expanding the chelate rings to six members. This was the final breakthrough to the molecular rubies.

Molecular Rubies

Corresponding the relationship to the gemstone ruby ($\text{Cr}^{3+}:\text{Al}_2\text{O}_3$) and its application in the first developed LASER in 1960,^[141] the new class of highly luminescent chromium(III) complexes was titled "Molecular Rubies".^[76] The rise of the rubies started with the first molecular ruby $[\text{Cr}(\text{ddpd})_2]^{3+}$ in 2015, showing dual emission peaking at 738 and 775 nm in solution.^[136] The N–Cr–N bite angles were extended by inserting NMe_2 bridges between the pyridine units of tpy (Fig. 1.7). With almost 90° bite angles, the nearly perfect octahedral geometry in $[\text{Cr}(\text{ddpd})_2]^{3+}$ results in a strong LFS with $\Delta_{\text{O}} \approx 32 B$, right to the second quartet-doublet crossing point in the TS diagram (Fig. 1.6).^[76] While in the parent complex $[\text{Cr}(\text{tpy})_2]^{3+}$, Δ_{O} is small enough, and with this the quartet-doublet energy gap, for thermally activated bISC to occur, resulting in a very low PL QY of less than 0.001 %, ^[135] this pathway is

closed in $[\text{Cr}(\text{ddpd})_2]^{3+}$ ($\Phi = 13.7\%$). ISC in $[\text{Cr}(\text{ddpd})_2]^{3+}$ is very efficient, likely due to strong SOC and the high density of states around the second crossing point in the TS diagram.^[44,125] Transient absorption spectroscopy of $[\text{Cr}(\text{ddpd})_2]^{3+}$ revealed, that the doublet states are reached within 3.5 ps after photo-excitation into to $^4\text{T}_2$ state. ISC, followed by IC and VR, occurs from the still hot $^4\text{T}_2$ state.^[117] Hence, $[\text{Cr}(\text{ddpd})_2]^{3+}$ is extremely photostable and nearly no fluorescence is observable.^[44] Standing in a thermal equilibrium, the excited doublet states show a common ES LT of more than one microsecond, based on the LAPORTE- and spin-forbidden transition back to the GS (Tab. 1.2).^[99] The underlying design strategy of $[\text{Cr}(\text{ddpd})_2]^{3+}$ was adopted in the $[\text{Cr}(\text{dqp})_2]^{3+}$ complex with the more rigid dqp ligand 2,6-di(quinolin-8-yl)pyridine.^[133]

By introduction of an inversion center into the TMC, LAPORTE's rule applies even more stringent. This was accomplished with the tripodal ligand tpe, yielding $[\text{Cr}(\text{tpe})_2]^{3+}$ (tpe = 1,1,1-tris(pyrid-2-yl)ethane).^[96] In this centrosymmetric complex, CT states are moved to higher energies and are separated from the purely MC transitions. They are now extremely forbidden and therefore only very weakly observable in the absorption spectra. The extinction coefficient of the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transition in $[\text{Cr}(\text{tpe})_2]^{3+}$ amounts to $\epsilon_{431\text{ nm}} = 30\text{ M}^{-1}\text{ cm}^{-1}$. The extremely forbidden nature of the doublet quartet transition in $[\text{Cr}(\text{tpe})_2]^{3+}$ leads to low extinction coefficients and radiative rates ($k_r \approx 20\text{ s}^{-1}$) and with this to a relatively small PL QY. Non-radiative decay rates are also small, resulting in a long ES LT. They can be exploited for bimolecular quenching reactions. In contrast to the MC reduction in $[\text{Cr}(\text{ddpd})_2]^{3+}$ and in combinations with the long ES LT, reduction of $[\text{Cr}(\text{tpe})_2]^{3+}$ is ligand centered, opening up a bouquet of opportunities concerning photoredox catalysis. These are discussed in section 1.3.3.

Bridge editing, *via* replacing the NMe_2 units by CH_2 , gave the $[\text{Cr}(\text{bpmp})_2]^{3+}$ complex (bpmp = 2,6-bis(2-pyridylmethyl)).^[97] Quantum chemical calculations were employed to predict the influence of electronic and geometrical change prior to experimental investigations. The intense emission of $[\text{Cr}(\text{bpmp})_2]^{3+}$ is strongly blue-shifted ($\lambda_{\text{em}} = 709\text{ nm}$) compared to $[\text{Cr}(\text{ddpd})_2]^{3+}$, while the ES LT and PL QY are in a similar range (Tab. 1.2). Due to the high charge of the TM ion, the methylene bridges are quite acidic and the complex shows pH dependent properties. At high pH values, the deprotonated complex is non-emissive.

As discussed in section 1.2.2, deuteration of ligands and solvent can dramatically increase the PL QY and ES LT of NIR emitters. Whereas deuteration of acetonitrile does not show a positive influence, employing D_2O instead of H_2O , raises the PL QY of $[\text{Cr}(\text{ddpd})_2]^{3+}$ from 11 % to 14 % and of $[\text{Cr}(\text{tpe})_2]^{3+}$ from 5.4 % to 8.2 % (plus HClO_4 or DClO_4).^[96,112] An extraordinary PL QY of 30 % could be achieved with $[\text{D}_9]\text{-ddpd}$, deuterated at the $\alpha\text{-CH}$ and NMe_2 protons.^[112] In $[\text{Cr}(\text{bpmp})_2]^{3+}$, deuteration of the ligand is only necessary at the $\alpha\text{-CH}$ of the pyridines ($[\text{D}_2]\text{-}$

bpmp), as the methylene bridge protons are expected to self-exchange with the deuterated solvent when coordinated. With this degree of deuteration, the PL QY could be increased from 20.0 % to 24.6 % in D₂O/DClO₄.^[97] The smaller relative increase in PL QY in [Cr(bpmp)₂]³⁺ compared to [Cr(ddpd)₂]³⁺ is traced back to poorer spectral overlap to the C-H(D) oscillators due to the higher doublet state energy in [Cr(bpmp)₂]³⁺.

Details on tailoring of ES energies and corresponding phosphorescence band maxima will be discussed in section 1.4.

1.3.3 Application of Molecular Rubies

Based on their suitable GS and ES properties, *i.e.* dual emission profile, ES energy and redox potentials, the molecular rubies were tested in a variety of applications, of which a selection is presented in the following.^[77]

The oxygen sensitivity of the luminescence QY and ES lifetime naturally make [Cr(ddpd)₂]³⁺ a great oxygen detector.^[136] Whereas its sensitivity towards molecular oxygen can be exploited for sensing, it is a huge drawback for all other kinds of application under atmospheric conditions. These methods include ratiometric temperature^[119] and pressure sensing,^[142] based on the Boltzmann distribution of both doublet states and pressure-induced geometrical distortions, respectively. Analog to the ruby itself (−0.8 cm^{−1} kbar^{−1}) but twenty times stronger, the emission is red-shifted upon increasing pressure on the sample (up to −14 cm^{−1} kbar^{−1}), with a more pronounced effect on solutions than crystals. It is assumed, that the doublet state energies change due to geometrical distortions under pressure, *e.g.* N-Cr-N angles. Supported by quantum chemical calculations, reasons for the non-uniform pressure sensitivity on the doublet manifold are rather seen in the different orbital populations in the intraconfigurational ESs ($\frac{\Delta E}{\Delta p}(^2T_1) \approx 2 \times \frac{\Delta E}{\Delta p}(^2E)$).^[143] While the ²E state is a true SF state with symmetric population of the *t*_{2g} orbitals (↑, ↑, ↓), the ²T₁ states, with unsymmetric occupation of the *t*_{2g} orbitals (↑, ↑↓, □) experience a stronger π effect by the central pyridines upon turning more coplanar under increased pressure.

The high ¹O₂ QY (61 %)^[117] makes [Cr(ddpd)₂]³⁺ a promising candidate for application in PDT. The complex meets necessary prerequisites for application in biological tissue: it shows outstanding PL QYs and ES LTs, is photostable, watersoluble and non-toxic in the dark. However, first experiments showed that the cell take-up is negligibly low.^[118] A strategy to reduce the overall charge and increase the lipophilicity of the complex needs to be developed to make it membrane permeable. More recently, [Cr(ddpd)₂]³⁺ was tested for the same purpose in a study investigating DNA strand break by ¹O₂ formation (DNA = deoxyribonucleic acid).^[144] The efficiency

was determined to 1–4 %.

Furthermore, utilizing the efficient formation of $^1\text{O}_2$, $[\text{Cr}(\text{ddpd})_2]^{3+}$ was employed in as PS for selective α -CH activation of amines.^[117] Photoinduced ET from $[\text{Cr}(\text{ddpd})_2]^{3+}$ is kinetically and thermodynamically unfavored, as it forms labile $[\text{Cr}(\text{ddpd})_2]^{2+}$. $[\text{Cr}(\text{dqp})_2]^{3+}$ and the centrosymmetric $[\text{Cr}(\text{tpe})_2]^{3+}$ complex exhibit ES properties suitable for photoredox catalysis with their non-innocent ligands dqp and tpe. The chromium(III) catalysts cannot only utilize oxygen from ambient reaction conditions to recover, but are also far more photostable than the typically employed complexes with MLCT ES character. Their exceptional performance in photoredox catalysis, *e.g.* radical cation [4+2] cycloadditions, aerobic bromination of methoxyaryls or SO_2 fixation, based on their ES redox potentials, is complemented by their typically long ES lifetimes.^[96,145–147]

$[\text{Cr}(\text{bpmp})_2]^{3+}$ was successfully tested in sTTA-UC.^[120] Following excitation with green light, ^3DPA was generated by an doublet-triplet EnT process (DPA = 9,10-diphenylanthracene). The UC QY of the blue emission from ^1DPA after TTA of two ^3DPA molecules was close to the theoretical maximum, with remarkable $\Phi_{\text{UC}} = 12\%$. When employing the sterically less hindered anthracene in the same setup, the dimer was detected by NMR-spectroscopy. It is formed in a [4+4] cycloaddition, which usually utilizes UV light.

$[\text{Cr}(\text{bpmp})_2]^{3+}$ and $[\text{Cr}(\text{H}_2\text{tpda})_2]^{3+}$ are suitable for pH sensing *via* on/off switching of the luminescence upon pH changes. The ligand protons of their CH_2 and N-H bridges, respectively, are acidified due to the high charge of the complex ions and can reversibly be (de)protonated over many cycles.^[97,100]

All of these examples together demonstrate that molecular rubies (and at some point also other 3d TMCs) are complementing and in some regards even outperforming usually employed 4d and 5d TMCs.^[35,37,41,48,77]

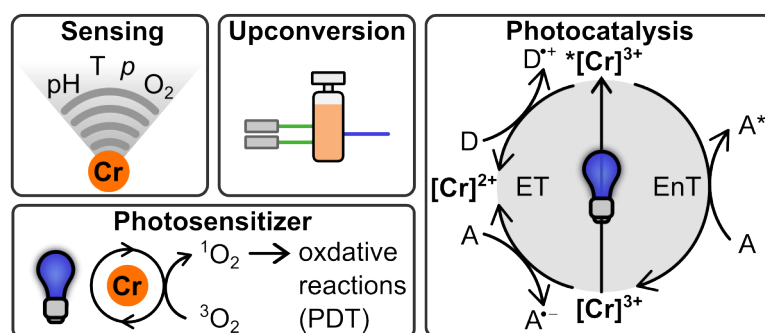


Fig. 1.8: Applications of and opportunities with molecular rubies.

1.4 Luminescence Energy Tuning

Depending on the nature of the ES, approaches to tune the luminescence energy differ.^[48]

The emission energy of $^3\text{MLCT}$ emitters depends largely on the energy difference between the ligand centered π^* and metal centered t_{2g} orbital energies. Hence, emission energies of $^3\text{MLCT}$ emitters depend largely on the metal (intrinsic LFS) and ligand. Using one ligand scaffold of a certain first coordination sphere, the electronic properties can be influenced by introduction of electron donating or accepting substituents.^[17,148] It should be kept in mind, that it is an intricate interplay between metal and ligand because changing the electronic properties of the ligand, will in turn always influence the metal centered t_{2g} orbital energies. Additionally, due to the dipolar nature of the CT ES, the solvent influences the ES energies (polarity; *i.e.* solvatochromism).^[70,149,150] As a result of many options to tackle the ES properties of a CT emitter, emission can range from the blue over the green and red spectral region, and even down to the NIR window. Many examples are known for iridium(III) complexes, of which several are even commercially available.^[17]

Looking at SF emitters, the difference to CT emitters becomes quite apparent: with no charge separation and intraconfigurational nature of the ESs, turning the obvious screws such as environment, LFS, TM ion, substituents on the ligand to influence the ES energies do not change the SF emission energy. It is noticeable from the shape of emission bands that tuning narrow SF emission over comparable wide spectral ranges is more challenging than for CT bands (Fig. 1.9). The energy of SF states depends on the interelectronic interaction (repulsion) of electrons in the degenerate d orbitals, quantified by the RACAH parameters B and C from ligand field theory.^[81,151] It becomes clear, that tuning the emission energy is not straightforward in SF emitters. The main strategy is to influence the M–L covalency and concomitantly the metal's d orbital size. It is called nephelauxetic effect, based on the greek words for cloud and expansion. The effect can be visualized with the simplified picture of an increased electron cloud upon coordination of a ligand to a TM ion (Fig. 1.10).^[81] As basis for emission energy tuning of chromium(III) complexes which are in the focus of this work, the effect will be elaborated in

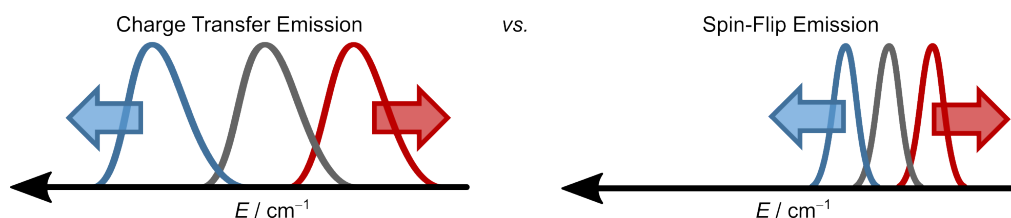


Fig. 1.9: Charge Transfer vs. Spin-Flip emission: While emission bands from CT excited states are quite broad and can be tuned over a wide spectral range, SF emission results in very sharp bands.

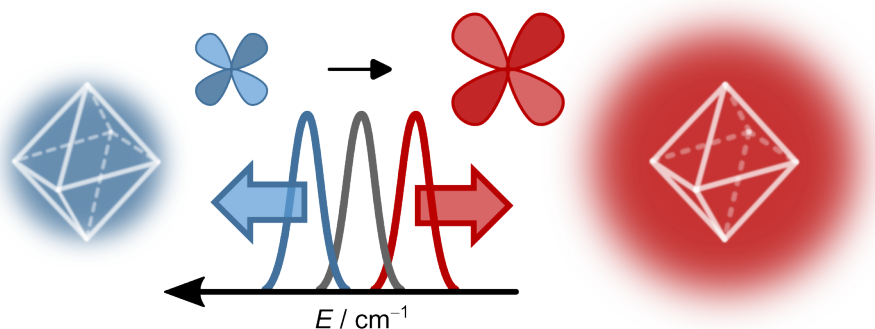


Fig. 1.10: Simplified visualization of the nephelauxetic effect: Electron cloud expansion upon formation of more covalent M–L bonds and concomitant SF energy shift.

more detail in the following section 1.4.1. SF states are usually of lower energy than CT states. Only depending on the interelectronic interaction, SF emission is mostly found in the NIR-I (750–1000 nm) to NIR-II (1000–1700 nm) spectral region. Some examples of SF emission on the verge of the low energy visible spectrum are known.^[97,129,130] Due to the low emission energies of SF emitters, the energy gap law (eq. 1.11) needs to be kept in mind when looking for low energy emission bands and explanations for short ES LTs or low PL QYs.^[152,153] The smaller the energy gap ΔE between an emissive ES and the GS to be recovered, the higher the non-radiative decay rate k_{nr} (γ = molecular parameter, ω = dominant vibrational frequency in the molecule).

$$k_{\text{nr}} \propto \exp\left(-\frac{\gamma \Delta E}{\hbar \omega}\right) \quad (1.11)$$

1.4.1 Nephelauxetic Effect

Whereas the efforts to enhance the PL QY in chromium(III) emitters were highly successful over the past years, yielding the molecular rubies, tuning the luminescence energy in the d^3 SF emitters is not so straightforward. Most of the reported highly emissive chromium(III) complexes emit between 670 nm and 780 nm (Fig. 1.11, Tab. 1.2). This is because the first coordination sphere of six pyridines, necessary for a sufficient LFS, remains rather similar in most examples. Only a few studies about specific luminescence energy tuning in chromium(III) complexes are known.^[138,139] In these examples, the nephelauxetic effect was tackled by alterations in the first coordination sphere of the ligand scaffold. Two out of the usually employed six pyridines were replaced by π donating amido moieties. In complexes with other TM ions, the nephelauxetic effect is exploited to lift the dark MC states above CT states in favor of stronger $^3\text{MLCT}$ emission (e.g. 3 d^6 complexes of iron(II), cobalt(III), chromium(0), manganese(I)).^[34,43]

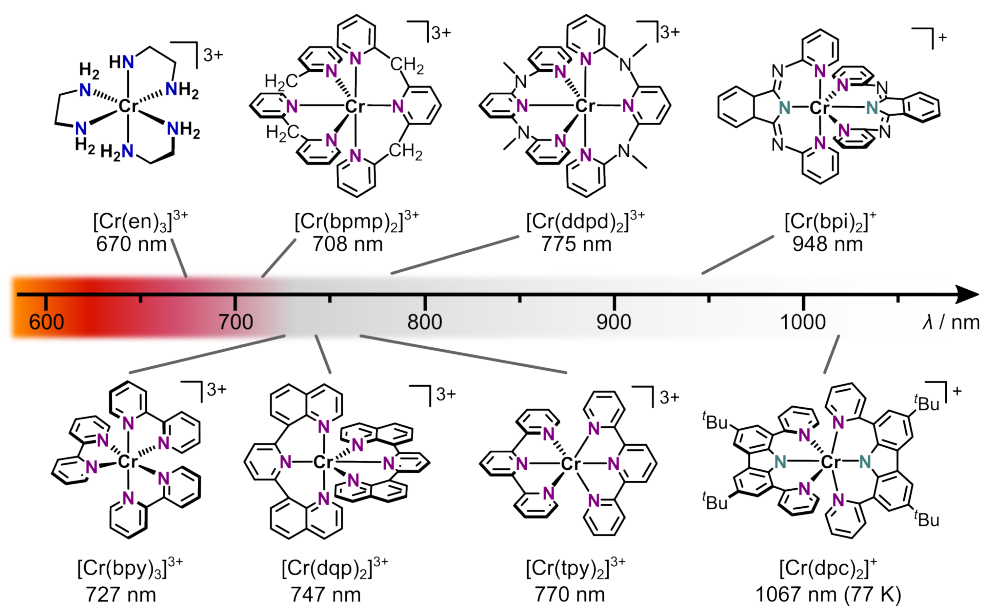


Fig. 1.11: Luminescent chromium(III) complexes arranged in order of their emission energy. Donor atoms of ligands colored according to their electronic character (blue: σ donor; purple: σ donor, π acceptor; cyan: σ donor, π donor).

Starting from the free chromium ion, the d electrons are centered closely around the metal center and the RACAH parameter B is at its highest value of $B_0(\text{Cr}^{3+}) = 918 \text{ cm}^{-1}$. It reduces upon coordination of a ligand and with increasing bond covalency. In TMCs the binding situation is often referred to as purely ionic ("coordination"). The nephelauxetic effect, based on increased M–L bond covalency, gives evidence for more than just an electrostatic nature of the M–L interactions.^[154,155] With this, the interelectronic repulsion between the d electrons reduces as the d orbitals can expand over metal orbitals onto the ligand centered orbitals. Due to the cloud expanding effect, the SF state energy reduces and corresponding emission from these states is red-shifted. Additionally, d orbitals are larger (less contracted) when the effective charge of the metal ion is lower (e.g. SF emission from molybdenum(III) complexes appears below 1000 nm).^[77]

The theoretical maximum for SF emission, derived from LF theory assuming $B = 4C$ in equations 1.9 and 1.9, for a chromium(III) complex would be 559 nm. Blue-shifted emission from SF emitters is however rather difficult to achieve. Moving from σ donating and π accepting pyridines to ligands with a smaller influence on the occupied t_{2g} orbitals (pure σ effect), such as $[\text{Cr}(\text{NH}_3)_6]^{3+}$, the LFS dramatically decreases. Consequently, in the group of complexes with only σ donating character, ES LTs and PL QYs are low because BISC is facilitated.^[77] $[\text{Cr}(\text{bpmp})_2]^{3+}$ is the molecular ruby with the highest emission energy so far. Being structurally closely related to $[\text{Cr}(\text{ddpd})_2]^{3+}$ and $[\text{Cr}(\text{H}_2\text{tpda})_2]^{3+}$, the reason for the blue shift of around 1200 cm^{-1} could not be fully explained yet, but was correctly predicted by quantum chemical calculations.^[97] Approaching blue-shifted emission via implementation of a higher oxidation state (e.g. manganese(IV) as d^3 TM ion) brings along chal-

lenges with close lying, dark LMCT states and higher covalency due to shorter M–L distances.^[37,88]

Besides the well known spectrochemical series (section 1.2.1), literature provides a nephelauxetic series of ligands. It is based on monodentate ligands and goes along with their increasing tendency to form covalent bonds and reversely with the electronegativity of the atom, with F^- on the one and I^- on the other end.^[156] This data has to be taken with care as the ligand character can drastically change when employed in a multidentate scaffold, which are typically used in photoactive TMCs.^[81]

In the $[Cr(dpc)_2]^+$ complex (dpc^- = deprotonated 3,6-di-*tert*-butyl-1,8-di(pyridine-2-yl)-carbazole), replacing two out of the six pyridines in the first coordination sphere in *trans* position using the π donating carbazole unit, lead to emission in the NIR-II region ($\lambda_{em} = 1067$ nm at 77 K).^[157] The increased M–L bond covalency and the complimentary π character of pyridines and amides in this complex lead to a push-pull effect of π electron density. The RACAH parameter is almost halved ($B = 470$ cm $^{-1}$) compared to the free ion. With an ES of such low energy, the energy gap law comes into play, accompanied by non-radiative decay via multiphonon relaxation, leading to a not unexpectedly low PL QY and relatively low ES LT (Tab. 1.2).

A pseudooctahedral chromium(III) complex with four pyrrol units did not show any luminescence.^[158] It is assumed that the π donating effect of the four pyrrols is so large, that the SF state energy is even lower than in $[Cr(dpc)_2]^+$.

In a series of chromium(III) complexes with a family of π donating isoindole ligands $bpi^{R,R}$ (bpi^- = deprotonated 1,3-bis(pyridin-2-ylimino)isoindolin-2-ide), the luminescence energy could be shifted over a wide range (780–985 nm) varying the substituents R on the pyridine moieties.^[138,159] With electron donating substituents R in the *para* position of the pyridine N, the emission was blue-shifted compared to R = H, while for a *meta* substituted example, the emission was red-shifted. Investigations of the influence on the emission energies due to the substituents revealed an LMCT contribution to the MC ESs. Based on this interpretation, the emission energy change in this series is not a consequence of the nephelauxetic effect.

Motivation and Aim of the Work

Molecular rubies show outstanding optical properties. With an ever growing interest in emitters based on 3d TMCs to replace their heavier homologues in various fields of application, it is desirable to extend our understanding about their photophysical properties.

Therefore, the overarching aim of this work is twofold: designing ligand functionalities and exploring emission energy tuning. The first objective aims to tailor the scaffold of the tridentate ligand ddpd with functionalities, required for various applications, while retaining the favorable optical properties of the chromium(III) complex. The second project is geared towards understanding the fundamentals of luminescence energies in spin-flip emitters by investigating chromium(III) complexes with different M–L bond characters.

Functionalization of Ligands for Molecular Rubies

Mitigating oxygen quenching is essential for employment of molecular rubies under ambient conditions. Because of the long excited state lifetime, their spin-flip emission is efficiently quenched by molecular oxygen in a DEXTER-type energy transfer. This project aims to shield the chromium center from oxygen quenching to enhance the luminescence quantum yields and excited state lifetimes of the complexes in air-saturated environments (Fig. 2.1a). Ligands with differing bulky substituents are designed to limit the accessibility for oxygen in the corresponding chromium complexes. Besides the photophysical properties, the impact of these different steric demands on the structure properties of the complexes are investigated.

Covalent attachment of molecular rubies could pave the way for their implementation in other applications (Fig. 2.1b). In this project, the functionality is introduced in the central backbone of the ddpd ligand. A fairly substitutionally labile functional group in the initial ligand will allow for further late stage functionalization. Homo- as well as heteroleptic chromium(III) complexes are targeted to fulfill the requirements of different applications.

Photodissociation of molecular rubies is investigated to discover application possibilities as photolabile groups, e.g. in controlled RNA interference. The emphasis lies on studying the photodissociation mechanism by irradiation of the prototypical $[\text{Cr}(\text{ddpd})_2]^{3+}$, coupled with absorption and emission spectroscopy. In addition, the influence of environmental conditions, such as solvent, proton and oxygen concentration on the dissociation process of the molecular rubies are explored.

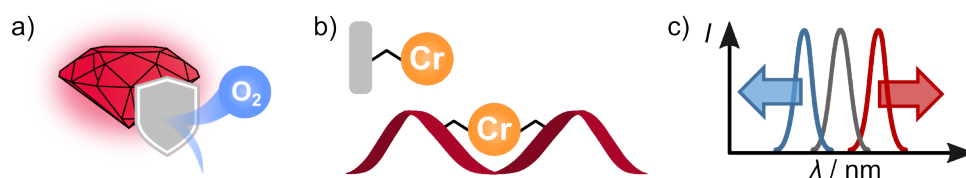


Fig. 2.1: Schematic illustration of the thesis' aim of work: a) shielding of molecular rubies from oxygen, b) functionalization of molecular rubies to enable mono- (grey) and bidentate (red) binding to materials and substrates (e.g. biomolecules, proteins, etc.) and c) luminescence energy tuning of chromium(III) emitters.

Tuning Ruby-like Emission Energies

Cyclometalated chromium(III) complexes are known since the late 1960s. However, their photophysical properties have been neglected so far. Long known cyclometalated chromium(III) complexes are investigated in terms of their excited state and luminescence properties (Fig. 2.1c). Different bidentate ligands such as pyridyl, dimethylamine and diphenylphosphane are investigated. Structural and electronic properties of these complexes are comprehensively characterized using single-crystal X-ray diffraction, cyclic voltammetry, and absorption as well as emission spectroscopy. Quantum chemical calculations are used for spectroscopic assignments and to predict trends in spin-flip emission energies.

The nephelauxetic effect describes the electron cloud expanding effect upon coordination of a ligand to a free metal ion and has a major influence on energies of spin-flip states. With spectroscopic and structural data of the cyclometalated complexes, in comparison to previously investigated luminescent chromium(III) complexes, ligand field effects will be analyzed and interpreted to establish a nephelauxetic series for ligand donors within chromium(III) complexes. The series is then used to understand and predict covalency effects on spin-flip emission energies.

The anticipated outcome of this research is multifaceted. Firstly, a deeper understanding of the photophysical properties of chromium(III) complexes, particularly in the NIR region is targeted. Secondly, molecular design strategies are developed to explore practical applications of molecular rubies in various fields.

This research is expected to contribute to the field of inorganic photochemistry as well as photophysics, particularly in the development of novel luminescent materials using earth-abundant transition metals, opening up possibilities for their use in applications like sensing or imaging.

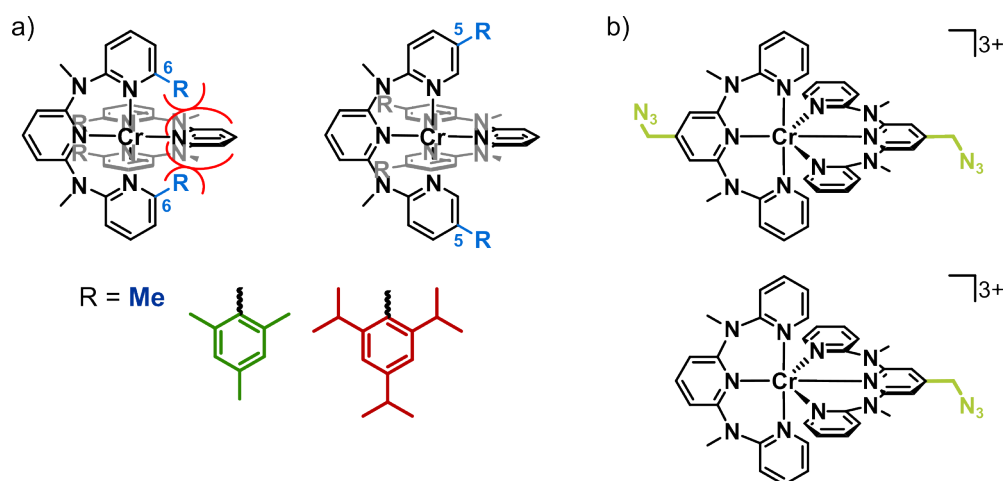
Results and Discussion

3.1 Overview

Most of the results of the research for this work have been published in peer-reviewed journals. In the following sections, the discussed publications are reprinted.

Molecular rubies show intense phosphorescence in the red to NIR spectral region. The first study *Bulky ligands protect molecular ruby from oxygen quenching* (section 3.2) addresses the oxygen-dependence of the phosphorescence quantum yield and excited state lifetime. The oxygen-sensitivity of chromium(III) spin-flip emitters arises from efficient DEXTER-type EnT of the long-lived doublet excited states (2T_1 , 2E) to 3O_2 . While this property can be exploited for oxygen sensing or usage of synthetic 1O_2 , it is typically considered a drawback for applications like pressure or temperature sensing, with $[Cr(ddpd)_2]^{3+}$ as prime example. In this study, $[Cr(ddpd)_2]^{3+}$ was protected from oxygen by introduction of bulky substituents on the terminal pyridines at the polypyridine ligand (Scheme 3.1a). Introduction of a methyl substituent on the α -position at the terminal pyridines hampers coordination of the ligand ($ddpd^{6Me}$) to the small chromium(III) ion as supported by DFT calculations. Hence, a series of substituents of increasing bulkiness from methyl over mesityl to 2,4,6-triisopropylphenyl were introduced in β -position ($ddpd^{5R}$), leading to a photoluminescence quantum yield of more than 5 % and an excited state lifetime of more than 500 μs under ambient conditions, *i.e.* under air. This is an almost tenfold increase compared to unprotected $[Cr(ddpd)_2]^{3+}$.

The second, study *Ligand Functionalization: Docking Molecular Rubies to Substrates* (section 3.3) aims to open up new application possibilities of molecular rubies. The previously explored scope of applications could be expanded if molecular rubies were to be (covalently) attached to biomolecules or other substrates. Depending on specific requirements, different functional groups and corresponding homo- or heteroleptic complexes can be used. The underlying design strategy is based on modifications of the central pyridine in the $ddpd$ ligand scaffold. Starting from the alcohol or halide functionalized ligand, many pathways to different functionalities are developed (Scheme 3.1b). At the central pyridine and with an additional linker (methylene bridge), the functional groups should not influence the first coordination sphere of the complex and decouple electronic communication between the complex and the substrate to retain the excellent luminescence properties of molecular rubies. This study focused on an azide functionality of the ligand, to click the



Scheme 3.1: Molecular structures of functionalized molecular rubies established in this study for a) shielding of the metal center from oxygen and b) attachment to substrates *via* click reactions.

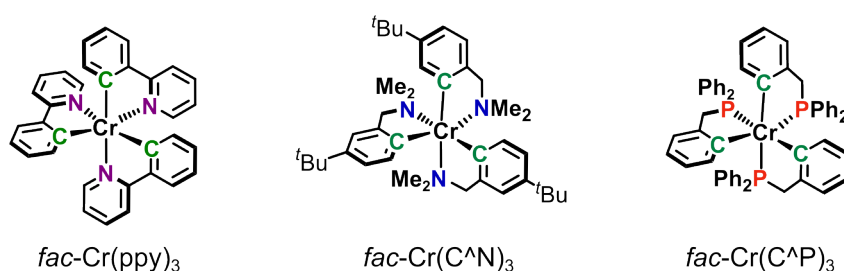
respective complex to alkyne functionalized oligonucleotides, as a first proof of concept application. The copper(I) mediated azide alkyne cycloaddition (CuAAC) to artificial and alkyne functionalized oligonucleotides was performed by Marlen Saalbach, supervised by Prof. Dr. Alexander Heckel (Goethe University, Frankfurt). The ligand was prepared in five steps and syntheses of homo- and heteroleptic complexes was successful. The work-up of the crude products turned out to be quite challenging. Therefore no structural analysis of the inspected complexes was possible, yet. Preliminary absorption and emission spectra, however, already show essentially unchanged band shapes and maxima. This in turn confirms similar excited state energies compared to unfunctionalized $[\text{Cr}(\text{ddpd})_2]^{3+}$.

While for some applications, such as photocatalysis, photostability of the sensitizer is essential, in other areas photodegradation is a desired process. Therefore, the photodissociation mechanism of $[\text{Cr}(\text{ddpd})_2]^{3+}$ was investigated within this project (section 3.3). The preliminary results gathered in this project already show a dependence of the photodegradation mechanism on oxygen and proton concentration, as well as the solvent and presence of (organic) substrates.

In molecular rubies and the most prominent examples of emissive chromium(III) complexes, the first coordination sphere is very similar, consisting of six pyridine units, to achieve the necessary strong ligand field. With this prerequisite, these chromium(III) complexes typically show SF luminescence between 670 nm and 780 nm. Being intraconfigurational and essentially independent of the ligand field splitting, the spin-flip excited state energies only depend on interelectronic repulsion of the three d electrons ($(t_{2g})^3$) in the chromium(III) ion. Therefore tuning the emission energy can be achieved by exploiting the nephelauxetic effect. With an enhanced M–L bond covalency and the concomitant d orbital expansion, the spin-flip emission should show a red-shift. A more covalent bond, compared to classical ligand

coordination, is expected from cyclometalating ligands. Whereas the syntheses of some cyclometalated chromium(III) complexes has been known for decades, *The overlooked NIR luminescence of Cr(ppy)₃* (section 3.4) was just recently discovered and published within this work. In deprotonated 2-phenylpyridine the typical strong field ligand motif of pyridine is combined with a phenyl unit. *fac*-Cr(ppy)₃ is the first reported chromium(III) complex showing phosphorescence at room temperature in solution above 900 nm. Details on non-radiative decay due to trigonal distortions in complexes with bidentate ligands are investigated. Quantum chemical calculations (DFT, CASSCF), correctly predicted the increased ligand field splitting and stronger nephelauxetic effect, compared to structurally related [Cr(bpy)₃]³⁺. This study gives first insights into luminescence energy tuning of chromium(III) emitters based on cyclometalation.

Building on the results of *fac*-Cr(ppy)₃, further cyclometalated chromium(III) complexes (Scheme 3.2) were investigated to elucidate the nephelauxetic effect in more detail and published in the paper *Luminescent Cyclometalated Chromium(III) Complexes* (section 3.5). The series emphasizes that not only the electronic but also structural properties of a ligand, and their interplay, influence the optical properties of the complex. With a bidentate carbanionic ligand containing an amine as second donor, the complex shows sharp emission at 765 nm (solid, 77 K). In contrast, the emission of a related complex with a phosphane ligand peaks at 865 nm (solid, 77 K). This complex showed a solvent-dependent equilibrium between the six-coordinate and a five-coordinate species, which was assessed using ³¹P-NMR spectroscopy. Both complexes are non-emissive at room temperature. Thermally activated pathways facilitate non-radiative decay due to twisting and trigonal distortions as the methylene bridges in the chelate ring are flexible and the ligands are bidentate. The combined results of emission and structural data show that interelectronic interaction follows the series NR₃ > py ≈ PR₃ > Ph[−].

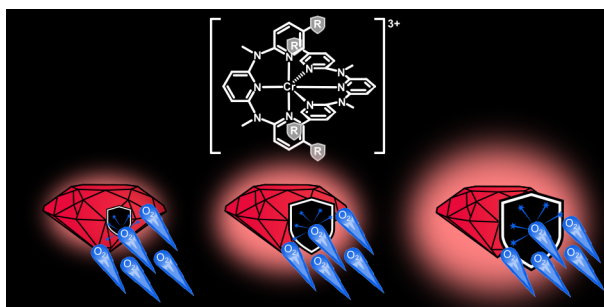


Scheme 3.2: Molecular structures of cyclometalated chromium(III) complexes investigated in this study.

3.2 Bulky Ligands Protect Molecular Ruby from Oxygen Quenching

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Molecular rubies show strong spin-flip emission ($\Phi_{Ar} = 13.7\%$) from long-lived doublet excited states (2T_1 , 2E), which is efficiently quenched by 3O_2 in a DEXTER-type EnT ($\Phi_{O_2} = 0.8\%$). $[Cr(ddpd)_2]^{3+}$ was protected from oxygen by introduction of bulky substituents on the terminal pyridines leading to a photoluminescence quantum yield of more than 5 % and an excited state lifetime of more than 500 μs under ambient conditions.

Author Contributions

Laura Stein designed and performed the syntheses, characterization, absorption, steady-state and time-dependent emission experiments, quantum chemical calculations, visualized the data and wrote the manuscript. Cui Wang performed preliminary optical characterizations and oxygen-dependent STERN-VOLMER studies, supervised by Ute Resch-Genger. Christoph Förster solved and refined the crystal structures. Katja Heinze conceptualized and supervised the study and revised the manuscript.

Supporting Information

for this article can be found on pp. 81.

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17664Bulky ligands protect molecular ruby from oxygen
quenching†Laura Stein,^a Cui Wang,^b Christoph Förster,^a Ute Resch-Genger^b and
Katja Heinze^{b,*}

Chromium(III) complexes can show phosphorescence from the spin-flip excited doublet states $^2E/{}^2T_1$ in the near-infrared with high photoluminescence quantum yields and extremely long lifetimes in the absence of dioxygen. The prototype molecular ruby, $[\text{Cr}(\text{ddpd})_2]^{3+}$ (ddpd = *N,N'*-dimethyl-*N,N'*-dipyridine-2-ylpyridine-2,6-diamine), has a photoluminescence quantum yield and a luminescence lifetime of 13.7% and 1.1 ms in deaerated acetonitrile, respectively. However, its luminescence is strongly quenched by $^3\text{O}_2$ via an efficient Dexter-type energy transfer process. To enable luminescence applications of molecular rubies in solution under aerobic conditions, we explored the potential of sterically demanding ddpd ligands to shield the chromium(III) center from O_2 using steady state and time-resolved photoluminescence spectroscopy. The structures of the novel complexes with sterically demanding ligands were investigated by single crystal X-ray diffraction and quantum chemically by density functional theory calculations. The O_2 sensitivity of the photoluminescence was derived from absolutely measured photoluminescence quantum yields and excited state lifetimes under inert and aerobic conditions and by Stern–Volmer analyses of these data. Optimal sterically shielded chromium(III) complexes revealed photoluminescence quantum yields of up to 5.1% and excited state lifetimes of 518 μs in air-saturated acetonitrile, underlining the large potential of this ligand design approach to broaden the applicability of highly emissive chromium(III) complexes.

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Introduction

Research on luminescent first-row transition metal complexes has tremendously increased in recent years to replace and complement the dominating precious and rare earth elements in molecular inorganic photochemistry.¹ Prominent examples are chromium(III) complexes with tridentate ligands and large bite angles which display a strong phosphorescence from spin-flip excited doublet states $^2E/{}^2T_1$ in the near-infrared (NIR) spectral region with extremely high quantum yields and lifetimes, yet typically only in the absence of molecular oxygen ($^3\text{O}_2$).^{2–4}

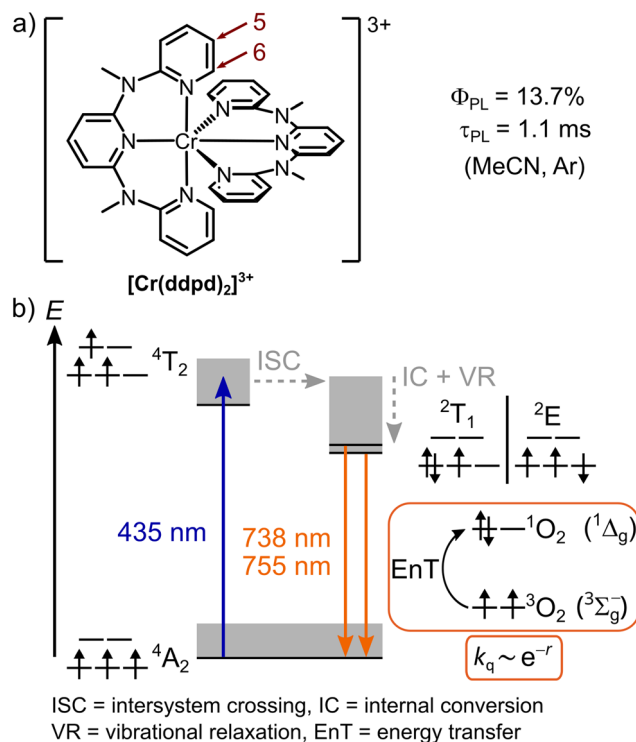
The prototypical complex is the so-called molecular ruby, $[\text{Cr}(\text{ddpd})_2]^{3+}$ ($[\text{Cr}^{5\text{H}}]^{3+}$, ddpd = *N,N'*-dimethyl-*N,N'*-dipyridine-2-ylpyridine-2,6-diamine, Scheme 1a) with a luminescence quantum yield of $\phi_{\text{PL}}^{\text{Ar}} = 13.7\%$ and an excited state lifetime of

$\tau_{\text{PL}}^{\text{Ar}} = 1.1$ ms at room temperature in deaerated acetonitrile solution ($\lambda_{\text{em}} = 738, 775$ nm).^{5,6} Modifying the ligand structure and substitution pattern enabled the tuning of the emission wavelength from 709 nm to 1067 nm.^{7,8}

Several unimolecular non-radiative decay pathways compete with the spin- and Laporte-forbidden radiative relaxation in octahedral chromium(III) complexes. This includes back-inter-system crossing to dissociative quartet states (4T_2 ; Scheme 1b), excited state distortion,⁹ and multiphonon relaxation¹⁰ promoted by CH, NH or OH overtones from ligands or solvent molecules.³ Large ligand field splitting and rigid ligand frameworks promoting high octahedricity and ligand deuteration helped to increase the quantum yield and lifetime of the excited state of $[\text{Cr}^{5\text{H}}]^{3+}$ up to $\phi_{\text{PL}}^{\text{Ar}} = 30\%$ and $\tau_{\text{PL}}^{\text{Ar}} = 2300$ μs in O_2 -free deuterated acetonitrile solution at room temperature.¹²

The dual NIR emission of $[\text{Cr}^{5\text{H}}]^{3+}$ was already exploited for O_2 and ratiometric temperature sensing as well as to optically probe hydrostatic pressure.¹³ The effective quenching of the chromium(III) emission by $^3\text{O}_2$ leads to a high quantum yield of the formed singlet oxygen ($\Phi(^1\text{O}_2)$ ca. 61% in acetonitrile),¹⁴ enabling the usage of $[\text{Cr}^{5\text{H}}]^{3+}$ as $^1\text{O}_2$ -generating photosensitizer for organic photo-oxidation reactions¹⁴ and photodynamic therapy.¹⁵ However, the high sensitivity to $^3\text{O}_2$ limits other potentially interesting applications of chromium(III) complexes

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Scheme 1 a) Molecular structure of $[\text{Cr}^{\text{III}}]^3+$ including the atom numbering of the ligand and (b) schematic Jablonski diagram of a transition metal complex with d^3 electron configuration in an octahedral environment with a large ligand field splitting. Relevant microstates and term symbols are indicated. The optical-spectroscopic data are given for $[\text{Cr}^{\text{III}}]^3+$ in acetonitrile solution at room temperature. Dexter-type energy transfer from doublet excited states to triplet oxygen ($^3\Sigma_g^-$) is indicated by respective microstates and term symbols.^{5,11} The grey boxes indicate vibrational levels.

as optical reporters, in bioimaging, and energy conversion schemes.

Mechanistically, quenching of long-lived electronically excited states with multiplicities differing from the ground state multiplicity by $^3\text{O}_2$ follows the Dexter energy transfer mechanism.¹¹ The doublet excited states of chromium(III) complexes are well suited to sensitize $^1\text{O}_2$ generation due to their much higher energy than the $^1\text{O}_2$ energy ($\Delta E = 0.6 \text{ eV}$), the favorable spin-statistics (67%), and the up to millisecond lifetimes of the excited doublet states.⁵ Based on the overlap of the donor and acceptor wavefunctions, the Dexter energy transfer rate constant k_q decreases exponentially with the donor-acceptor distance,¹⁶ which is typically below $10 \text{ \AA}$.¹⁷ To prevent this deactivation pathway, photoreactions, spectroscopic measurements and applications employing photoactive transition metal complexes are usually carried out under O_2 -free conditions.^{4,18} One strategy to protect the O_2 -sensitive luminophores from oxygen is to embed them in O_2 -impermeable matrices.¹⁸ For example, encapsulation of the molecular ruby in polystyrene nanoparticles coated with a silica shell and embedded in an oxygen-barrier poly(vinyl alcohol) film increased the quantum yield under air from $\phi_{\text{PL}}^{\text{air}} < 1\%$ to $\phi_{\text{PL}}^{\text{air}} = 15.2\%$.⁶

In the present study, we follow a different approach exploiting a rational ligand design concept: the coordinating ddpd ligand is derivatized with substituents of increasing bulkiness to mitigate close contacts of the chromium(III) center and O_2 and hence to reduce the overlap of their wavefunctions. The increased average $\text{Cr}\cdots\text{O}_2$ distance is expected to decrease the Dexter energy transfer rate constant k_q , thereby reducing the O_2 -sensitivity of the chromium(III) complexes and increasing the photoluminescence quantum yields $\phi_{\text{PL}}^{\text{air}}$ and lifetimes $\tau_{\text{PL}}^{\text{air}}$ in air-saturated systems.

Results and discussion

DFT calculations

The position at the ddpd ligand closest to the chromium(III) center with arguably the strongest shielding effect is the 6-position (Scheme 1a). According to density functional theory (DFT) modeling, the 6-methyl substituted derivative ddpd^{6Me} coordinates to chromium(III) giving $[\text{Cr}(\text{ddpd}^{\text{6Me}})_2]^3+$ ($[\text{Cr}^{\text{6Me}}]^3+$, Fig. 1b), however with significantly increased Cr–N distances to the terminal pyridines by $0.1 \text{ \AA}$ compared to the parent complex $[\text{Cr}^{\text{H}}]^3+$ (Table S3†). Possibly, interligand steric congestion, as observed in iron(II) complexes with 6,6''-halogenated 2,2':6',2''-terpyridyl (tpy) ligands,²⁰ hinders the successful coordination of ddpd^{6Me} to the small chromium(III) ion (ionic radius $0.62 \text{ \AA}$).²¹ Therefore, all attempts to coordinate ddpd^{6Me} to chromium(III) to form $[\text{Cr}^{\text{6Me}}]^3+$ failed. The next suitable position for introducing a shielding substituent R is position 5 at the terminal pyridine rings to give the ddpd^{5R} ligands (Scheme 1a). As these substituents R point away from the metal center, the substituent size clearly plays a key role to efficiently block the access of O_2 to the chromium center (Fig. 1). Therefore, we prepared ddpd ligands with methyl, mesityl and 2,4,6-triisopropylphenyl substituents at position 5 (ddpd^{5Me}, ddpd^{5Mes} and ddpd^{5Tripp}) and the corresponding chromium(III) complexes $[\text{Cr}(\text{ddpd}^{\text{5Me}})_2][\text{BF}_4]_3$ ($[\text{Cr}^{\text{5Me}}][\text{BF}_4]_3$), $[\text{Cr}(\text{ddpd}^{\text{5Mes}})_2][\text{BF}_4]_3$ ($[\text{Cr}^{\text{5Mes}}][\text{BF}_4]_3$) and $[\text{Cr}(\text{ddpd}^{\text{5Tripp}})_2][\text{BF}_4]_3$ ($[\text{Cr}^{\text{5Tripp}}][\text{BF}_4]_3$). Space-filling models of the DFT optimized complex geometries demonstrate the increasing steric demand of the ligand around the metal center (Fig. 1c–e).

Synthesis and characterization

The ddpd^{5R} ligands were synthesized according to the procedures outlined in Scheme 2 and analytically characterized (see ESI†).²² The methyl derivative ddpd^{5Me} was prepared from 2,6-diaminopyridine and 2-bromo-5-methyl pyridine followed by *N*-methylation with methyl iodide (Scheme 2a). The required 2-(*N*-methyl)-amino-5-aryl pyridines py^{5Mes}-NHMe and py^{5Tripp}-NHMe were obtained from 2,5-dibromopyridine by amination of the 2-position followed by Suzuki coupling of the 5-position with the respective aryl boronic acid (Scheme 2b). *N*-Substitution of py^{5Mes}-NHMe and py^{5Tripp}-NHMe with 2,6-dibromopyridine yielded the tridentate ligands ddpd^{5Mes} and ddpd^{5Tripp}, respectively (Scheme 2b).



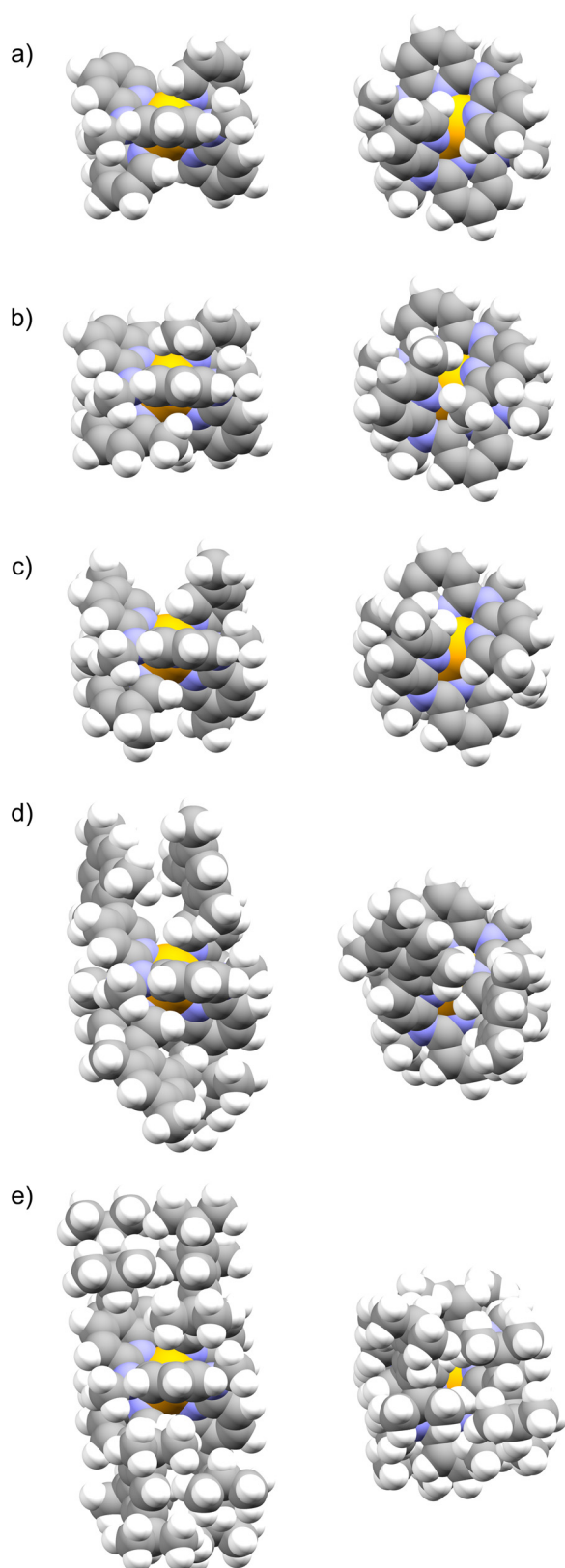
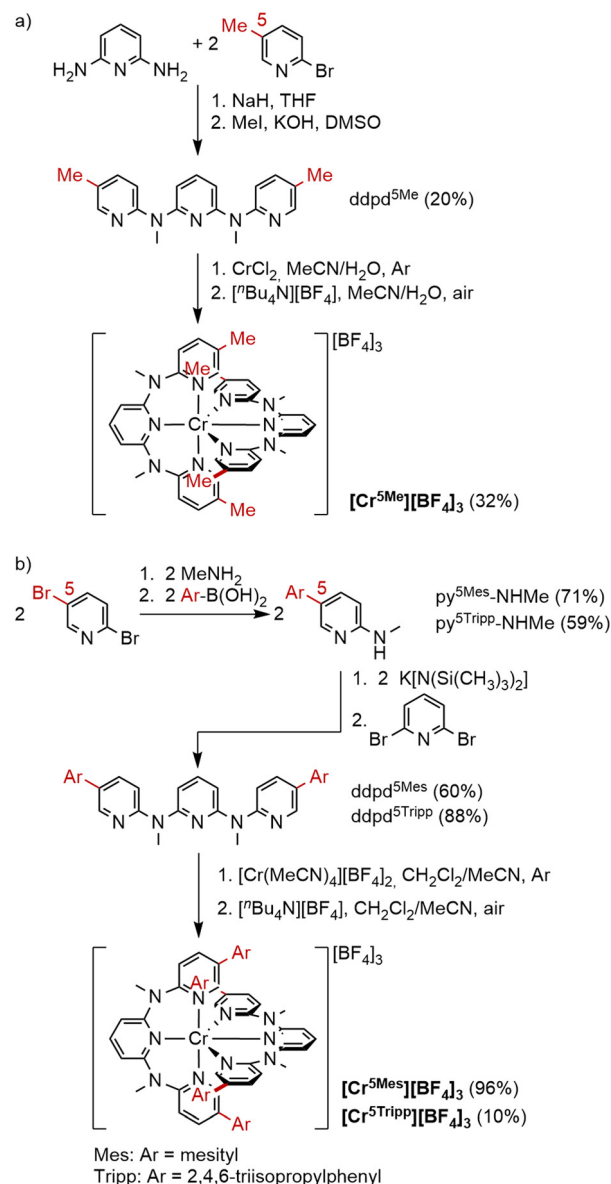


Fig. 1 Space-filling models of (a) $[\text{Cr}(\text{ddpd})]_2^{3+}$, (b) $[\text{Cr}(\text{ddpd}^{6\text{Me}})]_2^{3+}$, (c) $[\text{Cr}(\text{ddpd}^{5\text{Me}})]_2^{3+}$, (d) $[\text{Cr}(\text{ddpd}^{5\text{Mes}})]_2^{3+}$ and (e) $[\text{Cr}(\text{ddpd}^{5\text{Tripp}})]_2^{3+}$ from DFT calculations demonstrating the increasing shielding of the chromium center (orange: Cr, blue: N, grey: C, white: H). Left: front view, right: top view.



Scheme 2 Syntheses of substituted ligands $\text{ddpd}^{5\text{R}}$ and corresponding chromium(III) complexes $[\text{Cr}(\text{ddpd}^{5\text{R}})]_2[\text{BF}_4]_3$.

Coordination of $\text{ddpd}^{5\text{Me}}$ to chromium(III) was successful using a procedure analogous to the preparation of $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ in MeCN/H₂O giving $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ (Scheme 2a).⁵ The aryl substituted ligands $\text{ddpd}^{5\text{Mes}}$ and $\text{ddpd}^{5\text{Tripp}}$, however, are only poorly soluble in MeCN/H₂O mixtures. Consequently, different solvents and a different chromium precursor were required. With $[\text{Cr}(\text{MeCN})_4][\text{BF}_4]_2$ ^{2,3} in MeCN/CH₂Cl₂, these bulky ligands were successfully coordinated to chromium(II), yielding $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ and $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$, respectively, after oxidation (Scheme 2b). Slow diffusion of diethyl ether into concentrated acetonitrile solutions of $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$, $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ and $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ yielded orange crystals suitable for X-ray diffraction analyses (Table 2). As derived from DFT optimized geometries and crystal structures (Tables 1, 2 and S1–S3†), in these

Table 1 Selected bond lengths/Å and angles/° of complexes $[\text{Cr}^{\text{5R}}]^{3+}$ obtained from DFT calculations

	$[\text{Cr}^{\text{5H}}]^{3+}$	$[\text{Cr}^{\text{5Me}}]^{3+}$	$[\text{Cr}^{\text{5Mes}}]^{3+}$	$[\text{Cr}^{\text{5Tripp}}]^{3+}$
Cr–N1	2.059	2.056	2.062	2.064
Cr–N2	2.046	2.048	2.038	2.041
Cr–N3	2.059	2.056	2.057	2.060
Cr–N4	2.059	2.055	2.068	2.062
Cr–N5	2.046	2.047	2.045	2.044
Cr–N6	2.059	2.055	2.059	2.060
N1–Cr–N2	86.46	86.49	85.65	84.95
N2–Cr–N3	86.46	86.42	86.97	85.11
N1–Cr–N3	172.92	172.91	172.49	170.06
N4–Cr–N5	86.46	86.46	86.06	85.07
N5–Cr–N6	86.46	86.49	87.58	85.13
N4–Cr–N6	172.92	172.95	173.13	170.20
$S(\text{OC-6})^{19}$	0.26	0.26	0.32	0.52

complexes, a slight deviation from octahedral symmetry results with the largest substituent Tripp with the shape parameter¹⁹ $S(\text{OC-6}) > 0.5$. In the solid state, the average Cr–N bond from the central pyridines to the metal center is shortened (2.042 Å to 2.023 Å), while the average Cr–N bond to the terminal pyridines is elongated from 2.045 Å to 2.053 Å. Simultaneously, the intramolecular N–Cr–N angles increasingly deviate from 90° and 180° within this series. This is expected as the size of the aromatic substituents forces the ligand scaffold to twist more strongly out of plane than with small substituents like R = H or Me. Due to the torsion induced by the bulky Tripp substituent, the dihedral angle between the central pyridine planes becomes smaller ($\angle 10^\circ$, Table S1†) compared to the other ligands ($\angle 14^\circ$ – 19°). The more efficient overlap of the pyridine and metal centered t_{2g} orbitals presumably causes a stronger nephelauxetic effect and a bathochromic shift of the emission band for this complex (see below). Moreover, intermolecular π – π stacking occurs between the aromatic substituents (centroid-to-centroid distance in $[\text{Cr}^{\text{5Mes}}][\text{BF}_4]_3$ = 4.961 Å, Fig. S21† and $[\text{Cr}^{\text{5Tripp}}][\text{BF}_4]_3$ 5.700 Å, Fig. S22†) and even intramolecular interligand π – π stacking was observed in $[\text{Cr}^{\text{5Tripp}}][\text{BF}_4]_3$ (5.968 Å). This intramolecular π – π stacking might shield the chromium ion even more efficiently from the environment (Fig. 1e).

As a measure of the accessibility of the metal center within the ligand scaffold for subsequent luminescence studies without and in the presence of oxygen, the shortest Cr...F (BF_4^-) and Cr...N (MeCN) distances in the crystal structures were taken into account (Table S1 and Fig. S20–22†). Compared to the complex with R = Me, the distances to the counter ions increase, while they remain in the same range for MeCN contacts. This suggests better shielding from tetrahedral molecules than from linear molecules as well as a weaker electrostatic interaction between the counter ions and the cationic metal center in the solid state.

Optical properties of $[\text{Cr}(\text{ddpd}^{\text{5R}})_2][\text{BF}_4]_3$

The absorption and photoluminescence spectra of $[\text{Cr}^{\text{5R}}][\text{BF}_4]_3$ complexes with R = H, Me, Mes, Tripp were recorded in acetonitrile at room temperature under anaerobic conditions (Fig. 2a). The shapes of the respective absorption and emission spectra are relatively similar. Bathochromic shifts are noted for the $^4\text{A}_2 \rightarrow ^4\text{T}_2/\text{LMCT}$ absorption band from 435 to 455 nm (Fig. S23a†) and for the spin-flip emission bands from 738 nm $\rightarrow$ 742 nm/775 nm $\rightarrow$ 794 nm (Table 3 and Fig. 2). The bathochromic shift of the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ absorption band, combined with the more intense ligand-to-metal charge transfer absorption band, could be reproduced by time-dependent DFT calculations (Fig. S24†). The π – π^* transitions of the ligands in the UV region display larger changes, in particular for complexes with aryl substituted ligands (Fig. 2a), which is already evident from the ligand absorption bands (Fig. S13†). The quantum yields $\phi_{\text{PL}}^{\text{Ar}}$ and luminescence lifetimes $\tau_{\text{PL}}^{\text{Ar}}$ of the complexes in Ar-saturated acetonitrile solution are very similar (Table 4).

Oxygen quenching experiments

The photoluminescence of the complexes $[\text{Cr}^{\text{5R}}][\text{BF}_4]_3$ is quenched in the presence of O_2 , yet to very different extents (Table 4, Fig. 2 and S25†). The luminescence properties of $[\text{Cr}^{\text{5H}}][\text{BF}_4]_3$ and $[\text{Cr}^{\text{5Me}}][\text{BF}_4]_3$ in air-saturated acetonitrile solution are very similar, demonstrating that the shielding by methyl groups in position 5 is not effective. The DFT modeling and XRD data of the complexes with R = H and Me confirm

Table 2 Selected bond lengths/Å and angles/° of complexes $[\text{Cr}^{\text{5R}}][\text{BF}_4]_3$ obtained from single crystal XRD analyses

	$[\text{Cr}^{\text{5H}}][\text{BF}_4]_3$ ⁵	$[\text{Cr}^{\text{5Me}}][\text{BF}_4]_3$	$[\text{Cr}^{\text{5Mes}}][\text{BF}_4]_3$	$[\text{Cr}^{\text{5Tripp}}][\text{BF}_4]_3$
Cr–N1	2.0485(18)	2.0448(14)	2.0577(17)	2.0523(14)
Cr–N2	2.0393(18)	2.0294(14)	2.0268(17)	2.0222(14)
Cr–N3	2.0394(19)	2.0471(14)	2.0623(18)	2.0561(14)
Cr–N4	2.0446(17)	2.0492(13)	2.0579(18)	2.0576(14)
Cr–N5	2.0444(18)	2.0300(14)	2.0215(17)	2.0238(14)
Cr–N6	2.0485(18)	2.0403(13)	2.0549(18)	2.0449(14)
N1–Cr–N2	85.13(8)	85.83(6)	87.63(7)	84.91(6)
N2–Cr–N3	85.74(7)	86.18(6)	86.23(7)	85.26(6)
N1–Cr–N3	170.86(8)	172.00(5)	173.44(7)	170.02(6)
N4–Cr–N5	85.89(7)	86.00(5)	85.91(7)	84.48(5)
N5–Cr–N6	84.99(7)	86.08(5)	86.74(7)	84.98(6)
N4–Cr–N6	170.88(7)	171.81(5)	172.62(7)	169.35(6)
Cr...F (BF_4^-)	5.438(4)	4.682(2)	6.768(2)	5.556(2)
Cr...N (MeCN)	4.613(4)	4.694(2)	4.654(2)	4.513(2)
$S(\text{OC-6})^{19}$	0.43	0.35	0.31	0.56



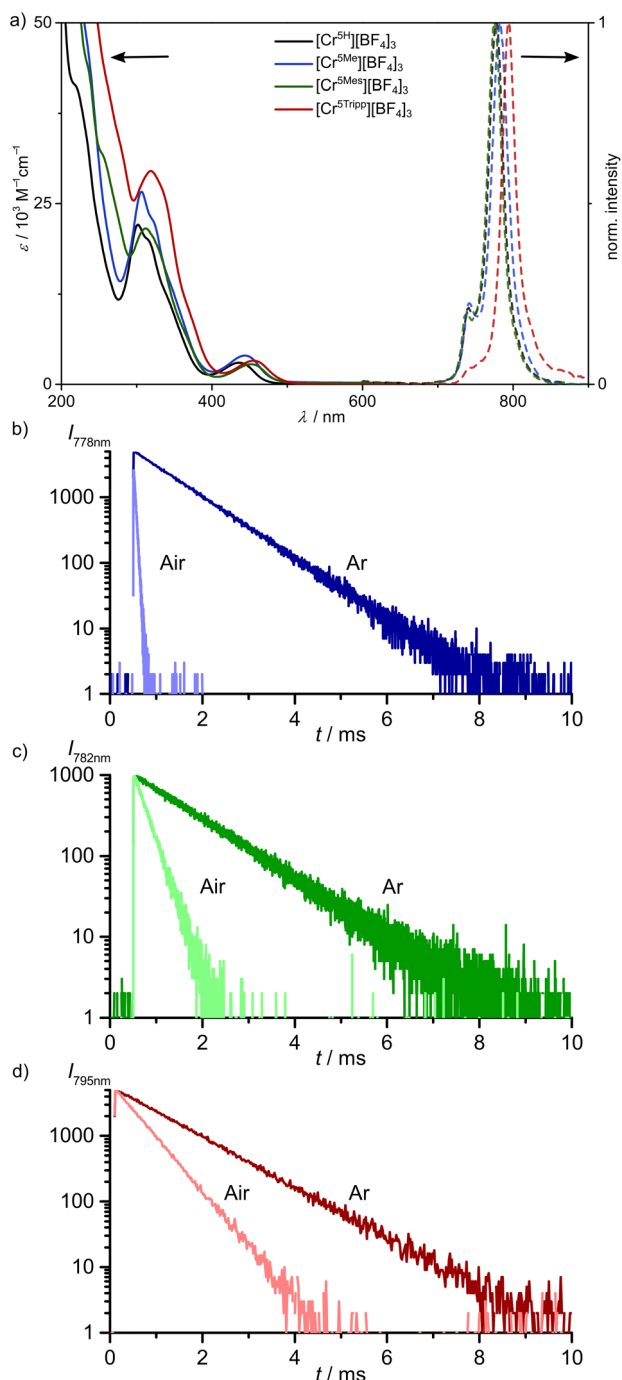


Fig. 2 (a) Absorption and normalized emission spectra of $[\text{Cr}^{5\text{R}}][\text{BF}_4]_3$ complexes with $\text{R} = \text{H}$ ($\lambda_{\text{exc}} = 435 \text{ nm}$, black), Me ($\lambda_{\text{exc}} = 441 \text{ nm}$, blue), Mes ($\lambda_{\text{exc}} = 450 \text{ nm}$, green) and Tripp ($\lambda_{\text{exc}} = 454 \text{ nm}$, red) in Ar-saturated acetonitrile. Luminescence decays of $[\text{Cr}^{5\text{R}}][\text{BF}_4]_3$ complexes with (b) $\text{R} = \text{Me}$, (c) $\text{R} = \text{Mes}$, (d) $\text{R} = \text{Tripp}$ in air- and Ar-saturated acetonitrile solution at 293 K.

this assumption as the accessibility of the chromium(III) ion seems to be very similar for both complexes (Fig. 1). On the other hand, mesityl and 2,4,6-triisopropyl substituents in position 5 clearly affect the photoluminescence quantum yields and luminescence lifetimes of the chromium(III) complexes in

Table 3 Optical data of the $[\text{Cr}^{5\text{R}}][\text{BF}_4]_3$ complexes in Ar-saturated acetonitrile solution at 293 K

Complex	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{em}}/\text{nm}$ ($\lambda_{\text{exc}}/\text{nm}$)
$[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$	444 (4), 323 (23, sh), 305 (27), 225 (53, sh)	741, 779 (441)
$[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$	453 (3), 312 (22), 257 (31), 236 (44, sh)	742, 782 (453)
$[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$	455 (3), 319 (30), 240 (55, sh)	740 (sh), 794 (455)

air-saturated acetonitrile as reflected by $\phi_{\text{PL}}^{\text{air}} = 2.2\%$ and 5.1% and $\tau_{\text{PL}}^{\text{air}} = 244 \mu\text{s}$ and $518 \mu\text{s}$, respectively. Compared to $\text{R} = \text{H}$ and Me , where the ratios of $\phi_{\text{PL}}^{\text{Ar}}/\phi_{\text{PL}}^{\text{air}}$ and $\tau_{\text{PL}}^{\text{Ar}}/\tau_{\text{PL}}^{\text{air}}$ amount to 17–25, for the Tripp substituted complex, these ratios drop remarkably to two (Table 4). This demonstrates the efficient shielding of the chromium(III) center from O_2 by the bulky Tripp substituents.

Compared to very recently reported chromium(III) complexes with 1,3-bis(2'-pyridylimino)-isoindoline ligands reported as showing long-lived NIR emission under inert and ambient conditions in acetonitrile ($\tau_{\text{PL}}^{\text{Ar}} = 8.0 \mu\text{s}$ and $25.0 \mu\text{s}$; $\tau_{\text{PL}}^{\text{air}} = 4.5 \mu\text{s}$ and $8.1 \mu\text{s}$),²⁴ the here reported lifetimes of $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ and $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ are larger by factors of 30 to 115.

Emission intensity and lifetime-based Stern-Volmer analyses with varying concentrations or partial pressures of O_2 in acetonitrile solution gave linear plots with Stern-Volmer constants $K_{\text{SV}}^{\text{int}}$ and $K_{\text{SV}}^{\text{LT}}$ matching within the measurement uncertainty. This confirms the diffusional quenching by O_2 (Table 4, Fig. 3 and S25†). The $K_{\text{SV}}^{\text{int}}$ and $K_{\text{SV}}^{\text{LT}}$ values drop significantly from $K_{\text{SV}} \approx 0.13 \text{ hPa}^{-1}$ for $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ and $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ over 0.02 hPa^{-1} for $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ to 0.01 hPa^{-1} for $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$. Similarly, the quenching rate constants $k_{\text{q}} = K_{\text{SV}}/\tau_{\text{PL}}^{\text{Ar}}$ decrease from $\approx 110 \text{ hPa s}^{-1}$ for $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ and $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ over 20 hPa s^{-1} for $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ to 11 hPa s^{-1} for $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$, equaling an overall shielding-related reduction by a factor of about 10. These results clearly demonstrate the superior shielding effect of the bulky ddpd^{5Tripp} ligand.

Cooling the complexes under aerobic and anaerobic conditions increases the luminescence lifetimes (Fig. S26 and Table S4†) of the complexes $[\text{Cr}^{5\text{R}}][\text{BF}_4]_3$ in acetonitrile solution, yet displaying a different degree of the temperature dependence for deaerated and atmospheric conditions (Fig. S27†). Under Ar-saturated conditions, for $\text{R} = \text{H}$, Me , Mes , the lifetimes are prolonged by a factor of $f = 5$ –7 upon cooling from 338 to 278 K. For the bulky substituent $\text{R} = \text{Tripp}$, the temperature dependence is significantly smaller (factor of $f = 2.4$) under these conditions. This indicates a higher activation barrier for thermally induced non-radiative processes, probably because the substituent Tripp enforces a rigid structure of the respective chromium(III) complex. Under atmospheric conditions, the increase in the luminescence lifetimes upon lowering the temperature is less significant for all complexes ($\text{R} = \text{H}$: $f \approx 1.1$, Me : $f \approx 1.3$; Mes : $f \approx 2.5$, Tripp : $f \approx 1.8$). Especially for the complexes with the ddpd ligands bearing the small substituents $\text{R} = \text{H}$ and Me , O_2 quenching is now the most sig-

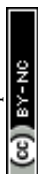
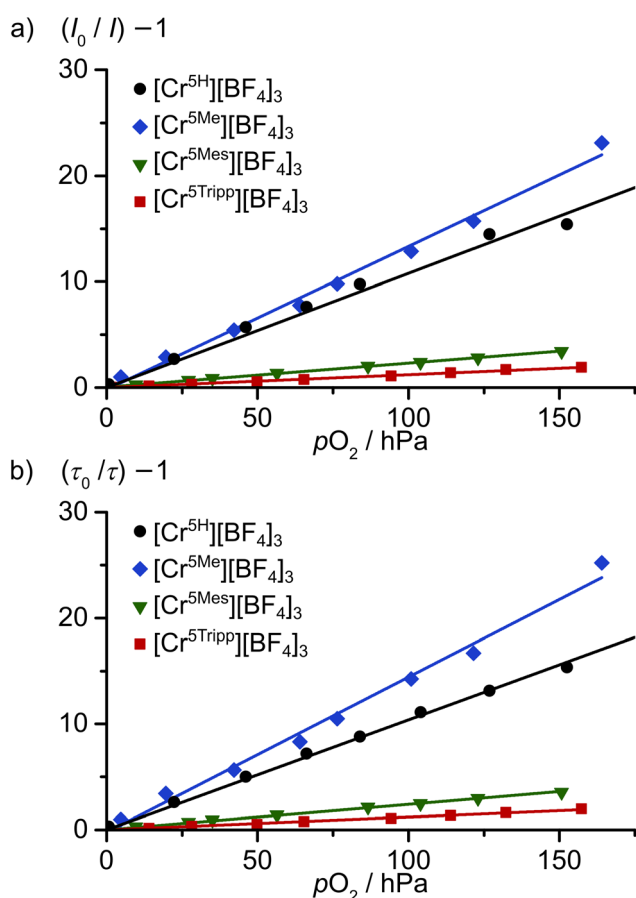


Table 4 Luminescence and O₂-quenching Stern–Volmer data of the [Cr^{5R}][BF₄]₃ complexes in acetonitrile solution at 293 K

	[Cr ^{5H}][BF ₄] ₃ ^{5,6}	[Cr ^{5Me}][BF ₄] ₃	[Cr ^{5Mes}][BF ₄] ₃	[Cr ^{5Tripp}][BF ₄] ₃
$\lambda_{\text{obs}}/\text{nm}$	778	778	782	795
$\phi_{\text{PL}}^{\text{Ar}}/\%$	13.7	13.9	12.1	11.3
$\tau_{\text{PL}}/\mu\text{s}$	1122	1258	1173	1131
$\phi_{\text{PL}}^{\text{air}}/\%$	0.8	0.8	2.2	5.1
$\tau_{\text{PL}}^{\text{air}}/\mu\text{s}$	52	52	244	518
$\phi_{\text{PL}}^{\text{Ar}}/\phi_{\text{PL}}^{\text{air}}$	17	17	5	2
$\tau_{\text{PL}}^{\text{Ar}}/\tau_{\text{PL}}^{\text{air}}$	20	25	5	2
$K_{\text{SV}}^{\text{int}}/\text{hPa}^{-1}$	0.116	0.135	0.023	0.012
$K_{\text{SV}}^{\text{LT}}/\text{hPa}^{-1}$	0.123	0.147	0.024	0.012
$k_{\text{q}}^{\text{int}}/\text{hPa s}^{-1}$	103.3	107.4	19.4	10.7
$k_{\text{q}}^{\text{LT}}/\text{hPa s}^{-1}$	109.6	116.5	20.0	10.5

**Fig. 3** (a) Intensity- and (b) lifetime-based Stern–Volmer plots of the [Cr^{5R}][BF₄]₃ complexes with O₂ in acetonitrile at 293 K.

nificant non-radiative decay process, as it is faster than other unimolecular, non-radiative (temperature-dependent) pathways.

Conclusion

This study reports the syntheses and structures of novel chromium(III) spin-flip emitters (molecular rubies) modified at position 5 of the tridentate chelate ligands with bulky substituents

to protect the chromium(III) center from O₂ quenching. Conceptually, the shielding of a spin-flip emitter from quenching by ³O₂ is more straightforward than the shielding of a phosphorescent charge-transfer emitter due to the metal-localized and ligand-delocalized nature of the respective participating wavefunctions. While small methyl substituents barely show a protective effect, the aryl substituents mesityl and 2,4,6-triisopropylphenyl effectively shield the chromium(III) center from a close contact with O₂. This reduces the Dexter-type energy transfer rate to O₂ from $k_{\text{q}} \approx 110 \text{ hPa s}^{-1}$ to 11 hPa s^{-1} and consequently increases the photoluminescence quantum yields and lifetimes of the respective chromium(III) complexes from 0.8 to 5.1% and from 52 to 518 μs , respectively, in air-saturated acetonitrile solution at 293 K. In the future, these favorable luminescence features of the chromium(III) complexes with sterically demanding ddpd ligands can enable applications of shielded molecular rubies, for example as reporters in time-gated luminescence detection schemes²⁵ or for circularly polarized NIR emission²⁶ under aerobic conditions.

Author contributions

L. S. performed the synthesis, characterization, DFT, UV-VIS, the quantum yield and lifetime measurements under Ar and air and temperature-dependent emission measurements under Ar and air, visualized the data and wrote the original draft. C. W. performed the oxygen-dependent Stern–Volmer studies and preliminary optical characterization. C. F. solved and refined the crystal structures. U. R.-G. supervised the Stern–Volmer studies and revised the manuscript. K. H. designed and supervised the project and finalized the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

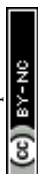
The authors acknowledge Dr Luca M. Carrella and Dr Dieter Schollmeyer for collection of XRD data and Dr Robert



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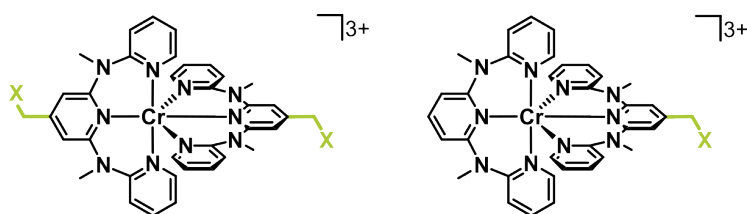
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3.3 Ligand Functionalization: Docking Molecular Rubies to Substrates

Molecular rubies have proven to be promising candidates for various kinds of applications. Among others, these include temperature, pressure, oxygen or pH sensing.^[77] The oxygen sensitivity, based on a DEXTER-type EnT process to atmospheric oxygen forming $^1\text{O}_2$, was exploited for oxidative reactions.^[117] Molecular rubies were intended to be tested for PDT, utilizing this same mechanism. However, cellular uptake is hindered due to the high charge of the complex.^[118] In addition, the formation of $^1\text{O}_2$ could be used to create light-triggered self-cleaning surfaces when the compound is linked to them. Besides $^1\text{O}_2$ formation, the red to NIR emission of molecular rubies is very appealing for biological applications, as it covers the biological transparent window. Therefore molecular rubies are imaginable as protein labels or markers for microscopy. With the growing list of further ideas and opportunities to expand the scope of applications, a strategy to design the ligand scaffold accordingly was established.

To attach molecular rubies to different kind of substrates or allowing for surface immobilization, *e.g.* in copper mediated azide alkyne cycloadditions (CuAAC), functional groups in the ligand scaffold are necessary. It was already shown that introduction of substituents on the terminal pyridines of ddpd shield the metal center from the environment, reducing the oxygen sensitivity of the emission intensity (Φ , τ), while keeping the optical properties (λ_{abs} , λ_{em}) unchanged. The functional group should be placed in *para* position of the nitrogen atom on the central pyridine of ddpd, as otherwise diastereomeres of the corresponding complexes would be formed. Suiting the scope of application and its requirements, homo- and heteroleptic complexes with the corresponding (un-)substituted ligands can be used (Scheme 3.3). In this work, a methylene bridge was incorporated between the ddpd ligand scaffold and the functional group to decouple electronic communication within the two units and leave the optical properties of the corresponding complexes untouched. This strategy can potentially be also used to reduce the overall charge and increase the lipophily of the complex.



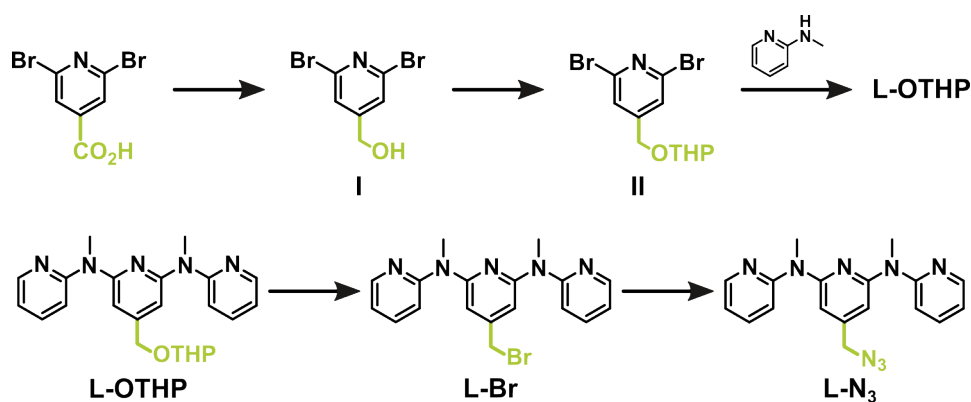
Scheme 3.3: Molecular structures of a homo- and a heteroleptic chromium(III) complex with functionalized ddpd ligands suitable for double and single sided attachment of the complex.

Supporting Information for this project can be found on pp. 118.

3.3.1 Synthesis, Characterization and Spectroscopy

Traditionally, ddpd is synthesized from 2,6-dibromopyridine and 2-methylaminopyridine.^[161] Sticking to the general synthesis procedure, a suitable substituent in *para* position of 2,6-dibromopyridine needed to be found. It should not hamper ligand and complex formation and allow for substitution with a wide range of functional groups for different kinds of applications.

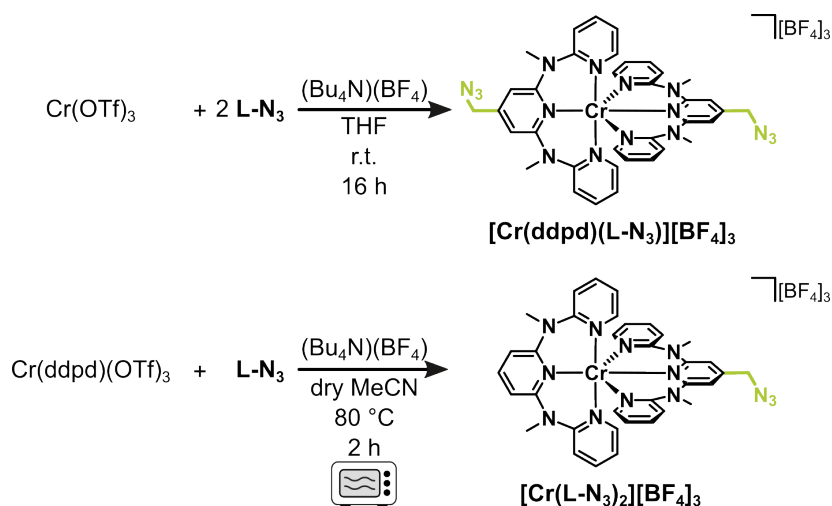
Starting from commercially available 2,6-dibromopyridine-4-carboxylic acid, **L-Br** was synthesized (Scheme 3.4) *via* and THP-protected (2,6-dibromopyridine-4-yl)methanol (**I**)^[162] (2,6-dibromo-4-(tetrahydropyran-2-yloxymethyl)-pyridine, **II**) in four steps similar to a reported procedure for substituted 2,6-di(pyrazol-1-yl)pyridines.^[163] The synthesis step to form the tripyridine was inspired by the reported synthesis of ddpd.^[161] Instead of KHMDS (potassium bis(trimethylsilyl)-amide), which is typically used as base, sodium hydride (NaH) was employed. With NaH, deprotonation can be monitored by gas formation (H₂) and fewer side products were obtained. After full deprotonation of the amine to the amide, the electrophile (**II**) was added. The reaction was performed at lower temperatures (66 °C) than in literature (101 °C) to inhibit the formation of oligomeric side products. Therefore, THF with a lower boiling point than 1,4-dioxane was chosen as solvent. Bromide was introduced in the same step as the protecting group was cleaved, using aqueous hydrobromic acid (48 %). From here, several functional groups can potentially be introduced by nucleophilic substitution of the halide. An azide functionality was introduced in a last step for click reactions with sodium azide as reagent (**L-N₃**). The overall yield starting from 2,6-dibromopyridine-4-carboxylic acid amounts to 16 %. **L-N₃** was characterized by electrospray ionization mass spectrometry (ESI⁺ MS) and NMR spectroscopy (¹H and ¹³C{¹H}). The chemical shifts of the methylene bridge demonstrates the change of substituent from OTHP over Br to N₃ according to their electronic properties (¹H: 4.40/4.65 → 4.23 → 4.24 ppm, ¹³C{¹H}: 67.5 → 35.7 → 54.3 ppm, Fig. S1–S6). In **L-OTHP** the methylene protons couple with



Scheme 3.4: Synthesis scheme for central substituted ddpd in four and five steps to bromide and azide functionality, respectively. For more details see pp. 118.

the THP protons and therefore the signals split. The mass spectra resemble the calculated isotopic patterns (Fig. S7–S9). Characteristic azide stretching appears around 2100 cm^{-1} in the IR spectrum of L-N_3 (Fig. S12). Absorption maxima at 234, 275, 300 (shoulder) and 336 nm in acetonitrile solution are accompanied by a shoulder around 390 nm (Fig. S15). Excitation of L-N_3 gives rise to an emission band peaking at 462 nm. A shoulder at 394 nm resembles the low energy absorption band.

Complex synthesis for homo- and heteroleptic chromium(III) complexes is performed *via* different routes (Scheme 3.5). Homoleptic complexes can usually be synthesized from a substitutionally labile chromium(III) precursor or from a chromium(II) source and subsequent oxidation. To prevent substitution of the azide functionality by halides from the traditional precursor CrCl_2 ,^[136] $\text{Cr}(\text{OTf})_3$ was chosen for the synthesis of $[\text{Cr}(\text{L-N}_3)_2]^{3+}$. Synthesis of heteroleptic chromium(III) complexes is more cumbersome. Introduction of a first tridentate ligand is simple by heating a chromium(III) salt with the corresponding ligand.^[135] Due to the low solubility of the green heteroleptic complexes CrLX_3 (L = tripyridine ligand, X = halide), reaction work up is fairly simple. For halide abstraction from the precursors, silver salts are employed, exploiting the extremely low solubility of silver halides. For the synthesis of $[\text{Cr}(\text{ddpd})(\text{L-N}_3)]^{3+}$, after halide abstraction using microwave irradiation, the reaction mixture was filtered, left over night, and filtered again before adding L-N_3 , to ensure complete precipitation of silver halide, prevent substitution of the azide and silver azide formation. Work up of the complexes from the reaction mixtures was tried *via* crystallization after anion exchange. For $[\text{Cr}(\text{ddpd})(\text{L-N}_3)][\text{BF}_4]_3$ orange needles from an ether diffusion into a concentrated acetonitrile solution were obtained. Crystallization of $[\text{Cr}(\text{L-N}_3)_2][\text{BF}_4]_3$ however failed in the course of this work and only orange to red oily precipitates were obtained.



Scheme 3.5: Synthesis scheme for homoleptic ($[\text{Cr}(\text{L-N}_3)_2]^{3+}$) and heteroleptic ($[\text{Cr}(\text{ddpd})(\text{L-N}_3)]^{3+}$) chromium(III) complexes with azide functionalized ddpd ligand.

ESI⁺-MS spectra of both complexes show expected m/z ranges of isotopic patterns (see Fig. S10–11). In the mass spectrum of $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$, there is no evidence for the formation of a homoleptic *bis*-ddpd or *bis*-L-N₃ complex as side product.

IR spectra of both complexes show the azide stretching frequencies around 2100 cm⁻¹. In line with the electron withdrawing character of the highly charged chromium(III) ion, the frequency is shifted to higher energy by 10 cm⁻¹ compared to the free ligand. The azide stretching amplitudes differ according to the numbers of azide substituents in the complexes compared to the polypyridine (1600–1400 cm⁻¹) and tetrafluoroborate (1050 cm⁻¹) stretching bands (Fig. S13–S14).

Additionally, successful preparation of $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$ and $[\text{Cr}(\text{L}-\text{N}_3)_2]^{3+}$ is confirmed as absorption and emission spectra of both complexes show similar optical properties compared to $[\text{Cr}(\text{ddpd})_2]^{3+}$ (Fig. 3.1). The resemblance with the spectra of $[\text{Cr}(\text{ddpd})_2]^{3+}$ indicate that the electronic properties of the substituted complexes are essentially unchanged compared to the unsubstituted complex. Therefore it can be assumed that the absorption bands around 435 and 300 nm, with a shoulder around 320 nm can be assigned to $^4\text{A}_2 \rightarrow ^4\text{T}_2/^4\text{LMCT}$ and $^4\text{A}_2 \rightarrow ^4\text{T}_1/^4\text{LMCT}$ transitions, respectively.^[136] Excitation of the complexes in solution gives rise to intense dual emission with maxima at 740 and 778 nm, from the doublet manifolds ($^2\text{T}_1/^2\text{E} \rightarrow ^4\text{A}_2$).^[44,142] As the work up did not give pure crystalline or powdered samples, absorption coefficients were not determined. The effects from poor purification of $[\text{Cr}(\text{L}-\text{N}_3)_2]^{3+}$ can be seen in the absorption spectrum deviating from that of $[\text{Cr}(\text{ddpd})_2]^{3+}$, whereas the spectrum of the latter and the spectrum of $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$ match almost perfectly. Excited state decay traces to evaluate the excited state lifetimes, were not recorded.

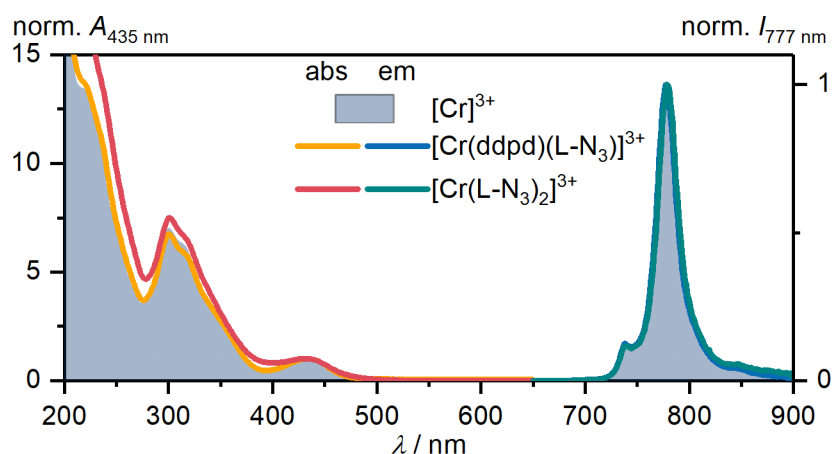


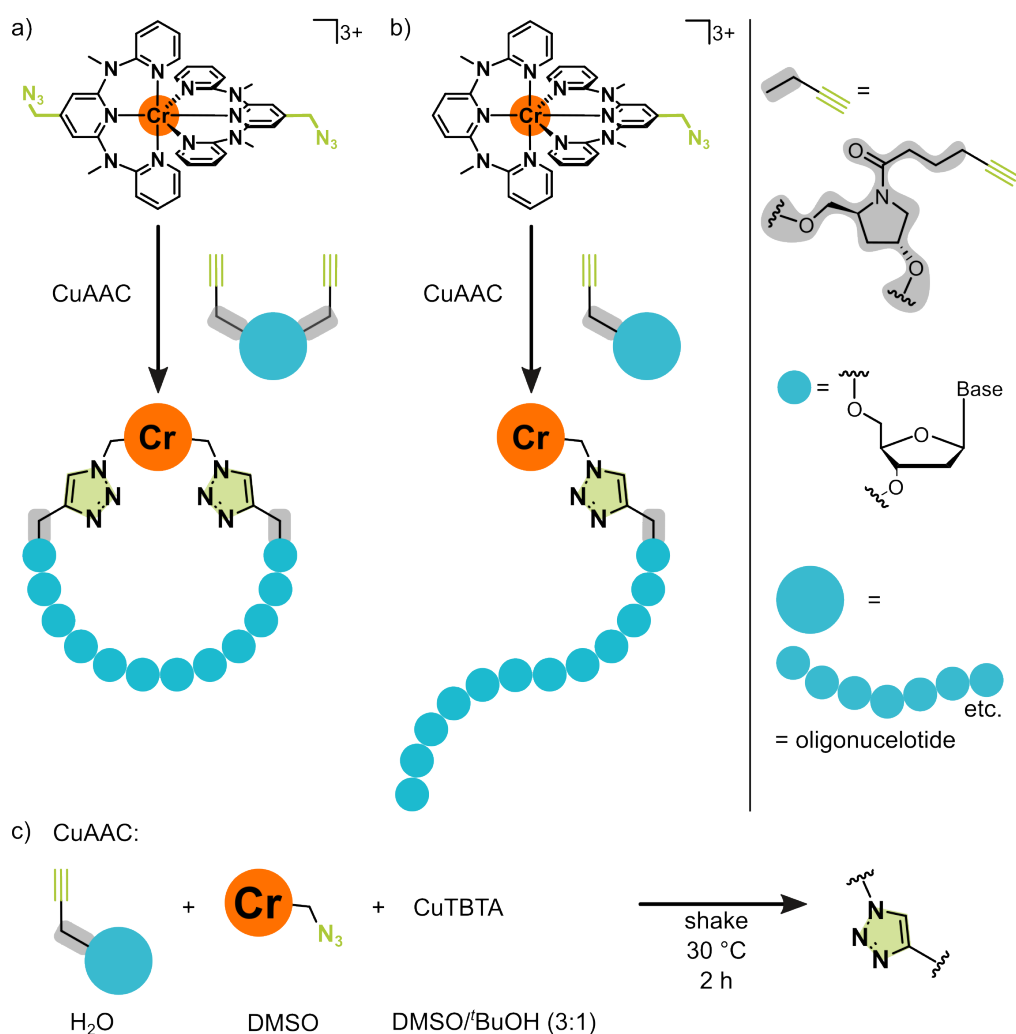
Fig. 3.1: Absorption and emission spectra ($\lambda_{\text{exc}} = 435$ nm) of homoleptic ($[\text{Cr}(\text{L}-\text{N}_3)_2]^{3+}$, red and cyan) and heteroleptic ($[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$, orange and blue) chromium(III) complexes in water. Spectra of $[\text{Cr}(\text{ddpd})_2]^{3+}$ (blue areas) are shown for comparison.

3.3.2 First Application

One idea to use the functionalized chromium(III) complexes is to test them as photolabile protecting group to control RNA interference (RNAi, RNA = ribonucleic acid). Since the discovery of RNAi in 1998^[164] and with insights into its mechanism, interest in this biological process has grown. A few years later, in 2006, the Nobel Prize in Physiology or Medicine was awarded for the "discovery of RNA interference – gene silencing by double-stranded RNA". RNAi acts as a naturally occurring mechanism to suppress certain genes, which is important for defending cells against *e.g.* viruses. Post-transcriptional gene silencing (PTGS) is based on mRNA (m = messenger) degradation and consequent inhibition of protein translation. Research on RNAi is extensive and covers a wide range of applications from medicinal therapeutics to biotechnology.^[165–168] Using artificial siRNA (si = small interfering), specific genes can be targeted and knocked-out. To further exploit the potential of RNAi, control over the mechanism's starting point is necessary, complementary to the spatiotemporal control of the RNA metabolism.^[169] It has been shown, that RNAi can be suppressed by introduction of protecting groups leading to cyclization of the oligonucleotide strand, while their activation can be induced upon irradiation, uncaging of the photolabile protecting group and setting free the siRNA.^[170,171]

Within the scope of this project, functionalized $[\text{Cr}(\text{ddpd})_2]^{3+}$ was introduced as photoactive group to an artificial siRNA, an alkyne substituted oligonucleotide, *via* CuAAC (Scheme 3.6). Synthesis of the functionalized oligonucleotide and the CuAAC reaction was performed by Marlen Saalbach, who is supervised by Prof. Dr. Alexander Heckel at the Goethe University in Frankfurt. Besides acting as protecting group, inhibiting RNAi activity, the molecular ruby would serve as an optical marker in the artificial siRNA. Based on the issues to isolate homoleptic $[\text{Cr}(\text{L}-\text{N}_3)_2]^{3+}$, the proposed cyclized product (Scheme 3.6a) was not synthesized. As proof of principle however, $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$ was clicked to a monofunctionalized oligonucleotide (Scheme 3.6b), yielding $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$ -oligo. The formation was checked by mass spectrometry after HPLC analysis (Fig. S22). Even though the MS data do not precisely coincide with the calculated masses, absorption and emission spectra of aqueous solutions of the product, confirm a successful click reaction and implementation of the molecular ruby (Fig. S23). The spectra show, that attachment of the oligonucleotide does not influence the optical properties of the complex.

With a quite low overall yield and issues concerning purification of the functionalized complexes $[\text{Cr}(\text{L}-\text{N}_3)_2]^{3+}$ and $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$, a first study on photodissociation of $[\text{Cr}(\text{ddpd})_2]^{3+}$ -type complexes was performed using $[\text{Cr}(\text{ddpd})_2]^{3+}$ itself.



Scheme 3.6: Synthesis scheme for CuAAC reaction products of a) homoleptic $[\text{Cr}(\text{L}-\text{N}_3)_2]^{3+}$ and b) heteroleptic $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$ chromium(III) complexes with alkyne functionalized oligonucleotides and c) details on CuAAC reaction protocol (TBTA = tris((1-benzyl-4-triazolyl)methyl)amine).

High-Power Irradiation of a Molecular Ruby

Many studies have shown that the reactivity, *i.e.* photoaquation, of polypyridyl chromium(III) complexes happens from the doublet ESs.^[172,173] Plausible reasons are given for an associative mechanism *via* a ground state intermediate species, which is hepta-coordinate $[\text{CrN}_6(\text{H}_2\text{O})]^{3+}$ and is additionally in line with thermal aquation reactions.^[92,174,175] Others suggested a complementary six-coordinate intermediate with monodentate pyridyl moieties (*i.e.* phenanthroline).^[176] The photoreaction quantum yields (Φ_{rct}) of intensively investigated $[\text{Cr}(\text{bpy})_3]^{3+}$ and $[\text{Cr}(\text{phen})_3]^{3+}$ are independent of the irradiation wavelength but pH dependent (*e.g.* pH 4.3: $\Phi_{\text{rct}} = 0.1\%$, pH 9.6 $\Phi_{\text{rct}} = 15\%$ for bpy complex).^[174,175] Under acidic conditions, this group of complexes is relatively stable (room temperature) towards photosubstitution reactions.^[140,175] It became quite clear that generalizations in terms of photoreactivity are not useful, but rather detailed studies on individual

systems are suggested to understand the photophysics and photochemistry of each complex.^[177]

$[\text{Cr}(\text{ddpd})_2]^{3+}$ is stable in neutral and alkaline air-saturated solutions ($\text{H}_2\text{O}/\text{MeCN}$) under irradiation (LED, 430 nm, 5 h), conditions under which $[\text{Cr}(\text{bpy})_3]^{3+}$ readily dissociates.^[136] Long-term experiments in the same study also showed the stability of $[\text{Cr}(\text{ddpd})_2]^{3+}$ towards high proton concentrations, while it slowly decomposes over time in alkaline solution. To discover possible photolysis pathways, the ES landscape of $[\text{Cr}(\text{ddpd})_2]^{3+}$, which was previously explored in a series of investigations, need to be taken into account.^[44] Insights into ES ordering and dynamics on ultrafast and long timescales were gained through various spectroscopic experiments and are supported by quantum chemical calculations (Fig. 3.2).^[44,117]

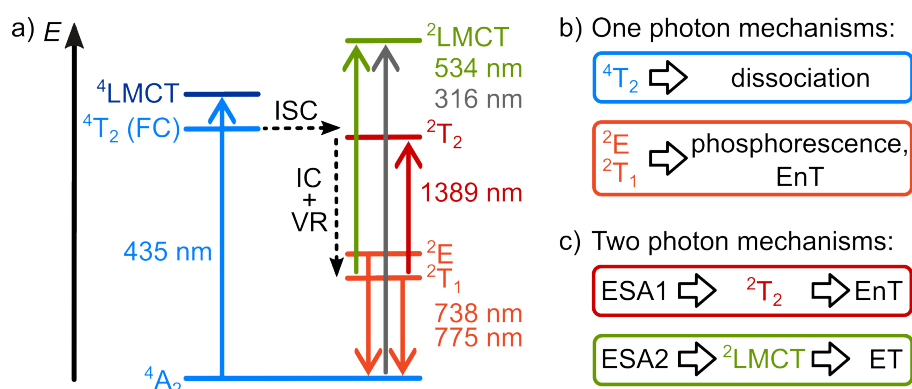


Fig. 3.2: a) Energy diagram of $[\text{Cr}(\text{ddpd})_2]^{3+}$, adapted from ref. [44]. Possible pathways for deactivation after b) one photon or c) two photon excitation (ESA = excited state absorption).

From this research, it is assumed, that photolysis in form of ligand dissociation can in principle occur from the JAHN-TELLER distorted 4T_2 states in a one photon mechanism or from the $^2\text{LMCT}$ state via ET to a substrate. As the long-lived excited doublet states 2E and 2T_1 are populated in less than 3.5 ps and thermally activated bISC is unfeasible in $[\text{Cr}(\text{ddpd})_2]^{3+}$, dissociation will likely not occur directly from the short-lived 4T_2 state. Photooxidation of substrates from the short-lived $^4\text{LMCT}$ or $^2\text{LMCT}$ states could be possible in a static quenching process, resulting in the labile $[\text{Cr}(\text{ddpd})_2]^{2+}$ complex, as has recently been found for a manganese(IV) complex.^[84] This work gives first insights into the photodissociation mechanism of $[\text{Cr}(\text{ddpd})_2]^{3+}$, summarized in a hypothesis about the reaction mechanism. Presented data and results from photolysis experiments are not entirely complete sets of reaction conditions, as they were preliminary experiments to pave the path for further detailed investigations (e.g. different counter ions were used and not all experiments were conducted at the same temperatures).

Photodissociation of $[\text{Cr}(\text{ddpd})_2]^{3+}$ was induced by two different light sources and monitored in two different procedures. High photon fluxes were necessary, as under conventional irradiation $[\text{Cr}(\text{ddpd})_2]^{3+}$ is quite stable.^[136] To observe spectral

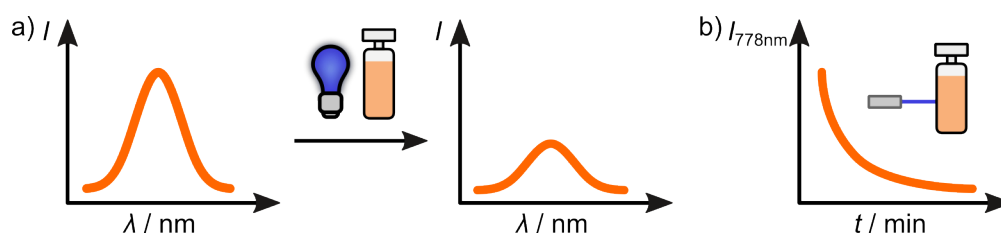


Fig. 3.3: Irradiation procedures: a) alternate measurement of emission spectra and irradiation (UHP LED) and b) continuous photolysis (cw LASER) and emission intensity measurement.

changes in a stepwise fashion, samples of $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ were irradiated with an UHP LED (UHP = ultra high power, $\lambda_{\text{max}} = 456 \text{ nm}$, $\text{FWHM} = 1155 \text{ nm}$, $P = 3.5 \text{ W}$) and absorption as well as emission spectra were recorded in between irradiation times (Fig. 3.3a). Excited state decays were additionally measured to check for the formation of photoproducts which could potentially quench the ESs (Tab. 3.1). This alternate procedure was chosen to detect photoproducts *via* NMR spectroscopy (Fig. S21). To obtain intensity decay traces (Fig. 3.3b), samples of $[\text{Cr}(\text{ddpd})_2][\text{Cl}]_3$ were irradiated with a cw LASER (cw = continuous wave, $\lambda_{\text{max}} = 450 \text{ nm}$, $P = 1 \text{ W}$) while simultaneously recording the emission intensity of the sample ($\lambda_{\text{obs}} = 778 \text{ nm}$). In initial experiments, large variations in intensities were found for the decay curves at lower temperatures (20°C to 40°C). Therefore, irradiation was performed at elevated temperatures (60°C) to decrease this error and to accelerate the overall reaction. Whereas at 80°C in the dark the emission intensity stayed almost constant (Fig. S20), for data interpretation, possible thermally activated secondary pathways for dissociation should be kept in mind. Additionally, all experiments were performed at the same temperature (60°C) to exclude an influence of the varying, temperature-dependent ES LTs of $[\text{Cr}(\text{ddpd})_2]^{3+}$ on the excited state dynamics.^[160] To further minimize influences on the dissociation mechanism, in these experiments chloride was chosen as counterion so that only one kind of anion, especially when adding HCl as proton source, was in solution.

Tab. 3.1: ES LTs of $[\text{Cr}(\text{ddpd})_2][\text{Cl}]_3$ at 60°C before and after irradiation (in parenthesis), irradiation times, and ES LT of $^1\text{O}_2$ at room temperature.^[178] ES LT of dark control reaction at 80°C in water at beginning and end of heating period of 10 min.

solvent	$\tau_{\text{O}_2} / \mu\text{s}$	$t_{\text{irrad}} / \text{min}$	$\tau_{\text{Ar}} / \mu\text{s}$	$t_{\text{irrad}} / \text{min}$	$\tau(^1\text{O}_2) / \mu\text{s}$
MeCN	38 (27)	20	244 (157)	10	30
MeCN + HCl	15 (11)	10	-	-	-
H ₂ O	120 (121)	15	463 (468)	15	2
H ₂ O (80°C)	-	-	146 (145)	-	-
H ₂ O + HCl	120 (121)	15	457 (461)	20	-

Intensity decay traces of $[\text{Cr}(\text{ddpd})_2][\text{Cl}]_3$ show a dependence on the solvent (water or acetonitrile), the pH (neutral or acidic) and the oxygen concentration (atmospheric O_2 pressure, deaerated with Ar). The influences and dependencies of the reaction conditions are attempted to be disentangled in the following.

Solvent: Photolysis was performed in aqueous and acetonitrile solutions (Fig. 3.4g, h, i). Photodissociation of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in acetonitrile solution is faster than in aqueous solution. In acetonitrile, the ES LT of $[\text{Cr}(\text{ddpd})_2]^{3+}$ changes upon irradiation and τ is shorter after irradiation (Tab. 3.1). This supports a hypothesis for the formation of a quencher during the dissociation mechanism. As this effect is not observed in aqueous solutions, it can be assumed that the quencher is deactivated in water. In aqueous solutions (pH 7), the intensity decay trace shows a gradient change in the first few minutes (Fig. 3.4a). Probably, a follow-up reaction takes place which further accelerates the reaction after an initiation phase. In acetonitrile the dissociation seems to be fast enough to outrun this initiation phase.

Oxygen: Irradiation experiments under ambient and deaerated conditions show that O_2 has a relatively small effect on the photodissociation mechanism (Fig. 3.4b, e). Interestingly, in acetonitrile O_2 accelerates dissociation of $[\text{Cr}(\text{ddpd})_2]^{3+}$, whereas it slows down this process in water. Reasons for this opposite effect can presumably be found in the different solubility of O_2 , and the ES LT of $[\text{Cr}(\text{ddpd})_2]^{3+}$ and $^1\text{O}_2$ in the two solvents (Tab. 3.1).^[178,179] Because the oxygen solubility in water is smaller ($0.29 \text{ mmol} \cdot \text{L}^{-1}$) than in acetonitrile ($1.9 \text{ mmol} \cdot \text{L}^{-1}$), quenching of the ^2ES by $^3\text{O}_2$ should be less likely in water. In addition, the probability for diffusion controlled bimolecular follow-up reactions with formed $^1\text{O}_2$ is lower because the ES LT of $^1\text{O}_2$ is shorter in water than in acetonitrile. To interpret this observation, the quenching constants k_q in water and acetonitrile were estimated with two-point STERN- VOLMER plots (ES LTs under aerated (τ) and deaerated (τ_0) conditions and oxygen solubility in the corresponding solvent), using equation 1.3. The quenching constants k_q in water ($k_q = 2.12 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$) and acetonitrile ($k_q = 1.17 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$) are almost similar and indicate that the longer ES LT of $^2[\text{Cr}(\text{ddpd})_2]^{3+}$ in water almost compensates the shorter ES LT of $^1\text{O}_2$ in water.

Presence of protons: Influences of pH changes were investigated by adding aqueous HCl to the complex solutions. Upon addition of acid, the dissociation process becomes slower in water, as well in acetonitrile (Fig. 3.4a and d). Deaerated aqueous solutions show no influence of the pH value on degradation, *i.e.* the intensity decay trace gradient (Fig. 3.4c). The observed initiation phase in neutral aqueous solution is prevented in acidic conditions. This supports the hypothesis that a quencher is formed, which can be removed from the reaction upon protonation. However, this proposed quencher undergoes further reactions and accelerates the dissociation process in pH neutral solutions. With a tenfold increase of acid concentration, degradation apparently accelerates (Fig. 3.4f). A high excess of H^+ could lead to protonation of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in the GS or ES.

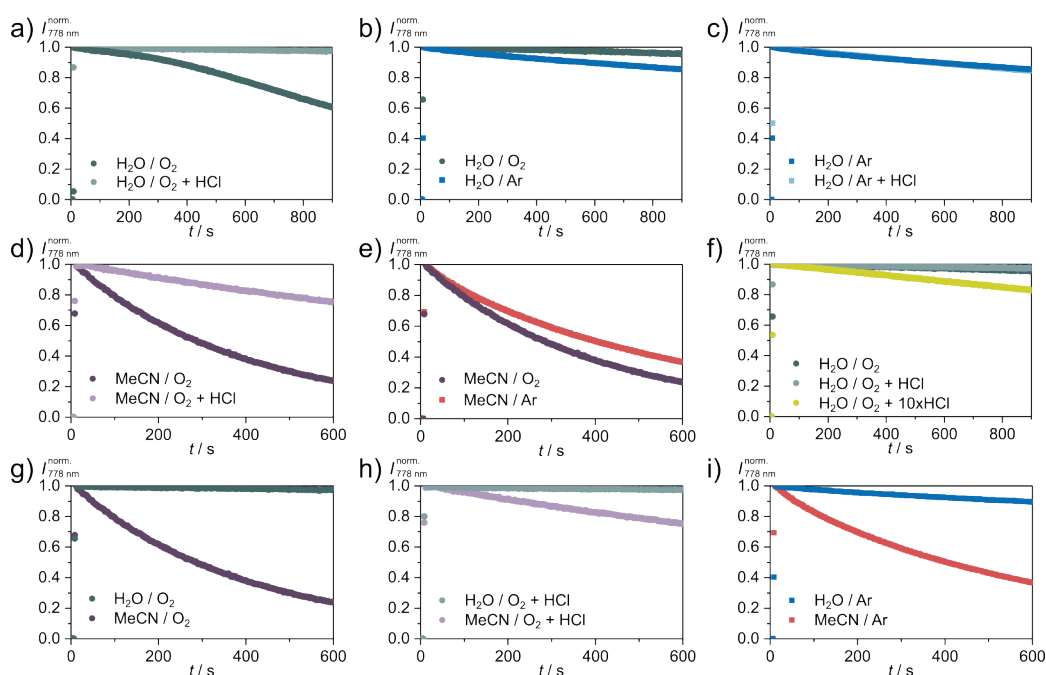


Fig. 3.4: Intensity decay traces of $[\text{Cr}(\text{ddpd})_2][\text{Cl}]_3$ emission under irradiation with CW LASER 450 in water (cyan with O_2 , blue without O_2) and acetonitrile (purple with O_2 , red without O_2) at 60°C . Symbols under acidified conditions (aqueous HCl) marked in lighter colors, excess of acid in green.

Secondary follow-up reactions of ddpd are imaginable and have been observed in similar systems with tertiary amines (Scheme 3.7b and c).^[117,180] Complementary to previously reported data on the photostability of $[\text{Cr}(\text{ddpd})_2]^{3+}$, with extremely high photon fluxes, photoanation products analog to $[\text{Cr}_2(\text{bpy})_4(\mu\text{-OH})_2]^{4+}$ and $\text{Cr}(\text{tpy})(\text{OH})_3$ could be possible ($[\text{Cr}]$ hydroxides in Scheme 3.7).^[76,181]

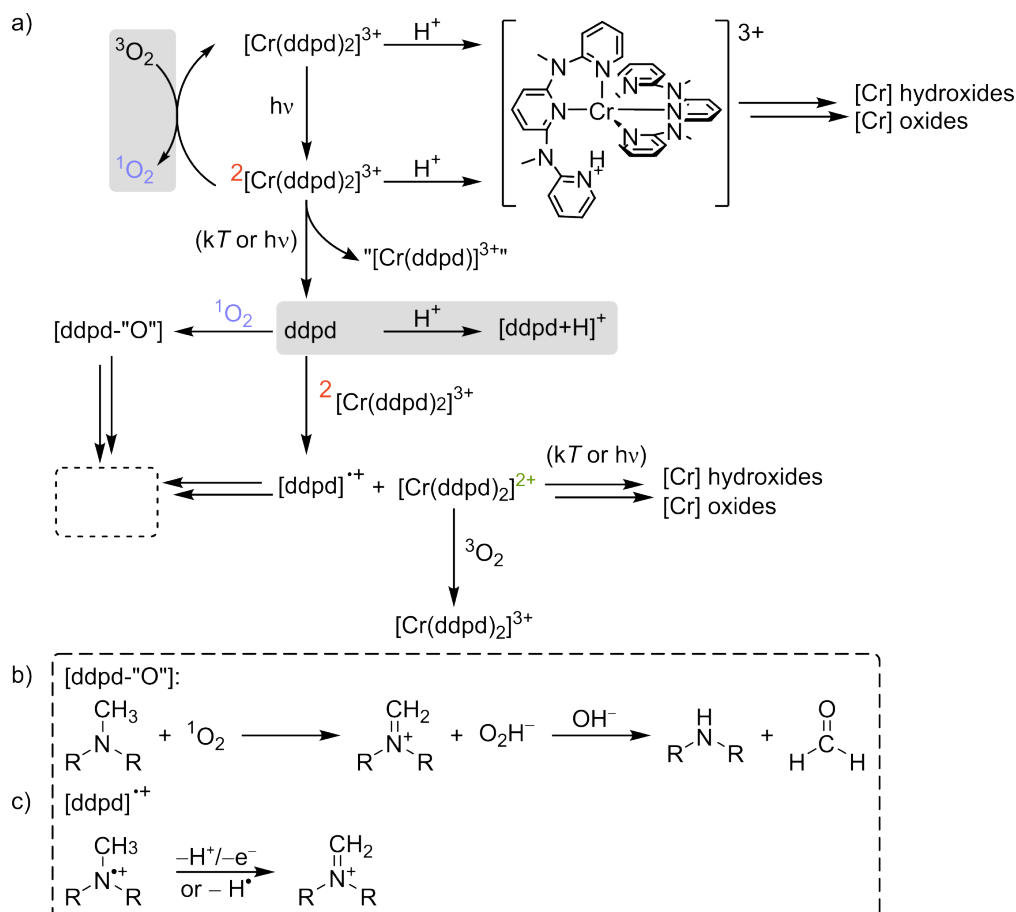
Preliminary NMR experiments showed that one equivalent of ddpd ligand per chromium complex is released upon continuous irradiation of $[\text{Cr}(\text{ddpd})_2]^{3+}$ (UHP LED, $\lambda_{\text{max}} = 456 \text{ nm}$, 2 h, Fig. S21). The spectra were recorded with disodium fumarate as internal standard.

Photolysis of heteroleptic $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$ -oligo was tested as proof of concept in water at 37°C over seven hours. The emission intensity of the $[\text{Cr}(\text{ddpd})_2]^{3+}$ unit decreased under irradiation with blue light of the UHP LED. Investigation of possible photoproducts is part of future research.

The various observations from the current state of investigation and their interpretation lead to the following conclusions, with a working hypothesis for the photodissociation mechanism of $[\text{Cr}(\text{ddpd})_2]^{3+}$, which is summarized in Scheme 3.7:

- Quenching with $^3\text{O}_2$ reduces the photodissociation rate in water compared to degassed samples. Therefore the photodissociative state is either in the $^2\text{E}/^2\text{T}$ manifold, which is efficiently quenched by $^3\text{O}_2$, or in the $^4\text{T}_2$ manifold, which is repopulated from the doublet states.

- Based on the high reactivity of $^1\text{O}_2$ follow-up reactions are likely.^[182]
- A photoproduct, which can accelerate further degradation, is formed. It can either be deactivated by addition of H^+ or undergo follow-up reactions leading to an acceleration of the initial photodissociation rate. Presumably, free ddpd is generated upon photodissociation of $[\text{Cr}(\text{ddpd})_2]^{3+}$ and formation of ddpd is confirmed by NMR spectroscopy.



Scheme 3.7: Possible pathways for the photodissociation mechanism of $[\text{Cr}(\text{ddpd})_2]^{3+}$ and possible follow-up reactions. Most relevant steps are indicated with grey boxes.

3.3.3 Conclusion and Outlook

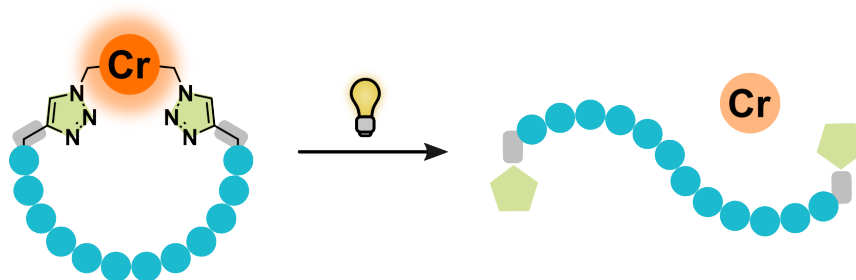
The combined results from this study lay the foundation for future projects. They give first insights on attachment opportunities of molecular rubies to various substrates for applications and into the photostability and photodissociation mechanism of $[\text{Cr}(\text{ddpd})_2]^{3+}$.

On the synthetic side, other substituents, starting from **L-OTHP** or **L-Br** can be introduced (THP = tetrahydropyran). After deprotection of **L-OTHP** and oxida-

tion of the free alcohol (e.g. KMnO_4), a carboxy substituent ($-\text{COOH}$) would for example be feasible, which is beneficial for surface attachment *via* condensation reactions.^[183] In the long run, ligand synthesis needs improvement to increase the overall yield.

While the heteroleptic complex $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$ could be isolated as orange needles, purification was quite challenging. Isolation of powdered or crystalline homoleptic complex $[\text{Cr}(\text{L}-\text{N}_3)_2]^{3+}$ was not possible in this work. The synthesis is in principle possible, as evident from the crude product's similar absorption and emission spectra compared to $[\text{Cr}(\text{ddpd})_2]^{3+}$. A new approach with fresh and acid free $\text{Cr}(\text{OTf})_3$ should be tested. For purification and crystallization, counter ion exchange to e.g. $[\text{OTf}]^-$ or $[\text{PF}_6]^-$ should be tested, depending on the application and further synthetic step requirements.

As proof of principle, mono-azide functionalized $[\text{Cr}(\text{ddpd})(\text{L}-\text{N}_3)]^{3+}$ was clicked to an alkyne functionalized synthetic oligonucleotide. In future projects, cyclization of oligonucleotides with difunctionalized $[\text{Cr}(\text{L}-\text{N}_3)_2]^{3+}$ and subsequent photorelease of chromium are to be tested for application in RNAi. Based on the findings from photolysis experiments with $[\text{Cr}(\text{ddpd})_2]^{3+}$, formation of the free oligonucleotide (plus triazole-ddpd moiety) and a non-emissive chromium species is expected, upon irradiation of the chromium-oligonucleotide (Scheme 3.8). HPLC combined with mass spectrometry could give insights into photoproducts.



Scheme 3.8: Reaction scheme of light driven cleavage of luminescent chromium(III) complex and cyclized oligonucleotide, yielding free, linear oligonucleotide and a non-emissive chromium species.

The photodissociation mechanism of $[\text{Cr}(\text{ddpd})_2]^{3+}$ needs to be investigated in more detail and the irradiation experiments performed so far need to be complemented by additional spectroscopic investigations (absorption and emission spectroscopy, mass spectrometry and HPLC) to ensure reproducibility. While it is crucial for application in RNAi to find out and know how to efficiently cleave $[\text{Cr}(\text{ddpd})_2]^{3+}$, for other applications it is important to avoid these conditions.

The preliminary results from this study show a dependence of the dissociation rate on the solvent, proton as well as oxygen concentration, and oxidizable substrates. A STERN-VOLMER study with suitable substrates, e.g. amines, should give further insights. In a first instance, additional ddpd should be tested. Based on the working hypothesis (Scheme 3.7), the oxidation potential of $^2[\text{Cr}(\text{ddpd})_2]^{3+}$ ($E^*(\text{Cr}^{3+/2+}) =$

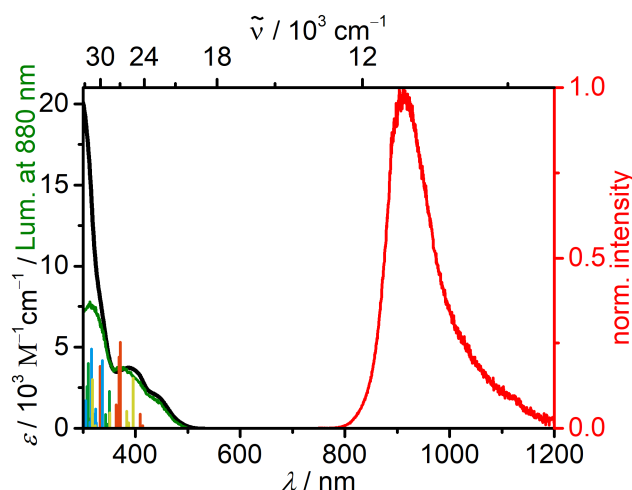
0.49 V vs. ferrocene)^[136] would need to fit the substrate (e.g. free ligand), for efficient acceleration of the dissociation process *via* this redox event. With its redox potential of 0.55 V vs. ferrocene (MeCN),^[184] oxidation of ddpd should be feasible. Furthermore, a deeper understanding on the proton concentration would be beneficial. For this, the pK_a value of ddpd should be determined. While it is already evident that high proton concentrations slow down the dissociation of [Cr(ddpd)₂]³⁺, by preventing follow-up reactions, the influence of alkaline conditions under irradiation need to be investigated. Of course, control experiments in the dark need to be performed to elucidate the influence of each variable in the absence of light and irradiation at different temperatures should give insight into thermally activated pathways. Furthermore, studies on the dark states, *i.e.* ²T₂ and ²LMCT, need to be performed to figure out if [Cr(ddpd)₂]³⁺ dissociation is a one or two photon process (Fig. 3.2). This can be achieved with varying irradiation power and TA spectroscopy.

All in all, the photodegradation mechanism of [Cr(ddpd)₂]³⁺ seems to be complex with an interplay of different pathways.

3.4 The Overlooked NIR Luminescence of $\text{Cr}(\text{ppy})_3$

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Chromium(III) complexes typically show spin-flip luminescence between 670 nm and 780 nm. With an enhanced M–L ($\text{Cr}-\text{C}^-$) bond covalency, the spin-flip emission of *fac*- $\text{Cr}(\text{ppy})_3$ is shifted above 900 nm. The strong nephelauxetic effect was correctly predicted by CASSCF-NEVPT2 calculations.

Author Contributions

Laura Stein performed the synthesis, characterization, quantum chemical calculations and visualized the data. Laura Stein and Robert Naumann performed emission spectroscopy experiments. Pit Boden performed step-scan FTIR experiments and luminescence spectroscopy in KBr pellets, supervised by Gereon Niedner-Schatteburg. Christoph Förster solved and refined the crystal structure. Katja Heinze conceptualized the study and wrote the manuscript.

Supporting Information

for this article can be found on pp. 136.

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The overlooked NIR luminescence of Cr(ppy)₃[†]

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Gereon Niedner-Schatteburg^b and Katja Heinze^{a*}

Cr(ppy)₃, a structural analog of the green phosphorescent Ir(ppy)₃, emits even in solution at room temperature from a weakly distorted spin–flip state at 910 nm (Hppy = 2-phenylpyridine). The low energy arises from an enhanced covalence of the Cr–C bonds as compared to Cr–N bonds. Lower temperature reduces thermally activated decay increasing the emission intensity.

Cyclometalated complexes, in particular of d⁶ metal ions such as Ru^{II},^{1,2} Ir^{III},^{3,4} or Fe^{II},^{5–7} possessing intense metal-to-ligand charge transfer (MLCT) absorptions, have shaped the field of organometallic photochemistry. The prototypical complex *fac*-Ir(ppy)₃ (Hppy = 2-phenylpyridine)^{8,9} with its intense green ³MLCT luminescence has paved the way to efficient luminescent materials for PHOLED applications,^{10,11} while cyclometalated Ru^{II} complexes are less luminescent.^{1,2} The first reported cyclometalated Fe^{II} counterparts are even non-luminescent^{5,6} and a phosphorescent iron(II) complex was reported only recently.⁷ In all d⁶ cases, ^{1/3}MLCT states play key roles for absorption and emission, while highly distorted metal centered excited triplet/quintet states (^{3/5}MC) provide non-radiative decay pathways in Ru^{II} and Fe^{II} complexes, which hamper efficient ³MLCT luminescence.^{1,10} Novel developments in the field of Earth-abundant complex chromophores beyond precious metal phosphors led to a paradigm change.^{12–16} Beside CT states, metal-centered spin–flip excited states can be highly luminescent between 709–775 nm as demonstrated with polypyridine Cr^{III} complexes.^{17–22} A higher covalent bonding in a carbazolato pyridine Cr^{III} complex [Cr(dpc)₂]⁺ (dpc = 3,6-di-*tert*-butyl-1,8-di(pyridine-2-yl)-carbazolato) shifted the emission to

lower energy ($\lambda_{\text{em}} = 1067 \text{ nm}$, 77 K). However, this went along with a poor quantum yield ($\Phi < 0.00089\%$).²³

We investigate the effect of cyclometalation on the spin–flip emission of Cr^{III} reporting the structure and photophysical properties of Cr(ppy)₃ as a 3d³ structural analog of the 5d⁶ complex Ir^{III}(ppy)₃.^{8,9} Cr(ppy)₃ was first prepared in 1967 by treating CrCl₃·3THF with 2-(*ortho*-lithiophenyl)pyridine²⁴ and later (1991) by treating CrPh₃(thf)₃ with 2-phenylpyridine.²⁶ Despite its existence for decades, neither the stereochemistry, nor emission properties of Cr(ppy)₃ were reported.^{24,26}

Single crystals of the facial isomer *fac*-Cr(ppy)₃ suitable for X-ray diffraction (XRD) analysis were obtained after heating CrPh₃(thf)₃ with 2-phenylpyridine in THF and recrystallisation from CH₂Cl₂/toluene (Fig. 1). *fac*-Cr(ppy)₃ crystallised in the tetragonal space group *P*4₂*c* as *fac*-Ir(ppy)₃ obtained from sublimation,²⁷ while Ir(ppy)₃ crystallised from solution as twinned crystals in the trigonal space group *P*3̄, resulting in superimposed Ir-coordinated C/N positions.²⁸

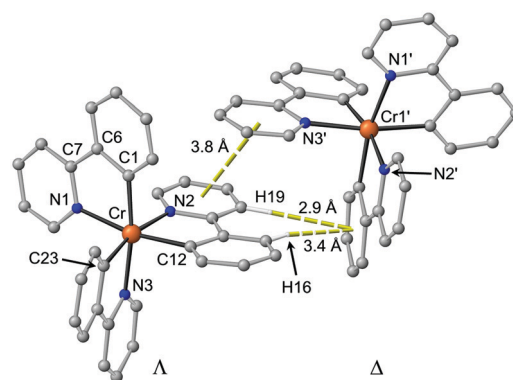


Fig. 1 Molecular structure of *fac*-Cr(ppy)₃ in the solid state with $\pi \cdots \pi$ and $\text{CH} \cdots \pi$ contacts between Δ and Λ isomers shown as yellow dashed lines. Hydrogen atoms (except those involved in $\text{CH} \cdots \pi$ contacts) are omitted for clarity. The $\pi \cdots \pi$ contact is denoted by the distance between ring centroids. $\text{CH} \cdots \pi$ contacts are denoted by the distance from the hydrogen atom to the ring centroid.

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[†] Electronic supplementary information (ESI) available. CCDC 2124885. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d2cc00680d



In the present XRD analysis, the C/N assignment and the facial configuration were confirmed by inspection of the thermal ellipsoids of the atoms of the alternative assignment and the resulting *R* factors. The Cr–C distances are shorter than the Cr–N distances ($d_{\text{av}}(\text{Cr–C}) = 2.059(2)$ Å, $d_{\text{av}}(\text{Cr–N}) = 2.145(2)$ Å; ESI,† Table S1 and Fig. S1). The Cr–N distances in $[\text{Cr}(\text{bpy})_3]^{3+}$ $[\text{PF}_6]_3$ (bpy = 2,2'-bipyridine; $d(\text{Cr–N}) = 2.042(5)$ Å) are significantly smaller, substantiating a trans influence of the carbon donor in *fac*-Cr(ppy)₃. Quantum chemical calculations yield $d(\text{Cr–C}) = 2.063$ Å and $d(\text{Cr–N}) = 2.146$ Å in very good agreement with the XRD data (ESI,† Table S1 and Fig. S1). The geometry of the $[\text{CrC}_3\text{N}_3]$ coordination sphere in *fac*-Cr(ppy)₃ is close to octahedral, similar to the $[\text{CrN}_6]$ coordination of $[\text{Cr}(\text{bpy})_3]^{3+}$ (ESI,† Table S2). $\pi \cdots \pi$ and $\text{CH} \cdots \pi$ contacts are observed between Δ and Λ isomers in the solid state of *fac*-Cr(ppy)₃ (Fig. 1), while no such contacts appear in the salt $[\text{Cr}(\text{bpy})_3][\text{PF}_6]_3$.²⁹ Analytical data of *fac*-Cr(ppy)₃ are compiled in the ESI† (Fig. S3 and S4).

While polypyridine Cr^{III} complexes are reduced either at the ligand to give radical anions or at the metal center to give Cr^{II},^{17,20,22,30,31} *fac*-Cr(ppy)₃ is not reduced up to potentials of -2.2 V vs. ferrocene (ESI,† Fig. S3), likely due to the electron-rich ppy[−] ligand. An irreversible oxidation is observed at a peak potential $E_p = +0.24$ V vs. ferrocene, which is assigned to an oxidation of the Cr-aryl moiety with a covalent Cr–C bond.

The optical properties of *fac*-Cr(ppy)₃ were probed in solution and in the solid state (ESI,† Fig. S5–S10). The absorption band at 440 nm ($\epsilon = 3000 \text{ M}^{-1} \text{ cm}^{-1}$ in CH_2Cl_2 , Fig. 2a) and around 450 nm in a KBr pellet (ESI,† Fig. S7) is assigned to transitions with ILCT/MLCT character (calcd. at 414 nm, $f = 0.0016$ (E); 409 nm, $f = 0.0041$ (A)) according to time-dependent DFT calculations and CT number analyses (Fig. 2a; ESI,† Fig. S2).^{32,33} The energetically next higher absorption band possesses a larger MLCT character (calcd. at 395 nm, $f = 0.0294$ (E); 387 nm, $f = 0.0016$ (A)) while the largely metal centered $^4\text{T}_2$ states are calculated at 350/348 nm ($f = 0.0108/0.0025$ (A/E)). The MLCT bands are responsible for the yellow-orange colour of the complex (Fig. 2b, inset). Excited states with MLCT/ILCT character are compatible with the oxidation of *fac*-Cr(ppy)₃ at $E_p = 0.24$ V and the reduction below -2.2 V vs. ferrocene (ESI,† Fig. S3), similar to the redox processes assigned for *fac*-Ir(ppy)₃ at 0.31 and -2.7 V in DMF.³⁴

Excitation of *fac*-Cr(ppy)₃ dissolved in deaerated 2-MeTHF or CH_2Cl_2 at 293 K results in sharp emission bands peaking at 910 nm with $\text{FWHM}_{293\text{K}} \approx 1185/1068 \text{ cm}^{-1}$, respectively (Fig. 2b; ESI,† Fig. S5). The band shifts to 890 nm and sharpens to $\text{FWHM}_{77\text{K}} \approx 540 \text{ cm}^{-1}$ at 77 K in frozen 2-MeTHF, revealing some fine structure (890, 910 (sh), 1020 (sh) nm). The integrated emission intensity increases *ca.* fivefold (Fig. 2b). The excitation spectra at 298 and 77 K in 2-MeTHF solution follow the absorption spectrum (ESI,† Fig. S6). This confirms that the emission arises from initially excited ILCT/MLCT states (350–500 nm) of *fac*-Cr(ppy)₃, which efficiently evolve to the emissive state in 2-MeTHF (ESI,† Fig. S6a). This also holds for excitation and emission properties in CH_2Cl_2 at 293 K (ESI,† Fig. S5 and S6b) and in the solid state (ESI,† Fig. S7). The

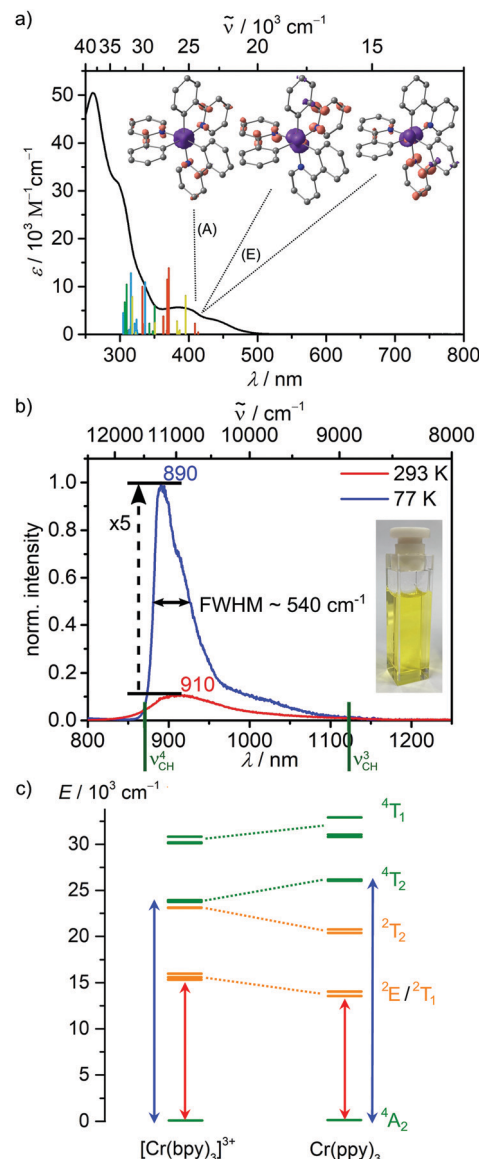


Fig. 2 (a) UV/Vis absorption spectrum of *fac*-Cr(ppy)₃ (black) in CH_2Cl_2 at 293 K including TD-DFT calculated transitions. The code indicates the character of the transition according to CT number analysis (green: MC, red: ILCT yellow: MLCT, orange: LMCT, blue: LLCT) and difference densities of the three lowest energy transitions (E and A, isosurface at 0.005 a.u., purple = electron depletion, orange = electron gain). (b) Emission spectra of *fac*-Cr(ppy)₃ in 2-MeTHF at 293 K (red) and 77 K (blue) ($\lambda_{\text{exc}} = 420$ nm) with the energies of CH overtones¹⁹ ν^3 and ν^4 indicated in green and a photograph of *fac*-Cr(ppy)₃ in 2-MeTHF (inset). (c) Quartet (green) and doublet (orange) energy levels of $[\text{Cr}(\text{bpy})_3]^{3+}$ and *fac*-Cr(ppy)₃ from CASSCF(7,12)-NEVPT2 calculations showing the increased ligand field splitting (blue arrows) and decreased spin-flip state energy (red arrows) for *fac*-Cr(ppy)₃ (labels according to octahedral symmetry, although the actual symmetry is lower).

luminescence lifetimes at 293 and 77 K in 2-MeTHF amount to 9.5 and 48 μs , respectively and to 9.3 μs in CH_2Cl_2 at 293 K (ESI,† Fig. S8 and S9). In the powder the decay is biexponential with 10 μs (76%) and 3 μs (24%) (ESI,† Fig. S10), possibly due to energy migration in the solid *via* the $\pi \cdots \pi$ and $\text{CH} \cdots \pi$ contacts (Fig. 1) as has been observed *e.g.* for Ir(ppy)₃.^{35,36}



Nanosecond laser flash photolysis experiments of *fac*-Cr(ppy)₃ in Ar-saturated CH₂Cl₂ yielded a transient absorption (TA) spectrum with excited state absorptions (ESA) throughout the visible region, superimposed to the ground state bleach below 500 nm (ESI,† Fig. S11). The TA spectrum of *fac*-Cr(ppy)₃ differs from reported TA spectra of pyridine and acetylacetonato Cr^{III} complexes displaying only a single ESA around 520–540 nm.^{22,37–40} The apparent ESA bands at 485 nm and 640 nm decay monoexponentially with $\tau = 10.2 \mu\text{s}$ and $9.9 \mu\text{s}$, respectively (ESI,† Fig. S11 and S12), in agreement with the luminescence decay.

Compared to [Cr(bpy)₃]³⁺ ($\lambda_{\text{em}} = 729 \text{ nm}$, HCl_{aq}),⁴¹ the spin-flip emission band of *fac*-Cr(ppy)₃ is bathochromically shifted by $\approx 2730 \text{ cm}^{-1}$. CASSCF(7,12)-NEVPT2 calculations on geometry-optimised [Cr(bpy)₃]³⁺ and *fac*-Cr(ppy)₃ complexes correctly predict the bathochromic shift of the spin-flip luminescence (1773 cm^{-1} ; Fig. 2c; ESI,† Table S5). With respect to the carbazolato pyridine Cr^{III} complex [Cr(dpc)₂]²⁺²³ the luminescence band of *fac*-Cr(ppy)₃ appears at higher energy by $\approx 1860 \text{ cm}^{-1}$ (77 K). Obviously, the combination of σ/π -donating carbanionic donors and π -accepting pyridines along all axes *x*, *y* and *z* in *fac*-Cr(ppy)₃, achieves a metal–ligand bond covalence in-between that of [Cr(bpy)₃]³⁺⁴¹ and [Cr(dpc)₂]²⁺.²³

Contrary to [Cr(dpc)₂]²⁺ emitting only at 77 K,²³ *fac*-Cr(ppy)₃ emits at 293 K in fluid 2-MeTHF or CH₂Cl₂ ($\Phi = 0.03\%$ in CH₂Cl₂; $\Phi = 0.02\%$ as powder). Although these quantum yields are still below the record values of molecular rubies of up to $\Phi = 20\%$ in solution,^{17–22} this marks a great advancement for open-shell complexes made from abundant transition metals emitting in the NIR region above 800 nm in fluid solution.

As the quantum yields increase at lower temperature, a thermally activated decay pathway is likely operative.⁴¹ For the tris(bidentate) Cr^{III} complex [Cr(bpy)₃]³⁺ ($\Phi = 0.25 \pm 0.02\%$, $\tau = 69 \pm 2 \mu\text{s}$ in 1 M HCl at 296–297 K) an activation barrier for thermal non-radiative deactivation of $43 \pm 1 \text{ kJ mol}^{-1}$ has been determined.⁴¹ A thermally activated trigonal twist has been suggested as possible non-radiative pathway for tris(bidentate) quasi-cage Cr^{III} complexes.⁴² Compared to the rather flexible bpy ligand in [Cr(bpy)₃]³⁺, the more rigid 1,10-phenanthroline ligand phen endows a higher Φ and τ in [Cr(phen)₃]³⁺ ($\Phi = 1.2 \pm 0.1\%$, $\tau = 304 \pm 4 \mu\text{s}$ in 1 M HCl at 296–297 K).⁴¹ Therefore, trigonal twisting and intraligand torsional modes might be operating in the excited *fac*-Cr(ppy)₃ complex as well, leading to thermally activated surface crossing. This implies that the relaxed excited doublet state is distorted relative to the ground state (see below).

Non-radiative multiphonon relaxation, *i.e.* electronic to vibrational energy transfer to overtones of high-energy oscillators, such as C–H modes, might not be very important for *fac*-Cr(ppy)₃ as the relevant overtones determined from a model ligand (Me₂-bpy; $\nu^3 = 8792 \text{ cm}^{-1}$ (1137 nm) and $\nu^4 = 11493 \text{ cm}^{-1}$ (870 nm))¹⁹ possess only a small spectral overlap with the emission band of *fac*-Cr(ppy)₃ at 910 nm (Fig. 2b). A further non-radiative pathway involving back-intersystem crossing to the metal centred quartet states appears unlikely as well, considering the strongfield ligand ppy[−]. TDDFT and CASSCF(7,12)-NEVPT2 calculations suggest an even larger

ligand field splitting (energy difference between ⁴T₂ and ⁴A₂ states) in *fac*-Cr(ppy)₃ than in [Cr(bpy)₃]³⁺ (by 2285 cm^{-1} ; Fig. 2c). Finally, energy transfer between uncharged *fac*-Cr(ppy)₃ complexes in solution and in the solid is a possible self-quenching pathway mediated by $\pi \cdots \pi$ and CH $\cdots\pi$ contacts (Fig. 1), while self-quenching of charged Cr^{III} complexes requires high chloride concentrations to form ion clusters in solution.^{43,44}

To obtain information on the potential distortion of the excited doublet state, step-scan FTIR spectra of *fac*-Cr(ppy)₃ were collected (KBr pellet, $\lambda_{\text{exc}} = 355 \text{ nm}$, 20 K). The spectra display ESA and bleaching bands (ESI,† Fig. S13a). The excited state FTIR spectrum consequently differs from the ground state spectrum (ESI,† Fig. S13b), confirming that the long-lived doublet state is distorted with respect to the ground state. At 20 K in KBr, this doublet state decays monoexponentially with $\tau = 9.8 \mu\text{s}$, as derived from a global fit of decay traces at 1286, 1397, 1442, 1461 and 1475 cm^{-1} (ESI,† Fig. S14 and Table S3). DFT geometry optimisations and frequency analyses (ESI,† Fig. S15 and S16) substantiate that the lowest energy doublet state is indeed distorted relative to the quartet ground state: Cr–C and Cr–N distances change from $2.063 \text{ \AA}$ to 2.044 , 2.053 and $2.055 \text{ \AA}$ and from $2.146 \text{ \AA}$ to 2.138 , 2.147 , $2.153 \text{ \AA}$, respectively, while the X–Cr–Y angles remain rather constant (ESI,† Fig. S17 and Table S1). In agreement with the experimentally obtained data, the DFT calculated vibrational frequencies for the quartet ground and the excited doublet state show similar shifts in energy (ESI,† Fig. S15 and S16, calculated frequencies scaled by 0.975).

The NIR luminescence of *fac*-Cr(ppy)₃ recorded in a KBr pellet between 290–5 K strongly increases below 100 K (ESI,† Fig. S18). While in solution the emission intensity increases *ca.* fivefold already at 77 K (Fig. 2b), the gain in intensity of the KBr pellet starts below *ca.* 80 K. This is compatible with a distorted excited state, which decays by thermal activation to the ground state. While the energy barriers appear higher in rigid matrices thanks to less distorted and hence more nested excited states the temperature dependence in frozen 2-MeTHF and KBr matrices is different (Fig. 2b, ESI,† Fig. S18).

Complexes *cis*-[Cr(bpy)₂(Ar)₂]⁺ reductively eliminate Ar–Ar under irradiation,⁴⁵ while *fac*-Cr(ppy)₃ is photostable in 2-MeTHF ($\lambda_{\text{exc}} = 420 \text{ nm}$, ESI,† Fig. S19) thanks to the absence of *cis*-positioned Ar ligands. Similarly, *trans*-[Cr(cyclam)(C $\equiv$ C–C₆H₄R)₂]⁺ appear to be photostable.⁴⁶ In CH₂Cl₂, some photoreactivity is observed for *fac*-Cr(ppy)₃ (ESI,† Fig. S20). Rather than photoreduction of CH₂Cl₂ itself ($E = -2.6 \text{ V}$)⁴⁷ by the excited complex ($E(^* \text{Cr(ppy)}_3 / [\text{Cr(ppy)}_3]^+) = -1.12 \text{ V}$), which is thermodynamically unfavourable, traces of HCl in the CH₂Cl₂ could lead to irreversible photooxidation of ^{*}Cr(ppy)₃ (ESI,† Fig. S3) and H⁺ reduction. Photo- and redox stable cyclometalated Cr^{III} complexes might be developed into useful photoreductants in the future.

fac-Cr(ppy)₃ is the first Cr^{III} spin-flip emitter with emission above 900 nm in solution at 293 K. The effect of carbanionic donors in place of pyridine donors is two-fold, namely the increase in energy of the metal centred quartet states, owing to



the larger ligand field strength, and the decrease of the energy of the spin-flip states, owing to the stronger Cr–C bond covalence (nephelauxetic effect). These insights on the photo-physics of the cyclometalated Cr^{III} complex *fac*-Cr(ppy)₃ are complementary to recent discoveries for first row transition metal CT emitters^{7,48–54} and demonstrate that fundamental ground-breaking studies can pave the way to fully exploiting Earth-abundant metals, *e.g.* in light harvesting, sensing, photocatalysis and optical devices.

K. H. designed the project and wrote the paper, L. S. and R. N. performed synthesis, characterization and DFT, P. B. and G. N. S. step-scan FTIR spectroscopy and luminescence in KBr.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

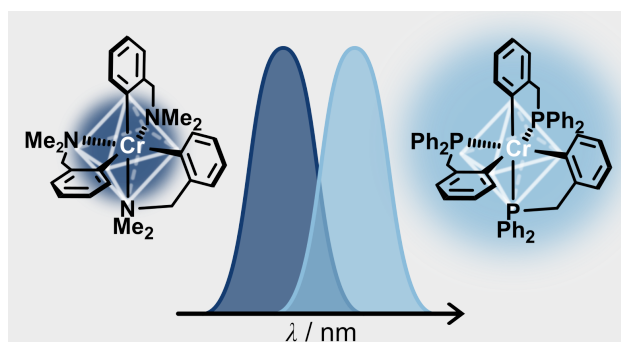
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3.5 Luminescent Cyclometalated Chromium(III) Complexes

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Cyclometalated amine and phosphane complexes were investigated towards their nephelauxtic effect and compared to *fac*-Cr(ppy)₃. Emission signals of the amine and phosphane complex peak at 765 nm and 865 nm, respectively. The phosphane complex shows a solvent-dependent equilibrium between the six-coordinate and a five-coordinate species, which was investigated using ³¹P-NMR spectroscopy. Both complexes are non-emissive at room temperature. With bidentate and flexible ligands, thermally activated pathways facilitate non-radiative decay. A short series for interelectronic interaction was established: NR₃ > py ≈ PR₃ > Ph[−].

Author Contributions

Laura Stein performed the syntheses, characterization, spectroscopic experiments, quantum chemical calculations, visualized the data and wrote the original draft. Christoph Förster solved and refined the crystal structures. Katja Heinze supervised the project and revised the manuscript.

Supporting Information

for this article can be found on pp. 158. Cartesian coordinates of calculated DFT-structures are found online at: <https://doi.org/10.1021/acs.organomet.4c00075>.

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1 Luminescent Cyclometalated Chromium(III) Complexes

2 Laura Stein, Christoph Förster, and Katja Heinze*

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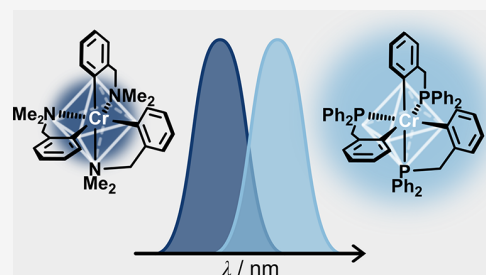


Article Recommendations



Supporting Information

ABSTRACT: Tris(cyclometalated) chromium(III) complexes *fac*-Cr(C[^]X)₃ with dimethylamine (X = NMe₂, *fac*-1) and diphenylphosphane (X = PPh₂, *fac*-2) donors were fully characterized by single crystal X-ray structure analyses, cyclic voltammetry, and absorption/emission spectroscopy. Both complexes are luminescent in the near-infrared spectral region in the solid state or in frozen solution. The phosphane complex *fac*-2 is hemilabile and forms a weakly emissive, five-coordinate complex with a dangling PPh₂ donor in fluid solution. Spectroscopic assignments are aided by quantum chemical calculations at the DFT and CASSCF/NEVPT2 levels of theory. *fac*-1 and *fac*-2 complement the cyclometalated pyridine complex *fac*-Cr(ppy)₃ (ppy⁻ = deprotonated 2-phenylpyridine) and allow establishment of a nephelauxetic series of aryl, pyridine, phosphane, and amine donors.



14 ■ INTRODUCTION

15 An outstanding property of pseudooctahedral chromium(III) complexes is their long-lived photoluminescence (PL) in the 16 red–near-infrared (NIR) spectral region,^{1–6} which enables 17 application in sensing of oxygen, pressure, temperature, or 18 pH.^{7–10} Furthermore, the high oxidation potential in their 19 long-lived excited states allows for oxidatively induced 20 photoredox catalysis, for example, with [Cr(bpy)₃]³⁺ deriva- 21 tives (Scheme 1; bpy = 2,2′-bipyridine).^{11–15} With the (t_{2g})³ 22 electron configuration of Cr^{III} in an octahedral ligand field, the 23 intraconfigurational emissive doublet excited states ((t_{2g})³; 24 ²E/²T₁; in octahedral symmetry) are only very weakly distorted 25 compared to the quartet ground state (⁴A₂) leading to sharp 26 spin-flip emission bands.⁴ These sharp bands contrast the 27 rather broad emission profiles from charge transfer states, as 28 seen for example from [Ru(bpy)₃]²⁺ or *fac*-Ir(ppy)₃ metal-to- 29 ligand charge transfer emitters (ppy⁻ = deprotonated 2- 30 phenylpyridine).⁶

31 As the ⁴A₂ ← ²E/²T₁ spin-flip emission is spin- and Laporte- 32 forbidden, the PL lifetimes (τ) are often very high up the 33 millisecond range.¹⁶ Much effort has been devoted to increase 34 the photoluminescence (PL) quantum yield (Φ) and PL 35 lifetime of chromium(III) complexes with record values of Φ = 36 30% and τ = 4500 μs achieved with complexes of tridentate 37 polypyridine ligands forming six-membered chelate rings.^{2,4,17} 38 The so-called molecular rubies, with [Cr(ddpd)₂]³⁺ as the 39 parent complex,¹⁰ meanwhile comprise a series of highly 40 emissive polypyridyl chromium(III) complexes, e.g., [Cr- 41 (H₂tpda)₂]³⁺ (H₂tpda = 2,6-bis(2-pyridylamino)pyridine),¹⁸ 42 [Cr(dqp)₂]³⁺ (dqp = 2,6-di(quinolin-8-yl)pyridine),¹⁹ [Cr- 43 (tpe)₂]³⁺ (tpe = 1,1,1-tris(pyrid-2-yl)ethane),¹⁶ or [Cr- 44 (bpmp)₂]³⁺ (bpmp = 2,6-bis(2-pyridyl-methyl)pyridine).⁹ 45 These photostable molecular rubies have already been utilized 46 in various applications, such as in photoredox catalysis,^{11–13} as

pressure or temperature sensors,⁷ in upconversion processes,²⁰ 48 or in circularly polarized emission.^{21,22} These developments 49 have been reviewed elsewhere.^{2–4,23–27} 50

The spin-flip emission bands of most known chromium(III) 51 complexes appear between 670 and 775 nm.^{2,4,5} Tuning the 52 spin-flip emission energy of chromium(III) complex is not 53 straightforward.^{9,28} The intraconfigurational doublet spin-flip 54 states ²E/²T₁ of an octahedral d³-ML₆ complex are essentially 55 independent of the ligand field strength Δ_o (Figure 1). They 56 rather depend on the nephelauxetic (cloud expanding) effect 57 resulting in less interelectronic repulsion as described by the 58 Racah parameter *B* relative to the free ion value *B*₀.^{29–31} 59

Replacing two out of the six pyridines in [Cr^{III}L₆]ⁿ 60 complexes by π-donating carbazoles or isoindolines in the 61 complexes [Cr(dpc)₂]⁺ (dpc⁻ = 3,6-di-*tert*-butyl-1,8-di- 62 (pyridine-2-yl)-carbazolato; λ_{em} = 1067 nm; Φ < 0.00089% 63 at 77 K) and [Cr(bpi)₂]⁺ (bpi⁻ = 1,3-bis(2′-pyridylimino)- 64 isoindolinato; λ_{em} = 930 nm; Φ = 0.11% at 298 K) shifts the 65 emission energy above 900 nm (Scheme 1).^{28,32–34} However, 66 the PL quantum yields are rather poor.^{28,32–34} 67

Alternatively to π-electron-rich amide donors, we reported 68 the spin-flip emission of the cyclometalated chromium(III) 69 complex *fac*-Cr(ppy)₃ at 910 nm (solution, 293 K, Scheme 1). 70 This spin-flip energy is indeed at much lower energy than that 71 of the isostructural polypyridine complex [Cr(bpy)₃]³⁺ (727 72 nm; Φ = 0.25% at 297 K).^{35–37} The PL of *fac*-Cr(ppy)₃ could 73

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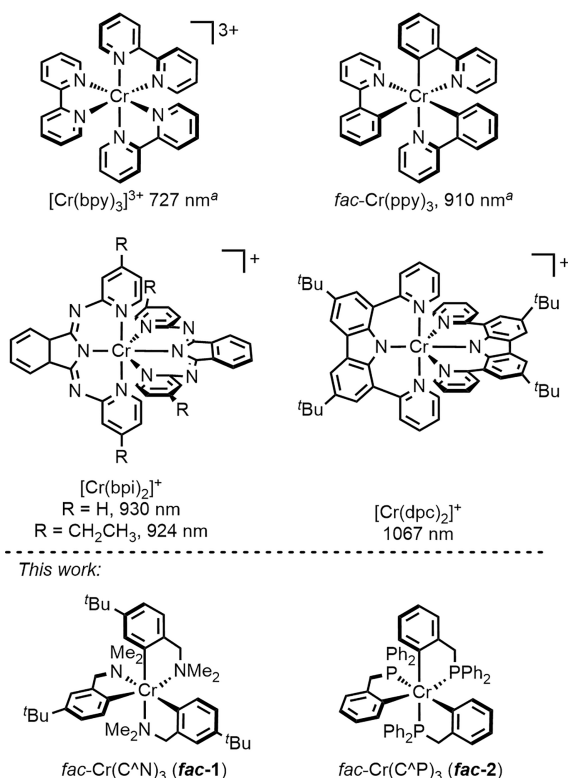
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Chapter 3 Results and Discussion

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Scheme 1. Chromium(III) Complexes Relevant to This Study with Their Luminescence Wavelengths at 77 K^a



^aRoom temperature.

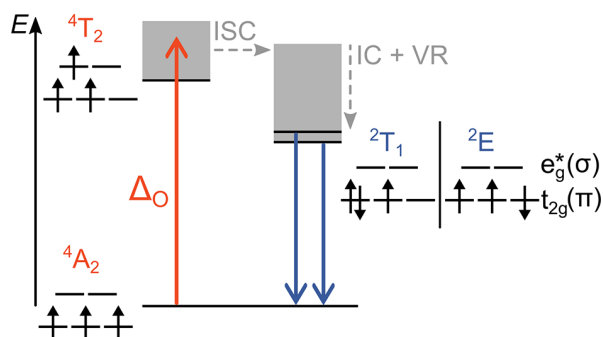


Figure 1. Energy diagram of an octahedral $d^3 \text{ML}_6$ complex with spin-allowed $4A_2 \rightarrow 4T_2$ (orange) and spin-forbidden $4A_2 \leftarrow 2E/2T_1$ (blue) transitions. Exemplary microstates of the spectroscopic terms are indicated. ISC = intersystem crossing, IC = internal conversion, and VR = vibrational relaxation.

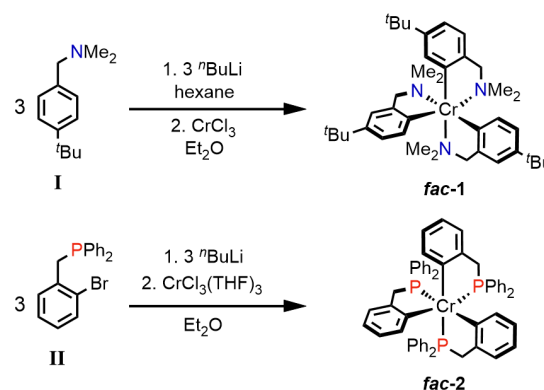
be observed in a fluid solution with $\Phi = 0.03\%$. The quantum yield is quite low compared to the molecular rubies. This might be due to the low emission energy (energy gap law³⁸ and multiphonon relaxation via CH overtones¹⁷ and/or an increased flexibility in the excited state such as trigonal twist and intraligand torsional motions involving the bidentate ligands.^{37,39} Bis(aryl) chromium(III) complexes with the aryl ligands in *cis* position are nonluminescent and undergo photolytic reductive elimination of the biaryl instead.⁴⁰ In this study, we explore the spin-flip PL of two further cyclometalated complexes $\text{fac-Cr}(\text{C}^{\text{N}})_3$ (**fac-1**) and $\text{fac-Cr}(\text{C}^{\text{P}})_3$ (**fac-2**) akin to first reported luminescent cyclometalated chromium(III) complex $\text{fac-Cr}(\text{ppy})_3$ (Scheme 1).

fac-1 and **fac-2** possess amine NMe_2 or phosphane PPh_2 donors instead of the pyridine donor. With these complexes we aim to establish a nephelauxetic series for phenyl, pyridine, amine, and phosphane donors and to predict trends of spin-flip emission energies in chromium(III) complexes, in particular cyclometalated complexes. The preparation of **fac-1** and **fac-2** was reported in the late seventies, but structural and photophysical data were lacking.^{41–45} Furthermore, **fac-2** represents one example of the very few reported phosphane chromium(III) complexes.^{46–48}

RESULTS AND DISCUSSION

Synthesis, Structural, and Electrochemical Characterization of fac-1 and fac-2. Cyclometalated chromium(III) complexes **fac-1** and **fac-2** were prepared according to literature procedures (Scheme 2)^{41–45} by treating the

Scheme 2. Synthesis of **fac-1** and **fac-2**



precursor complexes CrCl₃ and CrCl₃(THF)₃ with suspensions of the respective *ortho*-lithiated pro-ligands, **I** or **II**, in diethyl ether, respectively. Field desorption (FD) mass spectra and IR spectra of **fac-1** and **fac-2** are consistent with the composition (Figures S1–S4). Both complexes are prone to water hydrolysis, but to a different extent. While phosphane complex **fac-2** is fairly stable under ambient conditions in the solid state and solutions of **fac-2** decompose only within several minutes, amine complex **fac-1** nearly instantly hydrolyzes even in the solid state with traces of water (humidity). Possibly, the steric bulk of the PPh₂ donors protects the chromium(III) center from nucleophilic attack much more efficiently than does the smaller NMe₂ donors. Comparably rapid nucleophilic attack at chromium(III) has been observed in sterically unprotected complexes $[\text{Cr}(\text{bpy})_3]^{3+}$ and $[\text{Cr}(\text{tpy})_2]^{3+}$ leading to hydroxido complexes.^{3,49,50} **fac-1** is soluble in most common organic solvents like dried CH₂Cl₂, ethers, or DMF. It is even slightly soluble in hexane, likely because of the three *tert*-butyl substituents. **fac-2** is soluble in dried toluene, THF, DMF, and MeCN, but not in diethyl ether. **fac-2** is generally less soluble than **fac-1**. Recrystallization of complexes **fac-1** and **fac-2** from hexane or THF/Et₂O under inert conditions gave orange and red crystals, respectively, suitable for single crystal XRD analyses (Figure 2).

The molecular structures of **fac-1** and **fac-2** determined by single crystal XRD confirm the facial coordination modes of the bidentate C^N and C^P ligands. The Cr–C bond lengths of the amine complex **fac-1** (2.043(2)–2.083(2) Å) are similar to those of the pyridine complex $\text{fac-Cr}(\text{ppy})_3$ (2.059(2)–2.061(2) Å), suggesting a similar *trans* influence of NMe₂ and

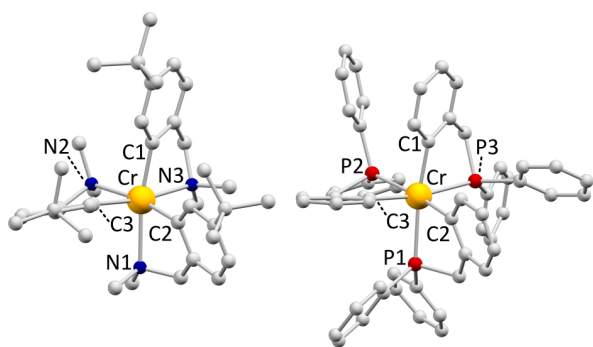


Figure 2. Molecular structures of *fac-1* (left) and *fac-2* (right) in the crystal with the indicated atoms in the first coordination sphere. Hydrogens omitted for clarity.

pyridine.³⁵ In the phosphane complex *fac-2*, the Cr–C bonds are significantly elongated to 2.107(2)–2.110(2) Å (Table 1;

Table 1. Average Bond Lengths [Å] and Angles [deg] of *fac-1*, *fac-2*, and *fac-Cr(ppy)₃* from XRD Analyses³⁵

	<i>fac-1</i> (X = N _{NMe2})	<i>fac-2</i> (X = P _{PPh2})	<i>fac-Cr(ppy)₃</i> (X = N _{py}) ³⁵
Cr–X	2.358	2.578	2.145
Cr–C	2.060	2.108	2.059
X–Cr–C _{ax}	169.9	172.0	168.6
X–Cr–C _{intra}	77.7	78.2	79.2
X–Cr–X	95.6	96.9	92.6
C–Cr–C	94.8	95.3	93.7

for further structural details, see Table S1). The Cr–X bond lengths increase from 2.140(2)–2.149(2) Å (X = N_{py}) and 2.336(1)–2.389(9) Å (X = N_{NMe2}) to 2.573(1)–2.588(2) Å (X = P_{PPh2}) in the series *fac-Cr(ppy)₃*, *fac-1*, and *fac-2*. Compared to amine (2.061–2.107 Å)^{51,52} and phosphane (2.458–2.519 Å)⁴⁸ chromium(III) complexes lacking aryl donors in *trans* position, these bond distances are elongated by up to ca. 0.33 and 0.13 Å, respectively. The *trans* influence of the carbanionic donor is also observed in the *fac-Cr(ppy)₃*/*[Cr(bpy)₃]³⁺* pair.³⁵ The deviation from octahedral symmetry in the cyclometalated complexes, in particular, *fac-1* and *fac-2*, is much more pronounced than in the *bpy* complex *[Cr(bpy)₃]³⁺* due to the very different Cr–C/Cr–X bond lengths (Tables S1 and S3). The five-membered chelate rings Cr–C–C–C–N of *fac-Cr(ppy)₃* are almost planar.³⁵ Due to the CH₂ group in the C^N and C^P chelate ligands the five-membered chelate rings of *fac-1* and *fac-2* adopt an envelope or half-chair conformations (Figure S11) which might allow for higher flexibility and hence less rigidity. This might also affect the photophysical properties (see below). DFT calculations (B3LYP, def2-TZVPP basis set, ZORA, solvent model CPCM(THF)) on *fac-1* and *fac-2* essentially reproduce the geometric parameters found in the solid state structures (Tables S1–S3) including the *trans* influence of the phenyl donor and the nonplanar chelate rings.

fac-Cr(ppy)₃ shows intermolecular $\pi\cdots\pi$ contacts between pyridine units in the solid state³⁵ similar to *fac-Ir(ppy)₃*,⁵³ while *fac-2* displays intermolecular contacts only between phenyl substituents of the PPh₂ units (centroid $\cdots$ centroid distance 3.9 Å), possibly due to steric shielding. In the solid state of *fac-1*, the *tert*-butyl substituents at the phenyl donor seem to suppress the intermolecular $\pi\cdots\pi$ contacts. However,

short intermolecular CH $\cdots\pi$ interactions exist between a methyl group (C5) of the *tert*-butyl substituent of a neighboring complex and the phenyl ring (C5 $\cdots$ centroid distance, 3.9 Å).

In DMF, *fac-1* and *fac-2* are reversibly reduced to the monoanions at $E_{1/2} = -1.81$ and -2.42 V and irreversibly oxidized at $E_p = 0.10$ and 0.25 V vs ferrocene, respectively (Figures S5–S8). A second irreversible oxidation follows for *fac-1* at 0.6 V, which might be assigned to oxidation of the amine. The very negative Cr^{III/II} redox potentials and the facile oxidations are likely due to the electron donating properties of the phenyl ligand. DFT calculations on [*fac-1*][−] and [*fac-2*][−] confirm the metal-centered reduction to low-spin chromium(II) according to the Mulliken spin densities (Table S4, Figures S14 and S15).⁵⁴ A metal-centered reduction of *fac-1* and *fac-2* to high-spin chromium(II) (quintet) would lead to Cr–P bond elongation ($d_{\text{d}}^{\text{av}} = 2.549$ Å, $d_{\text{hs-d}}^{\text{max}} = 2.845$ Å) and Cr–N bond breaking ($d_{\text{d}}^{\text{av}} = 2.409$ Å, $d_{\text{hs-d}}^{\text{max}} = 4.126$ Å), respectively (Table S4, Figures S14 and S15). Similarly, the calculations suggest an essentially metal centered oxidation to cations [*fac-1*]⁺ and [*fac-2*]⁺ (Table S4, Figures S14 and S15).

All chromium(III) complexes *fac-1* and *fac-2* are paramagnetic with magnetic moments corresponding to three unpaired electrons.^{41,45} Consequently, NMR resonances are expected to be severely broadened and shifted.⁵⁵ Indeed, the phosphane complex *fac-2* does not show a ³¹P NMR resonance between +2000 and −2000 ppm in the solid state NMR spectrum (Figure S9a) likely due to the coordination of the phosphorus nuclei to the paramagnetic Cr^{III} center. In THF-*d*₈ or toluene-*d*₈ solution, however, sharp ³¹P NMR resonances are observed at −12 and −10 ppm, respectively (Figure 3a and

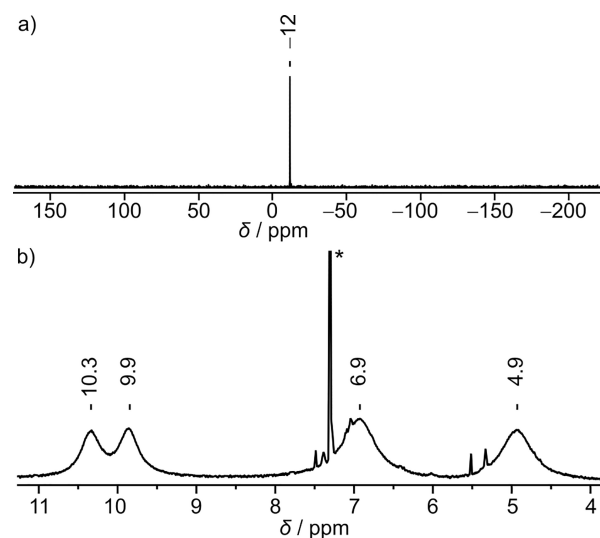
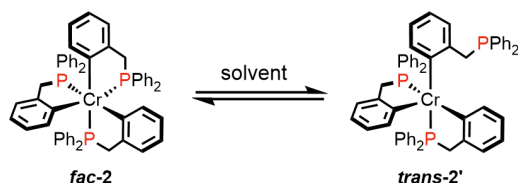


Figure 3. a) ³¹P{¹H} NMR spectrum and b) ¹H NMR spectrum of *fac-2/trans-2'* in THF-*d*₈ at 293 K. *, residual C₆H₆.

Figures S9b/S9c). This chemical shift is in the range of the resonance of the phosphane pro-ligand II.⁴³ This sharp resonance in the diamagnetic region suggests the presence of uncoordinated phosphane donors in solution. In addition, the ¹H NMR spectra of *fac-2* in THF-*d*₈ or toluene-*d*₈ display broad resonances at 10.3, 9.9, 6.9, and 4.9 ppm (Figures 3 and S10). These resonances shift with the inverse temperature, as expected for a paramagnetic species (Figures S10). We assign these resonances to protons of the uncoordinated PPh₂ units

(Figures 3 and S10). With careful baseline correction and integration of the two isolated resonances around 10 ppm (vs the resonance at 0.2 ppm as internal standard) at temperatures between 253–353 K in toluene, the integral of these resonances increases with temperature. This agrees with phosphane dissociation with increasing temperature, although thermodynamic data could not be estimated due to the limited temperature range. As the dried NMR sample does not display a ^{31}P NMR resonance in the solid state NMR spectrum, the phosphane dissociation/coordination appears to be reversible. Consequently, the C[∧]P ligand is a hemilabile ligand at a chromium(III) center (Scheme 3; *fac*-2/*trans*-2' equilibrium).

Scheme 3. Solvent Dependent Equilibrium Between *fac*-2 and *trans*-2'



This aligns with the observation that phosphane adducts of CrPh_3 without the chelate effect are merely five-coordinate $\text{CrPh}_3(\text{PR}_3)_2$ and resist coordination of a third phosphane donor.⁵⁶ We note at this point that the presence of six- and five-coordinate chromium(III) complexes in solution will likely affect the photophysical properties of *fac*-1 in solution. Consequently, we will discuss separately the photophysics, namely, absorption and luminescence properties of *fac*-1 and *fac*-2.

Optical Properties of *fac*-1. In MeCN, the cyclometalated amine complex *fac*-1 possesses intense spin-allowed ligand-centered transitions below 400 nm, while the six lowest-energy spin-allowed metal-centered transitions ($^4\text{A}_2 \rightarrow ^4\text{T}_2$ and $^4\text{A}_2 \rightarrow ^4\text{T}_1$; term symbols according to octahedral symmetry) appear around 402 and 470 nm, respectively (Figure 4a). These assignments are substantiated by TD-DFT calculations, which, however, calculate the transitions too high in energy by ca. 2400 cm^{-1} (Figure 4a, Figures S17 and 18). The energies of the ligand field bands are only weakly affected by the solvent with maxima at 402/470, 401/467, and 404/469 nm in MeCN, 2-MeTHF, and THF, respectively (Figure S24). The very weak spin-forbidden lowest-energy absorptions ($^4\text{A}_2 \rightarrow ^2\text{E}/^2\text{T}_1$) could be detected at 720 and 760 nm ($\epsilon = 1.3$ and $0.6\text{ M}^{-1}\text{ cm}^{-1}$) in highly concentrated MeCN solution (5 mM; Figure S29). CASSCF(7,12)-NEVPT2 calculations substantiate the assignments of the metal-centered transitions with 375/374/366 nm for $^4\text{A}_2 \rightarrow ^4\text{T}_1$, 460/443/440 nm for $^4\text{A}_2 \rightarrow ^4\text{T}_2$, and 697/693/683/674/665 nm for the five lowest spin-flip transitions ($^4\text{A}_2 \rightarrow ^2\text{E}/^2\text{T}_1$, Figure S23, Table S10). Due to the low complex symmetry, several of the five lowest spin-flip transitions are strongly mixed and an individual assignment to ^2E or $^2\text{T}_1$ parentage is not applicable for all states.

Excitation of solid *fac*-1 with 465 nm gives rise to a very sharp emission band at 765 nm ($\text{fwhm}_{\text{solid}} = 60\text{ cm}^{-1}$, 77 K; Figure S25) with a vibrational fine structure (first spacing 152 cm^{-1}). The very sharp emission band arises from undistorted excited doublet states, which possess dominant ^2E character according to CASSCF calculations, i.e., the same orbital occupancy as the ground state. The marginal distortion of the lowest energy doublet state is corroborated by DFT

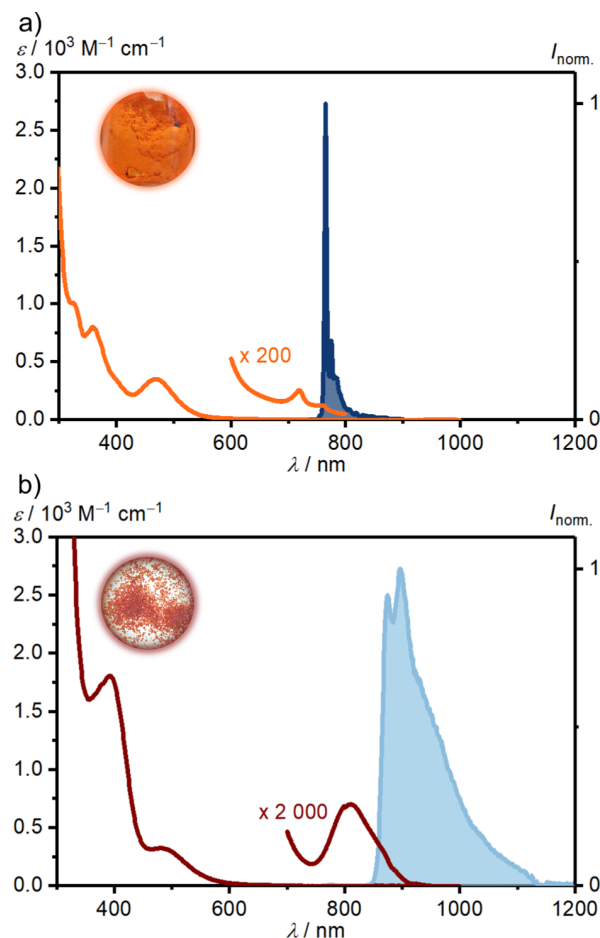


Figure 4. Absorption spectra at r.t. and normalized emission spectra at 77 K (blue) of a) *fac*-1 in acetonitrile and 2-MeTHF, respectively, and b) *fac*-2 in toluene and photographs of the solids (insets).

calculations with bond length and bond angle changes below $0.018\text{ \AA}$ and 0.4° , respectively (Table S2). At higher temperatures, a second emission band at 727 nm appears additionally. This higher energy spin-flip state (by ca. 685 cm^{-1}) is populated at higher temperature according to a Boltzmann distribution. This is a common behavior of d^3 spin-flip emitters with nondegenerate lowest-energy spin-flip states.⁵⁷

Corresponding spin-flip emission bands of *fac*-1 are obtained in 2-MeTHF solution at lower temperatures (765/725 nm; Figures 4a and S26). Above the melting point of the solvent, the emission intensity drops dramatically (Figure S26), pointing to efficient thermally activated nonradiative decay pathways. The emission maxima also match the spin-flip absorption spectra (Figure S29). The very small Stokes shifts below 90 cm^{-1} confirm the weak distortion of the doublet states. The shape of the structured 765 nm emission band is independent of the excitation into the ligand field states (465 nm) or into the higher energy spin-flip state (722 nm, Figure S27), confirming that both bands belong to the same species. In addition, the excitation spectra (300–550 nm; 600–818 nm) match very well, irrespective of the detection wavelength (755–818 nm; Figure S28).

The lowest spin-flip excited state of *fac*-1 decays monoexponentially in frozen 2-MeTHF at 77 K (Figures S31 and S32) with a lifetime of $\tau(77\text{ K}) = 930\text{ }\mu\text{s}$, typical for 283

chromium(III) luminophors.⁴ The decay rate is identical over the structured emission band (755, 765, 775, and 785 nm), confirming that all bands belong to the same emissive species and hence are vibronic in nature. The excited state lifetime is about 20 times longer than that of *fac*-Cr(ppy)₃ (890 nm, 48 μ s) under the same conditions.³⁵ Obviously, less efficient nonradiative relaxation pathways in *fac*-1 enable its longer PL lifetime. The higher emission energy of *fac*-1 renders nonradiative decay to the ground state (energy gap law) and multiphonon relaxation via CH overtones less efficient. Although the energies of the ⁴T₂ derived ligand field states of *fac*-1 are lower than those of *fac*-Cr(ppy)₃, the energy gap to the doublet states is sufficiently high to prevent back intersystem crossing (bISC) to the ⁴T₂ states from the doublet levels. Consequently, this relaxation pathway is not operative in both cases. When the temperature comes close to the solvent's melting point, the lifetime drops to $\tau(200\text{ K}) = 2\text{ }\mu\text{s}$. Close to room temperature, the emission signal becomes too weak to allow measuring the excited state decay with our experimental setup. Clearly, thermally activated pathways via excited state distortions such as trigonal twists or ligand torsions due to the flexible CH₂-based chelate bridge play a significant role in this temperature region. In the solid state, the overall decay is biexponential and faster ($\tau(\text{solid}, 77\text{ K}) = 163/62\text{ }\mu\text{s}$; Figure S30, Table S8). This observation suggests the presence of a further nonradiative pathway in the solid state of *fac*-1, possibly mediated by CH $\cdots\pi$ interactions in the solid state (see above).

Optical Properties of *fac*-2. As in toluene and in THF solution, six-coordinate *fac*-2 and derived five-coordinate species *trans*-2' seem to equilibrate according to the NMR studies (Scheme 3), and the spectra in solution will be a superposition of the spectra of both complexes (in variable unknown ratios). The absorption bands of *fac*-2 (Figure 4b) in toluene in the visible spectral region are unspecific and typical for chromium(III) complexes (492 nm; ⁴A₂ $\rightarrow$ ⁴T₂). TD-DFT calculations predict that the ligand field transitions are too high by 2600 cm⁻¹. The ⁴A₂ $\rightarrow$ ⁴T₁ transitions are hidden by intense phosphane $\rightarrow$ Cr charge transfer and intraligand transitions according to TD-DFT calculations on *fac*-2 (Table S10, Figure S19 and S20). Furthermore, the presence of *trans*-2' with different absorption bands might obscure the ⁴A₂ $\rightarrow$ ⁴T₁ transitions. In the NIR spectral region, a weak and broad absorption band at 810 nm is observed at high concentrations (10 mM; Figure S39). The large width of this band (fwhm = 1090 cm⁻¹) is untypical for pure spin-flip bands and might rather be associated with the five-coordinate complex *trans*-2' and might possess some charge transfer character.

In the solid state, only *fac*-2 is present and hence we will first discuss the emission of *fac*-2 in the solid state. The shape of the spin-flip emission band of *fac*-2 at 77 K strongly resembles that of *fac*-Cr(ppy)₃ (Figure 5, 938 nm) in the solid state,³⁵ yet occurs at higher energy (866 nm). According to CASSCF calculations, the emission of these two complexes arises from a lowest-energy doublet state with large ²T₁ character, i.e., with a spin-paired orbital population, which might impose a slight excited state distortion and thus leads to a broader emission band as compared to that of *fac*-1.^{7,10}

As characteristic for chromium(III) spin-flip emitters at higher temperature, emission from the next higher energy spin-flip state sets in peaking at 813 nm for *fac*-2. The energy difference between the emissive states amounts to 753 cm⁻¹ (Figure S34). Similar to *fac*-1, the PL decay is biexponential in

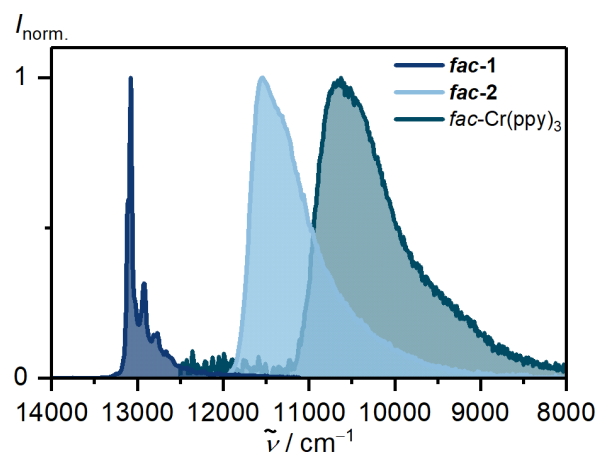


Figure 5. Normalized emission spectra of *fac*-1, *fac*-2 (solid state, 77 K), and *fac*-Cr(ppy)₃ (KBr pellet, 30 K).

the solid state ($\tau(\text{solid}, 77\text{ K}) = 109, 32\text{ }\mu\text{s}$ at 77 K; Figure S40) possibly due to intermolecular interactions (see above).

In solution, the PL characteristics are more complicated. Indeed, the shape and width of the emission band dramatically change from the solid to solution and between different solvents *n*-PrCN, toluene and 2-MeTHF (Figure 6). While the emission band profiles in the solid state and in *n*-PrCN can be reasonably approximated by three Voigt functions centered at ca. 11575, 11300, and 10750 cm⁻¹ (864, 885, and 930 nm), in toluene and in 2-MeTHF a further broad band centered at ca. 10090 cm⁻¹ (991 nm) is present. In 2-MeTHF this broad low-energy band becomes even more dominant than that in toluene. In addition, the band at ca. 930 nm possesses a higher intensity in toluene and 2-MeTHF than in *n*-PrCN or the solid state (Figure 6). Consequently, we suggest that a part of this band and the low energy band at ca. 990 nm arise from five-coordinate species *trans*-2', which is absent in the solid state, only marginally present in frozen *n*-PrCN, but quite prominent in frozen toluene and frozen 2-MeTHF. The amount of trapped *trans*-2' observed might be determined by the cooling and freezing rate rather than the type of the solvent. The large width of the low-energy band (fwhm = 1420 cm⁻¹ from the fitted Voigt function) is incompatible with a pure spin-flip transition from rather nested states. At higher temperature, the relative fraction of this band and the band at ca. 990 nm of the two low energy bands increases in toluene and in 2-MeTHF (Figures S35 and S36). This behavior is also consistent with a more pronounced dissociation of a phosphane donor at higher temperature, i.e., formation of *trans*-2' (Scheme 3). In contrast to *fac*-1 and in accordance with the presence of two species *fac*-2 and *trans*-2' in solution (Scheme 3), the shape of the structured emission band changes with different excitation wavelengths (390, 450, and 820 nm, Figure S37). Furthermore, the excitation spectra (400–580 nm; 650–880 nm) do not match as well with different detection wavelengths (860–930 nm; Figure S38) as the spectra of *fac*-1. The excitation spectrum of *fac*-2 in the NIR spectral region does not match the absorption spectrum of *fac*-2 (Figure S39). In addition, the biexponential PL lifetimes in 2-MeTHF at 77 K differ at different wavelengths, with $\tau_{865}(77\text{ K}) = 272/117\text{ }\mu\text{s}$ and $\tau_{930}(77\text{ K}) = 113/50\text{ }\mu\text{s}$ for 865 and 930 nm detection, respectively (Table S9).

We interpret the PL data of *fac*-2 in solution as follows: in toluene and even more pronounced in 2-MeTHF solution *fac*-

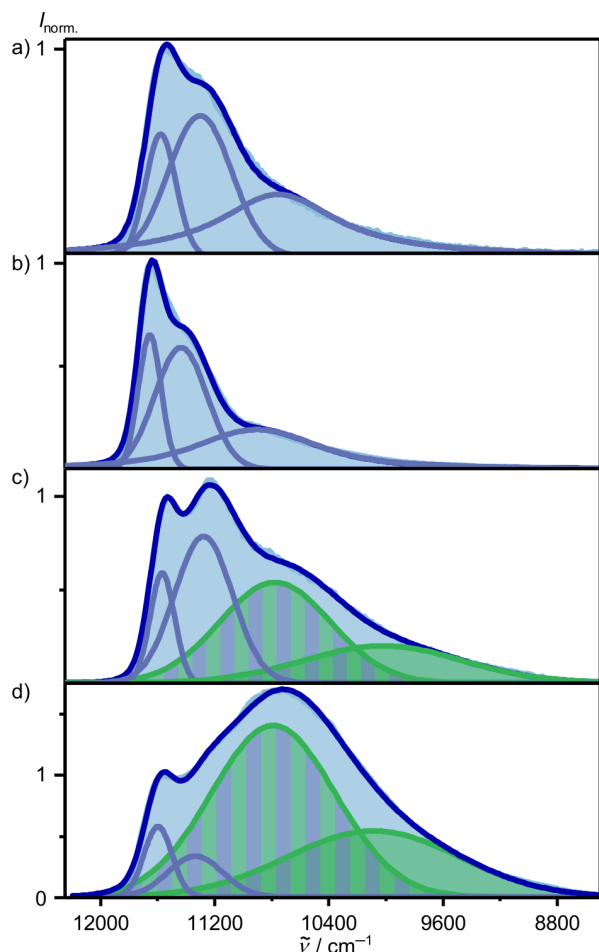


Figure 6. Normalized emission spectra of *fac-2/trans-2'* a) in the solid state, b) in *n*-PrCN, c) in toluene, and d) in 2-MeTHF at 77 K (light blue) and Voigt fits (cumulative in dark blue, assigned to *fac-2* in pale blue and assigned to *trans-2'* in green).

2 partially dissociates a phosphane donor giving the five-coordinate complex *trans-2'*. *trans-2'* possesses a characteristic broad absorption band at 810 nm and broad emission bands at ca. 930 and 990 nm with a comparably low PL lifetime of ca. 50 μ s (77 K). The large Stokes shift of ca. 1590 cm^{-1} precludes an assignment as pure spin-flip emission. DFT and TD-DFT calculations of *trans-2'* reveal a square-pyramidal geometry with a vacant coordination site *trans* to a phenyl donor (Figure S16). The lowest-energy quartet interconfigurational ligand field transitions of *trans-2'* are calculated by TD-DFT at lower energy (536, 585, and 592 nm; Figures S21 and S22) than for *fac-2* in agreement with a weaker ligand field strength. The TD-DFT calculations predict the ligand field transitions at energy too high by about 4500 cm^{-1} . This poor agreement might be due to the admixture of doublet character into these quartet states leading to coupled potential energy surfaces⁵⁸ which is not sufficiently reflected in the TD-DFT calculations. CASSCF(7,12)-NEVPT2 calculations of *trans-2'* (Figure S23) confirm the lower ligand field splitting, i.e., the energy of the lowest energy quartet states. The CASSCF(7,12)-NEVPT2 calculated pure doublet state energies of *trans-2'* without charge-transfer character admixture are only weakly affected by the loss of the phosphane donor (Figure S23). With some CT admixture, these low-energy states of *trans-2'* might be stabilized relative to the metal-centered doublet states of *fac-2*.

Discussion of Nephelauxetic Effects and Ligand Field Theory analysis. In the following, we will discuss the PL energies of the tris(bidentate) chromium(III) complexes [Cr(en)₃]³⁺ (670 nm),³⁶ [Cr(bpy)₃]³⁺ (727 nm),³⁶ *fac*-Cr(ppy)₃ (922 nm),³⁵ *fac-1* (765 nm), and *fac-2* (866 nm) in the context of the nephelauxetic effect (en = 1,2-ethylenediamine). Replacing a pyridine or amine donor by a carbanionic phenyl donor leads to a bathochromic shift of 2910 and 1855 cm^{-1} , respectively ([Cr(bpy)₃]³⁺ $\rightarrow$ *fac*-Cr(ppy)₃; [Cr(en)₃]³⁺ $\rightarrow$ *fac-1*). This suggests a significantly higher covalency of the Cr–C bond than of Cr–N bonds to pyridines or aliphatic amines. Similarly, replacing an aliphatic amine by pyridine or phosphane donors induces a bathochromic shift of 2225 and 1525 cm^{-1} , respectively (*fac-1* $\rightarrow$ *fac*-Cr(ppy)₃; *fac-1* $\rightarrow$ *fac-2*). Furthermore, a pyridine donor results in a slightly lower emission energy than a phosphane donor by 700 cm^{-1} (*fac-2* $\rightarrow$ *fac*-Cr(ppy)₃). These relationships lead to the short nephelauxetic series $\text{NR}_3 < \text{PR}_3 \cong \text{py} < \text{Ph}^-$.

The energies of the lowest energy doublet levels of the cyclometalated complexes *fac-1*, *fac-2*, *fac*-Cr(ppy)₃,³⁵ and [Cr(bpy)₃]³⁺ were calculated by the CASSCF(7,12)-NEVPT2 method at the DFT optimized ground state geometries (Figure S23). For the N/C donor ligands, the experimental trends are correctly reproduced with lowest doublet excited state energies of 13645, 14640, and 15330 cm^{-1} for *fac*-Cr(ppy)₃, *fac-1*, and [Cr(bpy)₃]³⁺, respectively. The order of the doublet state energies for the pyridine/phosphane pair *fac*-Cr(ppy)₃/*fac-2* is reversed (13645/12885 cm^{-1} ; difference of 760 cm^{-1}) in the calculations. These small differences and the reversal of the ordering suggest that π bonds of chromium(III) with pyridine and phosphane donors are rather similarly covalent. On the other hand, the Cr^{III}–P bond seems to be rather labile as seen by the facile phosphane dissociation and the formation of five-coordinate complexes (Scheme 3).⁵⁶ This hampers the applicability of phosphane ligands to luminescent and photoactive chromium(III) complexes.

Although the complexes under study possess a much lower symmetry than octahedral, we attempt a ligand field analysis to compare the ligand field parameters of the cyclometalated complexes *fac-1*, *fac-2*, and *fac*-Cr(ppy)₃ with those from mixed pyridine/amide complexes with carbazolato or iso-indolinato donors [Cr(dpc)₂]⁺ and [Cr(bpi)₂]⁺.^{28,32–34} The ligand field splitting Δ_o is simply given by the (average) energy of the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ ligand field transition(s), while the Racah parameter *B* can be estimated from the spin-flip transitions $^4\text{A}_2 \leftarrow ^2\text{E}/^2\text{T}_1$ with the assumption of $C = 4B$ according to eqs 1–3 (Table 2).⁵⁹ The nephelauxetic parameter β is then estimated using eq 4 and the free ion value of Cr³⁺, $B_0(\text{Cr}^{3+}) = 918 \text{ cm}^{-1}$.³¹

Table 2. Ligand Field Parameters Δ_o , *B*, and β of *fac-1*, *fac-2*, and Selected NIR Emissive Cr^{III} Complexes^a

	Δ_o/cm^{-1}	<i>B</i> (cm^{-1})	β
[Cr(dpc) ₂] ²⁸	19190	520	0.57
[Cr(bpi ^{H,H}) ₂] ³⁴	n.a.	n.a.	0.74
<i>fac</i> -Cr(ppy) ₃ ³⁵	26320	550	0.60
<i>fac-1</i>	21510	670	0.73
<i>fac-2</i>	20330	590	0.64

^aCalculated using eq 1 and 2 with λ_{em} at 77 K. For more details, see Table S11.

$$E(^4T_2) - E(^4A_2) = \Delta_o \quad (1)$$

$$E(^2T_1) - E(^4A_2) \approx 9B + 3C - 24\left(\frac{B^2}{\Delta_o}\right) \quad (2)$$

$$E(^2E) - E(^4A_2) \approx 9B + 3C - 50\left(\frac{B^2}{\Delta_o}\right) \quad (3)$$

$$\beta = \frac{B}{B_0} \quad (4)$$

The largest nephelauxetic effect, i.e., the lowest B or β values, is achieved with four pyridine and two carbazolato donors in $[\text{Cr}(\text{dpc})_2]^+$ ($B = 520 \text{ cm}^{-1}$; $\beta = 0.57$) followed by fac-2 $\text{Cr}(\text{ppy})_3$ ($B = 550 \text{ cm}^{-1}$; $\beta = 0.60$) with three pyridine and three phenyl donors *trans* of each other. Cyclometalated phosphane complex fac-2 possesses intermediate values ($B = 590 \text{ cm}^{-1}$; $\beta = 0.64$), while complexes fac-1 (three phenyls, three amines; $\beta = 0.73$) and $[\text{Cr}(\text{bpi}^{\text{HH}})_2]^+$ (four pyridines, two isoindolates; $\beta = 0.74$) possess the highest β values in this series. With two pyridine and four pyrrolato donors in the complex $[\text{Cr}(\text{MePDP})_2]^-$ the nephelauxetic effect might be so strong, that the doublet states shift to very low energies and hence luminescence is prevented (MePDP = doubly deprotonated of 2,6-bis(5-methyl-3-phenyl-1H-pyrrol-2-yl)pyridine).⁶⁰ Due to the mixed ligand nature and the resulting averaged values and possibly other geometric effects such as five- versus six-membered chelate rings, a simple trend cannot yet be derived from this limited series of NIR emissive chromium(III) complexes.

SUMMARY AND CONCLUSIONS

The spin-flip emission energy of cyclometalated chromium(III) complexes $\text{fac-Cr}(\text{C}^{\wedge}\text{X})_3$ ($\text{X} = \text{NMe}_2$ or PPh_2 ; fac-1/fac-2) can be tuned by the Cr–L bond covalency and the concomitant d orbital expansion. While the ligand field strength is high enough due to the strong phenyl donors to prevent excited state deactivation via back-intersystem crossing, nonradiative excited state decay is possible via intermolecular interactions in the solid state and flexible chelate rings in solution at higher temperature. The phosphane donor is even hemilabile, giving additionally five-coordinate complexes in fluid solution. In spite of these complex phenomena, the photoluminescence properties could be determined and a nephelauxetic series $\text{NR}_3 < \text{PR}_3 \cong \text{py} < \text{Ph}^-$ could be established. Amines and phosphanes appear as weaker and even labile ligands for chromium(III) complexes, hampering their usefulness in optical applications of chromium(III) complexes. On the other hand, stable and strong carbanionic donor ligands are highly useful ligands to achieve strong bathochromic shifts of the emission. Consequently, cyclometalation might be a valuable design strategy for stable and highly emissive chromium(III) complexes in the NIR spectral region.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.4c00075>.

General methods, synthetic procedures, crystal structure parameters, mass spectrometric and IR spectroscopic spectra, cyclic voltammetry, UV/vis/NIR absorption and

luminescence spectroscopic data and quantum-chemical calculations (PDF)

Cartesian coordinates of optimized geometries of fac-1 (quartet and doublet), $[\text{fac-1}]^+$, $[\text{fac-1}]^-$ (triplet and quintet), fac-2 (quartet and doublet), $[\text{fac-2}]^+$, $[\text{fac-2}]^-$ (triplet and quintet), *trans-2'*, and $\text{fac-Cr}(\text{ppy})_3$ from quantum chemical calculations (XYZ)

Accession Codes

CCDC 2306093–2306094 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

L.S. performed the syntheses, characterization, analytical measurements, and computational studies, visualized the data, and wrote the original draft. C.F. solved the crystal structures. K.H. conceptualized and supervised the project and finalized the manuscript.

Notes

The authors declare no competing financial interest.

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Summary and Outlook

Photoactive chromium(III) complexes have moved in the focus of interest in the field of photochemistry with the discovery of the first molecular ruby in 2015. Since then, research was intensely concentrated on their fundamental investigation, with a focus on luminescence quantum yield enhancement, and first applications. The scope and results of this work present ligand design strategies for molecular rubies to increase their application opportunities and contributed to a profound understanding of the photophysical behavior of cyclometalated chromium(III) complexes.

Each project line in this work commenced with the synthesis and characterization of (novel) luminescent chromium(III) complexes, to investigate their photophysical properties by means of optical spectroscopy and was guided by theoretical predictions of structural and excited state properties. The road ahead is both promising and demanding, requiring a series of investigations to further elucidate the potential of these complexes.

Functionalization of Ligands for Molecular Rubies

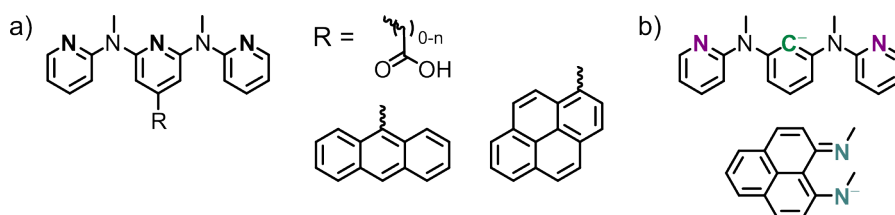
A first idea to use a ddpd ligand, with a substituent on the α -H of the terminal pyridines, to protect the chromium ion could not be implemented experimentally. Theoretical calculations on the ground state geometry support the unfeasible formation of a homoleptic chromium(III) complex with α methyl substituted ddpd through quite elongated Cr-N bonds. Compared to traditional $[\text{Cr}(\text{ddpd})_2]^{3+}$, introduction of bulky substituents mesitylene and triisopropylphenyl in β position of the terminal pyridines, increased the excited state lifetimes and photoluminescence quantum yields in air-saturated environments four- and tenfold, respectively. This improvement gives rise to a large pool of applications, *e.g.* sensing, under ambient conditions.

Secondly, addition of a backbone functionality in the central pyridine of the ddpd ligand has long been sought. Research on this objective in the frame of this work yielded an azide functionalized ddpd ligand in a five step synthesis, starting from commercially available 2,6-dibromopyridine-4-carboxylic acid, with an overall yield of 16 %. The ligand can now be used as anchor group to covalently bind a molecular ruby to various substrates, such as proteins, oligonucleotides or surfaces. As proof of concept, the mono-functionalized complex was attached to an oligonucleotide *via* a copper catalyzed azide alkyne click reaction.

Incorporation of aromatic groups, like pyrene or anthracene moieties, at this position could result in an antenna effect, increasing the molar absorption coefficient, consequently the brightness of molecular rubies and with this the scope of opportunities for optical applications (Scheme 4.1a).

To make molecular rubies suitable for biological applications, further ligand modification strategies, based on the developed substitution patterns, could aim for decreasing the overall charge while increasing the lipophilicity of the complexes (Scheme 4.1a). The interaction of these complexes with biological systems has not been explored, yet. The biocompatibility and potential toxicity of these complexes are critical aspects that need to be assessed before they can be employed in medical applications such as bioimaging and PDT. *In vitro* studies, along with the exploration of their cellular uptake mechanisms, would provide valuable insights into their biomedical applications.

Additionally, the durability and stability of these complexes under practical working conditions are of paramount importance. The preliminary study within the scope of this work could show that photodissociation of $[\text{Cr}(\text{ddpd})_2]^{3+}$ depends on various factors, such as the solvent, proton and oxygen concentration, leading to several pathways in the mechanism. Yet, high photon fluxes are required. Further investigations supporting the previous findings are necessary and should be accompanied by other spectroscopic methods such as TA spectroscopy, to reveal if a one or two photon mechanism is operating. For fundamental research, it will be interesting to reveal if photodissociation can arise directly from an intraconfigurational state or *via* bISC. Long-term photostability studies, including the effects of continuous irradiation and thermal stress on the luminescence properties, would provide vital information regarding their suitability for applications. Whereas properties need to be tailored for stability under extreme conditions, such as photocatalysis, other applications exploit photolability. With insights into the photodissociation mechanism, the systems could then be designed accordingly.



Scheme 4.1: Molecular structures of a) ligands to attach molecular rubies to oxidic surfaces (-COOH) and to improve their absorption properties (anthracene, pyrene) and b) ligands suitable for chromium(III) emitters with enhanced M-L bond covalency to investigate the nephelauxetic effect.

Tuning Ruby-like Emission Energies

Besides working towards application of molecular rubies the research presented in this work could shed light on the fundamentals of tailoring the chromium(III) emission energy. Most chromium(III) complexes emit in the spectral region between 700 and 780 nm. The investigation of cyclometalated chromium(III) complexes showed how excited state properties of spin-flip emitters can be influenced by the M–L bond covalency and the concomitant d orbital expansion.

The synthesis of a group of cyclometalated chromium(III) complexes has been known for decades, but their emission properties were never investigated. In this work, three cyclometalated chromium(III) complexes were investigated and their photophysical properties were characterized. Introduction of carbanionic phenyl ligands leads to a red-shift of the emission compared to well-explored pyridyl complexes. Within the investigated group of complexes, the emission energy was tuned from 765 to 890 nm (77 K).

fac-Cr(ppy)₃, the structural analog of famous *fac*-Ir(ppy)₃, is the first chromium(III) complex showing emission in solution at room temperature above 910 nm. As correctly predicted by CASSCF calculations of [Cr(bpy)₃]³⁺ and *fac*-Cr(ppy)₃, the strong σ donating character of the phenyl ligand in *fac*-Cr(ppy)₃ results in an increased ligand field splitting while its π donating character, lowers the doublet excited state energies and thus the emission energy. A second study on cyclometalated amine and phosphane complexes gave further insights into the nephelauxetic effect. With only a weak σ donating and no π character of the amine, the ligand field splitting and the nephelauxetic effect ($\lambda_{\text{em}} = 765$ nm) in the respective complex is smaller. The phosphane complex shows a solvent-dependent structural equilibrium. ³¹P-NMR spectroscopy studies suggest dissociation of a phosphor donor in solution, forming a five-coordinate species. This effect was additionally observed in solvent-dependent emission band shape changes. From the solid state sample, the emission maximum of the phosphane complex was determined as 865 nm.

A nephelauxetic series was established, comparing the results of these two studies with reported data on other chromium(III) emitters. The interelectronic interaction decreases with increasing the M–L bond covalency and concomitant d orbital expansion. It follows the series $\text{NR}_3 > \text{py} \approx \text{PR}_3 > \text{Ph}^-$.

The emission of all three investigated cyclometalated complexes shows a strong temperature-dependence. The amine and phosphane complexes are even non-luminescent at room temperature. Thermally activated pathways are dominant in these examples for two reasons: These complexes with bidentate ligands show trigonal distortion in the excited state and in the amine and phosphane complexes methylene bridges in the ligand scaffold dramatically increase the flexibility. Together, these distortions lead to potential surface crossing which then results in efficient non-radiative decay.

In the future, besides carbanions, amides could be explored as ligands for chromium(III) complexes with increasing M–L bond covalency (Scheme 4.1b). Analog to the development of molecular rubies, tridentate cyclometalating ligands with six-ring chelates should be employed to achieve higher photoluminescence quantum yields and longer excited state lifetimes. Additionally, the cyclometalating ligands, based on phenyl moieties, should be more rigid to prevent distortions and non-radiative decay. For implementation in optical devices, a blue-shifted emission would be desirable. Hence, in the future new ligand designs with a lower nephelauxetic effect could be explored. With usually concomitant decreasing ligand field splittings, facilitating back ISC, when moving to smaller nephelauxetic effects, this will be an attractive challenge for future research in the field.

The results presented in this work built a strong foundation, while a row of exciting questions remain unanswered and give rise to innovate and inspiring future research in the field of luminescent chromium(III) complexes.

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6.1 Supporting Information: Bulky Ligands Protect Molecular Ruby from Oxygen Quenching

Bulky Ligands protect Molecular Ruby from Oxygen Quenching

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Supplementary Information

General procedures

All reagents (pyridines, boronic acids, solvents, etc.) were used as received from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer, Sigma-Aldrich and TCI). Air and/or moisture-sensitive reactions were performed in dried glassware under an inert gas atmosphere (argon, quality 4.6). 1,4-Dioxane was refluxed over sodium, THF over potassium, dichloromethane and acetonitrile over calcium hydride and distilled under argon prior to use in moisture-sensitive reactions. A glovebox (UniLab/MBraun, Ar 4.8, O₂ < 1 ppm, H₂O < 1 ppm) was used for storage and weighing of sensitive compounds.

NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400.1 MHz (¹H), 100.7 MHz (¹³C{¹H}). All resonances are reported in ppm versus the solvent signal as internal standard [CDCl₃ (¹H: δ = 7.26, ¹³C: δ = 77.16)]. ¹ (s) = singlet, (d) = doublet, (t) = triplet, (m) = multiplet.

ESI⁺ mass spectra were recorded on an Agilent 6545 QTOF-MS spectrometer with analyte solutions in acetonitrile.

Elemental analyses of ligands and [Cr(ddpd^{5Me})₂][BF₄]₃ were performed by the central analytical service of the department of chemistry of the University of Mainz using an Elementar Vario EL Cube. Elemental analyses of complexes [Cr(ddpd^{5Mes})₂][BF₄]₃ and [Cr(ddpd^{5Tripp})₂][BF₄]₃ were performed by the Mikroanalytisches Labor Kolbe, c/o Fraunhofer Institut UMSICHT, Oberhausen, Germany.

IR spectra were recorded with a Bruker Alpha II FT-IR spectrometer with a Platinum Di-ATR unit under inert conditions in a glovebox.

UV/Vis absorption spectra were recorded on a Jasco V770 spectrometer using 1.0 cm quartz cells.

Emission spectra and luminescence decay curves were recorded at 293 K on an Edinburgh Instruments spectrometer (FLS 1000) equipped with the cooled red and NIR sensitive photomultiplier detectors PMT-980 and N-G09 PMT-1700, together covering the 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 the μ s-xenon flashlamp μ F2 (pulse width ca. 2 μ s) 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 $\pm 10\%$.

The solution samples of the complexes (10⁻⁴ M) were prepared in long neck 1.0 cm quartz cuvettes with a Schott valve containing a stir bar. The spectroscopy grade acetonitrile was stirred in a beaker to ensure complete air saturation of the solvent. After measurement of the air saturated solutions the sample solutions, were purged for about 30 minutes with argon using a cannula. The absence of molecular oxygen was verified by the missing ¹O₂ emission band at around 1275 nm after excitation.

Temperature dependent luminescence decay curves were recorded from 278 K to 338 K in 5 K steps with 300 s equilibration time, while stirring the solution.

Emission spectra for Stern-Volmer analyses were recorded on an Edinburgh Instruments spectrometer (FSP 920) using a xenon arc lamp. Luminescence decay curves in the μ s-range were measured with the same spectrometer using a μ s xenon flashlamp and multi-channel scaling mode. All luminescence measurements were performed using magic angle conditions (polarization 0° in the excitation and 54.7° in the emission channel). Oxygen was removed from the solvents by purging with argon and the oxygen concentration in the sample solutions was measured using a Neofix-GT (sensor Phosphor-R) optical detection system (OceanOptics).

Stern-Volmer studies with oxygen: The solution samples were sealed in a long-neck (ca. 15 cm) quartz cuvette with a precision seal rubber septum cap. After purging the samples with Ar using a long needle (that reaches the bottom of the cuvette) for 30 min, the emission spectra, and decays were recorded. These data were used as the starting point (*I*₀ or τ_0) of the Stern-Volmer studies. The lifetime data under Ar-saturation were obtained by independently measuring the freshly prepared samples at least twice to ensure reproducibility of the data.

After recording the starting point emission data, the oxygen partial pressure was determined with a commercial fiber-optic oxygen meter Firesting O₂ from PyroScience and a solvent-resistant oxygen probe tip (OXSOLVPT), which was calibrated with air-saturated and oxygen-free solutions before measurements. The needle-shaped oxygen probe tip can pierce the septa cap and reach the cuvette bottom. The oxygen concentration was read out on-live on the PyroScience program. Measuring the sample for 1-2 min, a stable *p*O₂ readout was recorded. This value is usually found in the range of 0.01 and 0.5 hPa, as there was still traces of air in the needle-shaped oxygen probe tip, which dissolved in the sample solutions. This value will be taken as the starting *p*O₂ point correlated to the Ar-saturated data (*I*₀ or *τ*₀).

An increase of the oxygen concentration was achieved by opening the septa cap for a few seconds to let air in and sealing the cuvette again. The sealed cuvette was shaken for ca. 1 min on a lab dancer. The oxygen concentration was determined again until a stable *p*O₂ readout was obtained. Followed by subsequent emission measurements, the oxygen concentration was controlled again. In some cases, the averaged *p*O₂ values (before and after emission measurements) are used for the Stern-Volmer studies. This measuring cycle was repeated 9 to 10 times with different *p*O₂ to obtain a reliable Stern-Volmer plot.

Density functional theory (DFT) calculations were carried out using the ORCA program package 5.0.3.² All calculations were performed using the B3LYP functional³ employing the RIJCOSX approximation.⁴ Relativistic effects were calculated at the zeroth-order regular approximation (ZORA) level.⁵ 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.⁶ Geometry optimizations were performed using Ahlrichs' polarized valence triple- ζ basis set (def2-TZVP).⁷ Atompairwise dispersion correction was performed with the Becke-Johnson damping scheme (D3BJ).⁸ 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 assignment of the state characters has been done dividing the molecule into three fragments (metal center and two ligands) and calculating charge transfer (CT) numbers, as implemented in the TheoDore software package.^{9,10}

Crystal Structure Determinations

Intensity data for crystal structure determination of [Cr(ddpd^{5Me})₂][BF₄]₃ were collected with a STOE IPDS-2T diffractometer from STOE & CIE GmbH with an Oxford cooling using Mo-K α radiation (λ = 0.71073 Å). The diffraction frames were integrated using the STOE X-Area¹¹ software package and were corrected for absorption with MULABS¹² of the PLATON software package.¹³ Intensity data for crystal structure determination of [Cr(ddpd^{5Me})₂][BF₄]₃ and of [Cr(ddpd^{5Tripp})₂][BF₄]₃ were collected with a STADIVARI diffractometer from STOE & CIE GmbH using Mo-K α radiation (λ = 0.71073 Å). The diffraction frames were integrated using the STOE X-Area¹¹ software package and were corrected for absorption with STOE LANA¹⁴ of the STOE X-Area software package.¹¹

The structures were solved with SHELXT¹⁵ and refined by the full-matrix method based on *F*² using SHELXL¹⁶ of the SHELX¹⁷ software package and the ShelXle¹⁸ 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-2125020 ([Cr(ddpd^{5Me})₂][BF₄]₃), 2125021 ([Cr(ddpd^{5Me})₂][BF₄]₃) and 2125019 ([Cr(ddpd^{5Tripp})₂][BF₄]₃).

Syntheses

ddpd and [Cr(ddpd)₂][BF₄]₃ (Cr^{5H}) were synthesized according to literature procedures.^{19,20}

Synthesis of ddpd^{6Me} (adapted from literature procedures of similar compounds^{21,22}): 2,6-Bis(methylamino)pyridine (1.00 g, 7.29 mmol, 1.0 eq) was added to a suspension of potassium bis(trimethylsilyl)amide (3.34 g, 16.76 mmol, 2.3 eq) in 1,4-dioxane (100 mL). After stirring for 30 min, 2-bromo-6-methylpyridine (3.13 g, 2 mL, 18.22 mmol, 2.5 eq) was added. The solution was refluxed for 5 days. After cooling to room temperature, water (150 mL) was added. The aqueous phase was extracted three times with CH₂Cl₂ (50 mL). The brown solution of the combined organic phases was washed twice with water (50 mL), dried over MgSO₄ and concentrated under reduced pressure. The red-brown residue was subjected to column chromatography (SiO₂, PE/EtOAc, gradient 6:1 → 1:1 + 5 vol% NEt₃) to yield ddpd^{6Me} as a pale-yellow oil. Yield: 370 mg, 1.16 mmol, 16%.

¹H NMR (400 MHz, CD₃CN, 296 K) δ / ppm = 7.44 (m, 3 H, H¹, H^{6,6a}), 7.03 (d, ³J = 8.3 Hz, 2 H, H^{5,5a}), 6.76 (d, ³J = 7.4 Hz, 2 H, H^{7,7a}), 6.66 (d, ³J = 8.0 Hz, 2 H, H^{2,2a}), 3.48 (s, 6 H, H^{9,9a}), 2.41 (s, 6 H, H^{10,10a}).

¹³C{¹H} NMR (101 MHz, CD₃CN, 296 K) δ / ppm = 158.1 (C^{3,3a}), 157.7 (C^{4,4a}), 157.3 (C^{8,8a}), 139.5 (C¹), 138.3 (C^{6,6a}), 117.1 (C^{7,7a}), 113.3 (C^{5,5a}), 106.1 (C^{2,2a}), 36.3 (C^{9,9a}), 24.5 (C^{10,10a}).

MS (ESI⁺, MeCN): Calcd. for C₁₉H₂₂N₅⁺: m/z = 320.19. Found: m/z (%) = 320.19 (100, [ddpd^{6Me}+H]⁺).

UV/Vis (MeCN): $\lambda_{\max}$ / nm (ϵ / 10³ M⁻¹cm⁻¹): 236 (72.1), 273 (88.2), 335 (11.3).

Emission (MeCN): λ_{em} / nm (λ_{exc} / nm): 423, 373 (sh) (334).

Synthesis of ddpd^{5Me} (adapted from literature procedures of similar compounds^{21,22}): A solution of 2,6-diaminopyridine (1.27 g, 11.63 mmol, 1.0 eq, dried under reduced pressure overnight at 40 °C) in THF (30 mL) was added to a suspension of NaH (1.40 g of 60 wt%, 34.89 mmol, 3.0 eq) in THF (30 mL). After stirring for 30 min, 2-bromo-5-methylpyridine (5.00 g, 29.07 mmol, 2.5 eq) was added. The solution was refluxed for 3 days. After solvent evaporation, the residue was dissolved in CH₂Cl₂ (50 mL) and extracted twice with water (2 x 25 mL). The organic phase was concentrated under reduced pressure and used in the next step without further purification. The brown solid was added to a suspension of powdered KOH (1.62 g, 28.83 mmol, 2.5 eq) in DMSO (50 mL) and the mixture was stirred at ambient temperature for 30 min. Methyl iodide (1.5 mL, 2.25 g, 15.86 mmol, 1.4 eq) was added to the red-brown suspension and stirring was continued for 15 h. Water (30 mL) was added and the yellow aqueous suspension was extracted with a 1:1 (v/v) mixture of Et₂O/THF (3 x 10 mL). The combined organic phases were washed with saturated aqueous Na₂CO₃, dried over MgSO₄, and concentrated under reduced pressure. The red-brown residue was subjected to column chromatography (SiO₂, PE/EtOAc, gradient 3:1 → 1:1 + 5 vol% NEt₃) to yield ddpd^{5Me} as a pale-yellow oil. Yield: 760 mg, 2.38 mmol, 20%.

¹H NMR (400 MHz, CD₃CN, 296 K): δ / ppm = 8.14 (s, 2 H, H^{8,8a}), 7.41 (m, 3 H, H¹, H^{6,6a}), 7.18 (d, ³J = 8.4 Hz, 2 H, H^{5,5a}), 6.53 (d, ³J = 8.0 Hz, 2 H, H^{2,2a}), 3.45 (s, 6 H, H^{9,9a}), 2.24 (s, 6 H, H^{10,10a}).

¹³C{¹H} NMR (101 MHz, CD₃CN, 296 K): δ / ppm = 157.3 (C^{3,3a}), 156.7 (C^{4,4a}), 148.7 (C^{8,8a}), 139.6 (C¹), 138.6 (C^{6,6a}), 127.8 (C^{7,7a}), 117.0 (C^{5,5a}), 104.5 (C^{2,2a}), 36.3 (C^{9,9a}), 17.7 (C^{10,10a}).

MS (ESI⁺, MeCN): m/z (%) = 320.19 (100, [ddpd^{5Me}+H]⁺), 382.11 (5, [ddpd^{5Me}+Cu]⁺).

Elem. anal. calcd. for C₁₉H₂₁N₅ (319.18): C, 71.45; H, 6.63; N, 21.93. Found: C, 71.11; H, 6.53; N, 22.16.

UV/Vis (MeCN): $\lambda_{\max}$ / nm (ϵ / 10³ M⁻¹cm⁻¹): 238 (13.8), 274 (18.3), 336 (19.9).

Emission (MeCN): λ_{em} / nm (λ_{exc} / nm): 431, 370 (sh) (334).

Synthesis of 5-bromo-N-methylpyridine-2-amine. 2,5-Dibromopyridine (15.18 g, 62.80 mmol, 1 eq) and methylamine solution (33 wt% in EtOH; 80 mL, 642.62 mmol, 10 eq) were stirred and heated in an autoclave for 24 h at 160 – 170 °C. After cooling to room temperature, the solvent was removed under reduced pressure yielding an orange solid. The crude product was dissolved in 1 M aqueous HCl solution (100 mL), yielding a yellow solution with a small amount of insoluble residue. The mixture was extracted with CH₂Cl₂ (30 mL) and the organic phase containing the starting material was discarded.

The aqueous phase was brought to pH 11 with 1 M aqueous NaOH solution, resulting in the precipitation of a colorless solid. The mixture was extracted with CH₂Cl₂ (3 x 50 mL) dissolving the solid in the organic phase. The organic phase was dried over MgSO₄, filtered and the solvent was removed under reduced pressure resulting in 2-methylamino-5-bromopyridine as a colorless solid. Yield: 11.54 g, 61.70 mmol, 98%.

¹H NMR (400 MHz, CD₂Cl₂, 296 K): δ / ppm = 8.08 (dd, ³J_{HH} = 2.6, 0.7 Hz, 1H, H¹), 7.48 (dd, ³J_{HH} = 8.9, 2.5 Hz, 1H, H³), 6.31 (dd, ³J_{HH} = 8.9, 0.7 Hz, 1H, H⁴), 4.94 (s, 1H, NH), 2.86 (d, ³J_{HH} = 5.2 Hz, 3H, H⁶).

¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 296 K): δ / ppm = 158.3 (C⁵), 148.5 (C¹), 139.5 (C³), 107.5 (C⁴), 106.5 (C²), 28.9 (C⁶).

MS (ESI⁺, MeCN): m/z (%) = 186.99 (100, [py^{5Br}-NHMe+H]⁺).

Syntheses of 5-mesityl-*N*-methyl-pyridine-2-amine and 5-(triisopropylphenyl)-*N*-methyl-pyridine-2-amine (adapted from an analogous literature procedure²³): 5-Bromo-*N*-methylpyridine-2-amine (1.00 eq), Pd(OAc)₂ (0.05 eq), XPhos (2-(dicyclohexylphosphano)-2',4',6'-triisopropyl-1,1'-biphenyl, 0.16 eq), K₃PO₄ (3.00 eq) and the corresponding boronic acid (1.16 eq; **Ar** = **Mes** 2.41 g, 14.7 mmol; **Ar** = **Tripp** 1.73 g, 7.0 mmol) were suspended in a 5:1 mixture of 1,4-dioxane (10 mL) and H₂O (2 mL). The solution was degassed and stirred at 90 °C for 48 h under argon. The reaction mixture was allowed to cool to room temperature, diluted with EtOAc (30 mL), washed with H₂O (3 x 25 mL) and brine (60 mL). The organic layer was dried over MgSO₄ and the solvent was evaporated under reduced pressure. The orange oily residue was recrystallized from hexane, giving **5-mesityl-*N*-methyl-pyridine-2-amine** and **5-(triisopropylphenyl)-*N*-methyl-pyridine-2-amine**, respectively, as colorless powders.

5-mesityl-*N*-methyl-pyridine-2-amine: Yield: 71%, 2.00 g, 8.8 mmol.

¹H NMR (400 MHz, CD₂Cl₂, 296 K): δ / ppm = 7.88 (dd, J = 2.3, 0.9 Hz, 1H, H⁵), 7.26 (dd, J = 8.5, 2.3 Hz, 1H, H³), 6.99 – 6.94 (m, 2H, H^{11,13}), 6.51 (dd, J = 8.5, 0.9 Hz, 1H, H²), 5.09 (s, 1H, H⁷), 2.96 (s, 3H, H⁹), 2.33 (s, 3H, H¹⁷), 2.07 (s, 4H, H^{15,16}).

¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 296 K): δ / ppm = 158.5 (C¹), 147.9 (C⁵), 138.7 (C³), 136.8 (C^{10,14}), 136.6 (C¹²), 135.8 (C), 128.1 (C¹¹, C¹³), 125.0 (C⁴), 105.7 (C²), 29.0 (C⁹), 20.8 (C¹⁷), 20.7 (C^{15,16}).

MS (ESI⁺, MeCN): m/z (%) = 227.15 (100, [py^{5Mes}-NHMe+H]⁺).

5-(triisopropylphenyl)-*N*-methyl-pyridine-2-amine: Yield: 59%, 1.08 g, 3.5 mmol.

¹H NMR (400 MHz, CD₂Cl₂, 296 K): δ / ppm = 7.88 (dt, J = 2.2, 1.0 Hz, 1H, H⁵), 7.28 (ddd, J = 8.4, 2.4, 1.0 Hz, 1H, H³), 7.08 (s, 2H, H^{11,13}), 6.49 (d, J = 8.0 Hz, 1H, H²), 4.89 (b, J = 5.6 Hz, 1H, H⁷), 3.02 – 2.87 (m, 5H, H^{9,21}), 2.74 (pd, J = 6.8, 1.1 Hz, 2H, H^{15,18}), 1.31 (dd, J = 7.0, 1.0 Hz, 6H, H^{22,23}), 1.11 (td, J = 7.0, 1.0 Hz, 12H, H^{16,17, 19,20}).

¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 296 K): δ / ppm = 158.5 (C¹), 148.3 (C¹²), 148.1 (C⁵), 147.8 (C^{10,14}), 138.8 (C³), 134.0 (C⁸), 124.5 (C⁴), 120.5 (C^{11,13}), 105.4 (C²), 34.4 (C²¹), 30.3 (C^{15,18}), 28.9 (C⁹), 23.9 (C^{16,17,19,20,23}).

MS (ESI⁺, MeCN): m/z (%) = 311.25 (100, [py^{5Tripp}-NHMe-H]⁺).

Synthesis of ddpd^{5Mes} (adapted from an analogous literature procedure¹⁹): Potassium bis(trimethylsilyl)amide (2.49 g, 12.48 mmol, 3.2 eq) was suspended in freshly dried 1,4-dioxane (50 mL) under an argon atmosphere. Addition of 5-mesityl-*N*-methyl-pyridine-2-amine (2.00 g, 8.84 mmol, 2.3 eq) resulted in a yellow solution. A solution of 2,6-dibromopyridine (0.91 g, 3.84 mmol, 1.0 eq) in 1,4-dioxane (10 mL) was added. The reaction mixture was refluxed for 64 h. After cooling to room temperature, water (100 mL) was added. The solution was extracted with a 1:1 (v/v) mixture of Et₂O/THF (4 x 50 mL). The combined organic phases were washed with saturated aqueous Na₂CO₃ solution (3 x 50 mL), dried over MgSO₄ and the solvent was removed under reduced pressure, yielding a brown oil. The crude product (2.4 g) was dissolved in as little diethyl ether as possible. Tetrafluoroboric acid diethyl ether complex (2.5 eq, 9.6 mmol, 2.6 mL) in diethyl ether (50 – 55 wt%) was added dropwise to the solution of the crude product, resulting in the formation of a colorless precipitate (1.54 g). A concentrated solution of this solid was recrystallized by diffusion of diethyl ether into the solution. The

tetrafluoroborate salt of protonated ddpd^{5Mes} was suspended in water (100 mL). Diethyl ether (25 mL) was added and the pH of the aqueous phase was brought to 9 with a 1 M aqueous NaOH solution. The aqueous phase was extracted with diethyl ether (3 x 30 mL). The combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure yielding ddpd^{5Mes} as a colorless solid. Yield: 1.21 g, 2.30 mmol, 60%.

¹H NMR (400 MHz, CD₂Cl₂, 296 K): δ / ppm = 8.12 (dd, J = 2.3, 0.9 Hz, 2H, H^{5,28}), 7.49 (t, 1J = 8.0 Hz, 1H, H²¹), 7.39 (dd, J = 8.5, 1.0 Hz, 2H, H^{2,31}), 7.35 (dd, J = 8.5, 2.3 Hz, 2H, H^{3,30}), 6.99 – 6.93 (m, 4H, H^{11,13,34,36}), 6.81 (d, 1J = 8.0 Hz, 2H, H^{20,22}), 3.64 (s, 6H, H^{23,25}), 2.32 (s, 6H, H^{17,40}), 2.06 (s, 12H, H^{15,16,38,39}).

¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 296 K): δ / ppm = 20.7 (C^{15,16,38,39}), 35.6 (C^{23,25}), 105.6 (C^{20,22}), 114.5 (C^{2,31}), 128.1 (C^{11,13,34,36}), 129.5 (C^{8,32}), 135.2 (C^{12,35}), 136.5 (C^{1,14,33,37}), 137.0 (C^{4,29}), 137.9 (C^{3,30}), 138.3 (C²¹), 148.0 (C^{5,28}), 156.3 (C^{9,19}), 156.3 (C^{1,26}).

MS (ESI⁺, MeCN): m/z (%) = 528.31 (100, [ddpd^{5Mes}+H]⁺), 550.29 (6, [ddpd^{5Mes}+Na]⁺), 1077.60 (6, [2 ddpd^{5Mes}+Na]⁺).

Elem. Anal. calcd. for C₃₅H₃₇N₅ (527.30): C, 79.66; H, 7.07; N, 13.27. Found: C, 79.27; H, 7.02; N, 12.99.

UV/Vis (MeCN): $\lambda_{\max}$ / nm (ϵ / 10³ M⁻¹cm⁻¹): 243 (sh, 20.7), 279 (26.0), 337 (26.7), 371 (sh, 4.9).

Emission (MeCN): λ_{em} / nm (λ_{exc} / nm): 415, 370 (sh) (337).

Synthesis of ddpd^{5Tripp} (adapted from an analogous literature procedure¹⁹). Potassium bis(trimethylsilyl)amide (0.966 g, 3.36 mmol, 2.4 eq) was suspended in freshly dried 1,4-dioxane (20 mL) under an argon atmosphere. Addition of 5-(triisopropylphenyl)-*N*-methyl-pyridine-2-amine (1.00 g, 3.22 mmol, 2.3 eq) resulted in an orange-colored solution. A solution of 2,6-dibromopyridine (0.332 g, 1.44 mmol, 1.0 eq) in 1,4-dioxane was added. The reaction mixture was refluxed for 64 h. After cooling to room temperature, water (50 mL) was added and 1,4-dioxane was removed under reduced pressure. The aqueous phase was extracted with CH₂Cl₂ (3 x 50 mL). The brown CH₂Cl₂ solution was dried over Na₂SO₄ and the solvent was removed under reduced pressure. Suspending the crude product in diethyl ether (20 mL) led to the formation of a colorless precipitate. This solid was filtered and washed with diethyl ether (3 x 10 mL), giving ddpd^{5Tripp} as a colorless powder. Yield: 0.89 g, 1.28 mmol, 88%.

¹H NMR (400 MHz, CD₂Cl₂, 296 K): δ / ppm = 8.16 (t, J = 1.6 Hz, 2H, H^{5,28}), 7.52 (t, J = 8.0 Hz, 1H, H²¹), 7.39 (d, J = 1.6 Hz, 4H, H^{2,3,30,31}), 7.10 (s, 4H, H^{11,13,34,36}), 6.86 (d, J = 8.0 Hz, 2H, H^{20,22}), 3.66 (s, 6H, H^{23,25}), 2.95 (hept, J = 6.9 Hz, 2H, H^{17,40}), 2.72 (hept, J = 6.9 Hz, 4H, H^{15,16,38,39}), 1.31 (d, J = 6.9 Hz, 12H, H^{41,42,48,51}), 1.13 (dd, J = 13.3, 6.9 Hz, 24H, H^{43,44,45,46,47,49,50,52}).

¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 296 K): δ / ppm = 156.3 (C^{1,9,19,26}), 148.7 (C^{12,35}), 148.1 (C^{5,28}), 147.5 (C^{10,14,33,37}), 138.4 (C²¹), 138.2 (C^{3,30}), 133.5 (C^{4,29}), 129.0 (C^{8,32}), 120.6 (C^{11,13,34,36}), 114.1 (C^{2,31}), 105.8 (C^{20,22}), 35.6 (C^{23,25}), 34.4 (C^{17,40}), 30.4 (C^{15,16,38,39}), 23.9 (C^{41,42,48,51}), 23.9 (C^{43,44,45,46,47,49,50,52}).

MS (ESI⁺, MeCN): m/z (%) = 696.50 (21, [ddpd^{5Tripp}+H]⁺), 718.48 (23, [ddpd^{5Tripp}+Na]⁺), 1414.98 (100, [2 ddpd^{5Tripp}+Na]⁺), 1430.95 (6, [2 ddpd^{5Tripp}+K]⁺).

Elem. Anal. calcd. for C₄₇H₆₁N₅ (696.04): C, 81.10; H, 8.83; N, 10.06. Found: C, 80.99; H, 9.07; N, 9.93.

UV/Vis (CH₂Cl₂): $\lambda_{\max}$ / nm (ϵ / 10³ M⁻¹cm⁻¹): 248 (sh, 20.5), 281 (29.4), 341 (32.1).

Emission (CH₂Cl₂): λ_{em} / nm (λ_{exc} / nm): 402, 370 (sh) (320).

Synthesis of [Cr(ddpd^{5Me})₂][BF₄]₃ ([Cr^{5Me}][BF₄]₃, adapted from an analogous literature procedure²⁰): ddpd^{5Me} (725 mg, 2.3 mmol, 1.8 eq) was dissolved in MeCN (20 mL) and water (20 mL) was added. The solution was degassed with argon for one hour. Adding CrCl₂ (155 mg, 1.3 mmol, 1.0 eq) yielded a dark green to blue solution. After stirring overnight, an aqueous NH₄BF₄ solution (4 mL, 1 M) was added and the solution was exposed to air. The solution turned orange. The solvents were removed under reduced pressure and the residue dissolved in MeCN (30 mL). Insoluble residues were filtered and the orange solution was subjected to crystallization with Et₂O, resulting in orange crystals suitable for X-ray crystallography. Yield: 381 mg, 0.4 mmol, 32%.

MS (ESI⁺, MeCN): m/z (%) = 230.10 (74, [Cr(ddpd^{5Me})₂]³⁺), 388.65 (100, {[Cr(ddpd^{5Me})₂][BF₄]}²⁺), 864.31 (54, {[Cr(ddpd^{5Me})₂][BF₄]₂}⁺).

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 1601 (m), 1580 (m), 1506 (s), 1447 (s), 1387 (s), 1337 (m), 1251 (w), 1225 (w), 1176 (w), 1153 (m), 1051 – 1015 (vs br, BF), 948 (s), 826 (s), 807 (s), 747 (m), 674 (m), 591 (m), 519 (m), 492 (m), 449 (m), 419 (m).

Elem. anal. calcd. (%) for C₃₈H₄₂B₃CrF₁₂N₁₀ (951.23) x 2 H₂O: C, 46.23; H, 4.70; N, 14.19. Found: C, 46.22; H, 4.84; N, 14.29.

UV/Vis (MeCN): $\lambda_{\max}$ / nm (ϵ / 10³ M⁻¹cm⁻¹): 444 (4.0, MC + LMCT), 323 sh (22.4, MC + LMCT), 305 (26.5, LMCT), 225 sh (52.7, $\pi\pi^*$).

UV/Vis (H₂O): $\lambda_{\max}$ / nm (ϵ / 10³ M⁻¹cm⁻¹): 444 (4.0, MC + LMCT), 324 sh (22.1, MC + LMCT), 306 (26.6, LMCT), 222 sh (52.9, $\pi\pi^*$).

Emission (MeCN): λ_{em} / nm (λ_{exc} / nm): 740, 778 (444).

Emission (H₂O): λ_{em} / nm (λ_{exc} / nm): 741, 779 (444).

Syntheses of [Cr(ddpd^{5Mes})₂][BF₄]₃ ([Cr^{5Mes}][BF₄]₃) and [Cr(ddpd^{5Tripp})₂][BF₄]₃ ([Cr^{5Tripp}][BF₄]₃). The precursor [Cr(MeCN)₄][BF₄]₂ was prepared according to a literature procedure.²⁴ All following reactions were performed in a glove box under inert conditions. The ligand (ddpd^{5Mes}, 1.40 g, 2.65 mmol; ddpd^{5Tripp}, 0.39 g, 0.56 mmol, 2.0 eq) was dissolved in CH₂Cl₂ (10 mL). [Cr(MeCN)₄][BF₄]₂ (1.0 eq) was dissolved in MeCN (10 mL). The pale blue chromium complex solution was added dropwise to the clear brownish ligand solution. The reaction mixture was stirred overnight under inert conditions and then for 2 hours under air, resulting in a dark yellow solution. A solution of [ⁿBu₄N][BF₄] in MeCN (2 mL) was added (2.0 eq). After stirring for three hours, the CH₂Cl₂ was removed under reduced pressure and the remaining orange MeCN solution was subjected to crystallization with Et₂O, resulting in orange needles suitable for X-ray crystallography. Rapid addition of Et₂O to a concentrated MeCN solution of the complex yields a yellow powder.

[Cr^{5Mes}][BF₄]₃: Yield: 680 mg, 1.3 mmol, 96%.

MS (ESI⁺, MeCN): m/z (%) = 368.85 (72, [Cr(ddpd^{5Mes})₂]³⁺), 596.78 (100, {[Cr(ddpd^{5Mes})₂][BF₄]}²⁺), 1280.56 (60, {[Cr(ddpd^{5Mes})₂][BF₄]₂}⁺).

IR (ATR): $\tilde{\nu}$ = 1603 (m), 1576 (w), 1502 (m), 1480 (m), 1448 (s), 1374 (m), 1333 (w), 1234 (w), 1150 (w), 1104 – 1006 (vs br, BF), 944 (w), 849 (w), 810 (w), 762 (w), 736 (w), 585 (w), 519 (w), 449 (w), 406 (w) cm⁻¹.

Elem. anal. calcd. (%) for C₇₀H₇₄B₃CrF₁₂N₁₀ (1367.56): C, 61.47; H, 5.45; N, 10.24. Found: C, 61.13; H, 5.48; N, 10.20.

UV/Vis (MeCN): $\lambda_{\max}$ / nm (ϵ / 10³ M⁻¹cm⁻¹): 453 (2.8, MC + LMCT), 312 (21.6, LMCT), 257 (31.2), 236 sh (43.5, $\pi\pi^*$).

Emission (MeCN): λ_{em} / nm (λ_{exc} / nm): 742, 782 (450).

[Cr^{5Tripp}][BF₄]₃: Yield: 140 mg, 0.08 mmol, 10%.

MS (ESI⁺, MeCN): m/z (%) = 481.31 (62, [Cr(ddpd^{5Tripp})₂]³⁺), 765.47 (100, {[Cr(ddpd^{5Tripp})₂][BF₄]}²⁺), 1616.93 (36, {[Cr(ddpd^{5Tripp})₂][BF₄]₂}⁺).

IR (ATR): $\tilde{\nu}$ = 2959 (m), 2870 (w), 1601 (m), 1504 (m), 1444 (s), 1378 (s), 1333 (w), 1232 (w), 1148 (w), 1110 – 989 (vs br, BF), 946 (m), 878 (w), 812 (m), 760 (m), 649 (w), 581 (w), 519 (m), 457 (w), 406 (w) cm⁻¹.

Elem. anal. calcd. (%) for C₉₄H₁₂₂B₃CrF₁₂N₁₁ (1442.92) x MeCN x Et₂O: C, 66.01; H, 7.48; N, 8.47. Found: C, 65.70; H, 7.20; N, 8.14.

UV/Vis (MeCN): λ_{max} / nm (ϵ / $10^3 \text{ M}^{-1}\text{cm}^{-1}$): 455 (3.3, MC + LMCT), 319 (29.5, LMCT), 240 (sh, 55.1, $\pi\pi^*$).

Emission (MeCN): λ_{em} / nm (λ_{exc} / nm): 740 (sh), 794 (454).

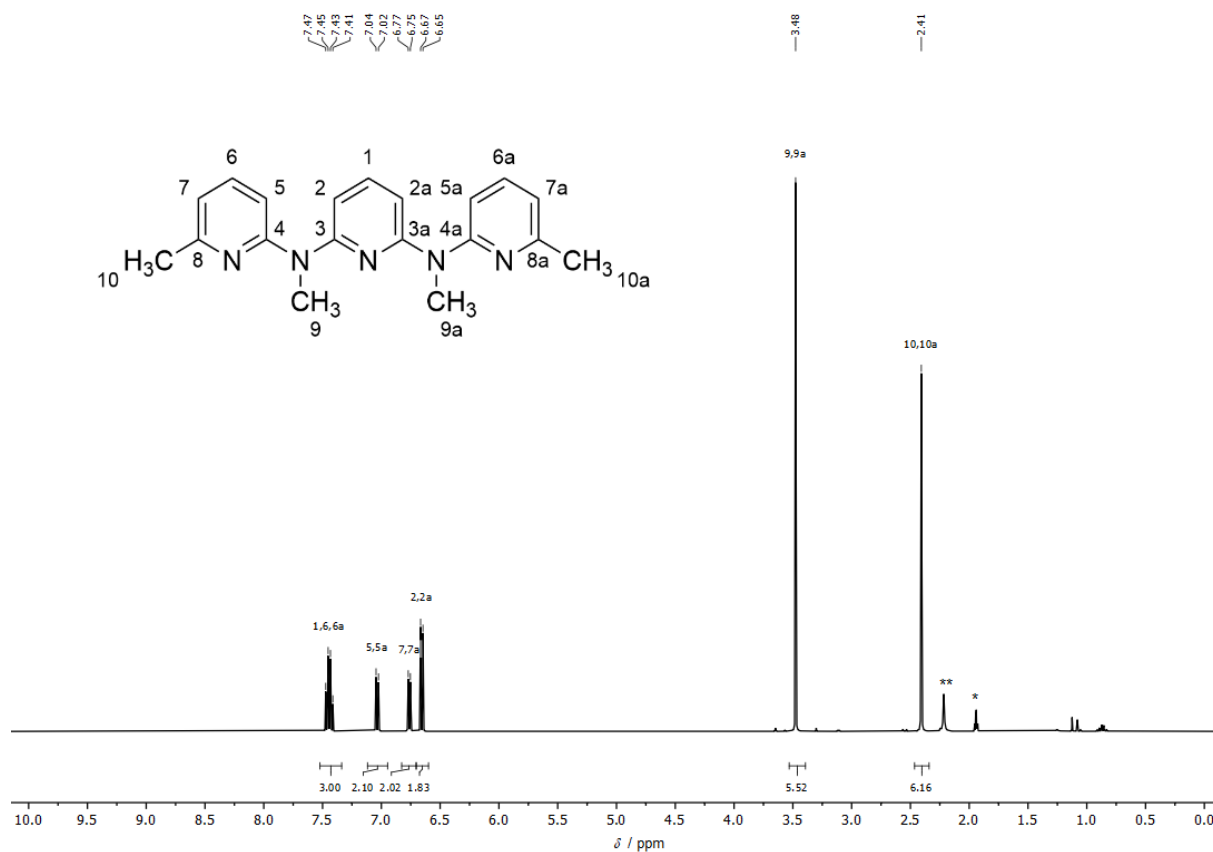


Figure S1. ¹H NMR spectrum of ddpd^{6Me} in CD₃CN. * CH₂DCN, ** water.

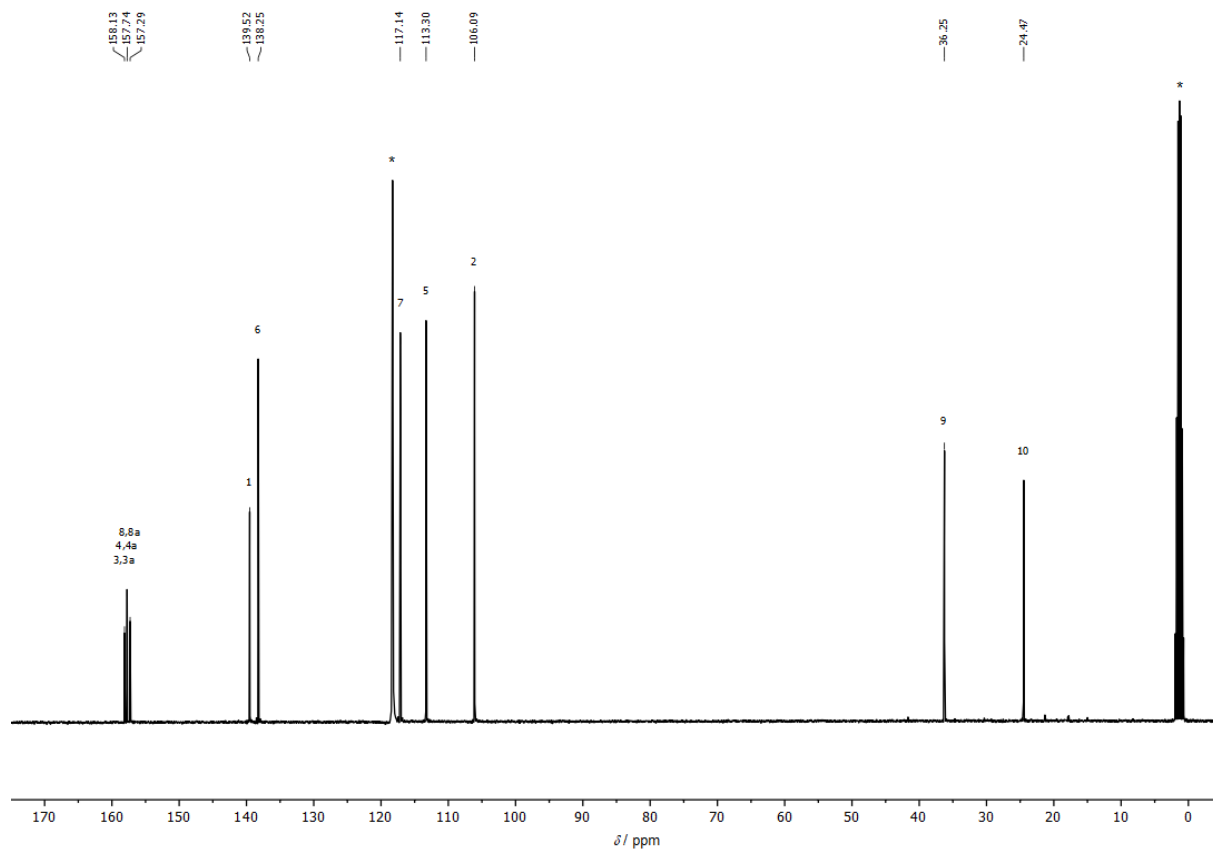


Figure S2. ¹³C{¹H} NMR spectrum of ddpd^{6Me} in CD₃CN. * CH₂DCN.

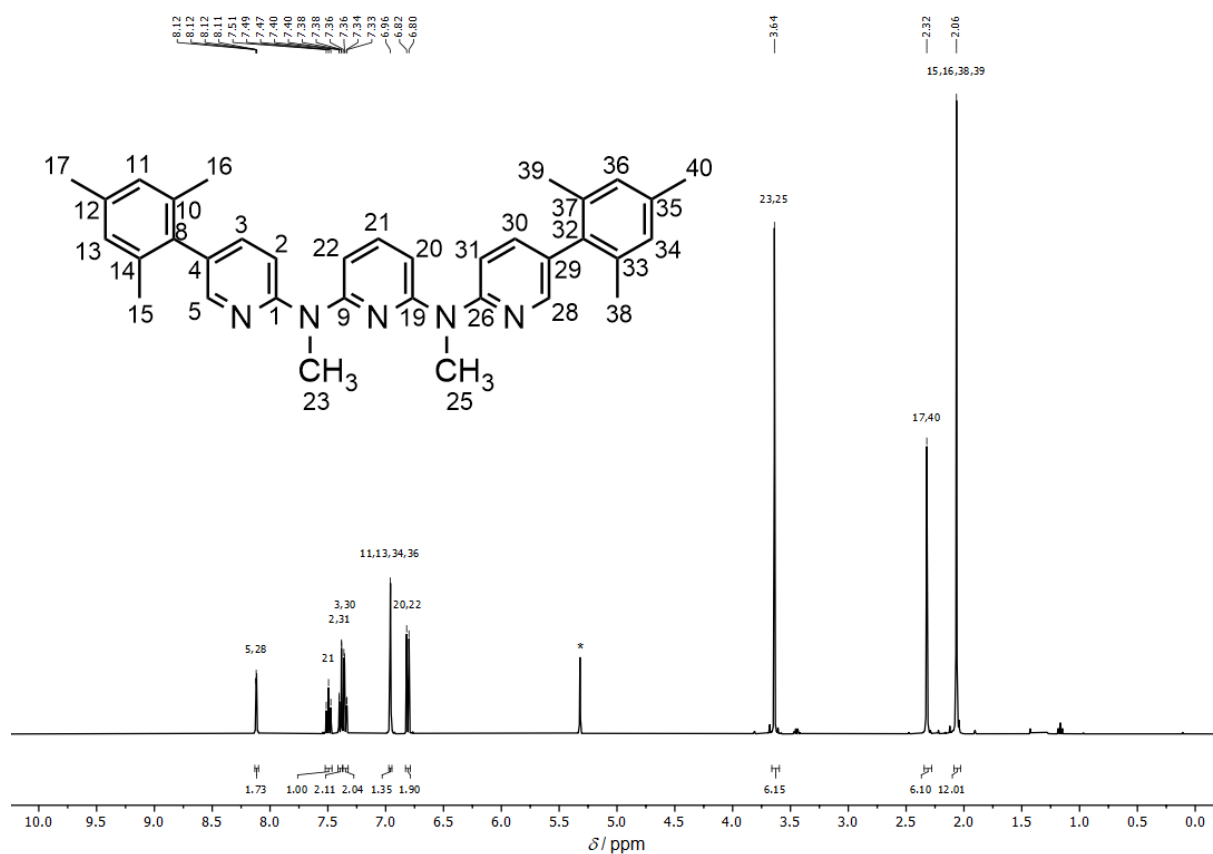


Figure S5. ¹H NMR spectrum of ddpd⁵Mes in CD₂Cl₂. * CHDCl₂.

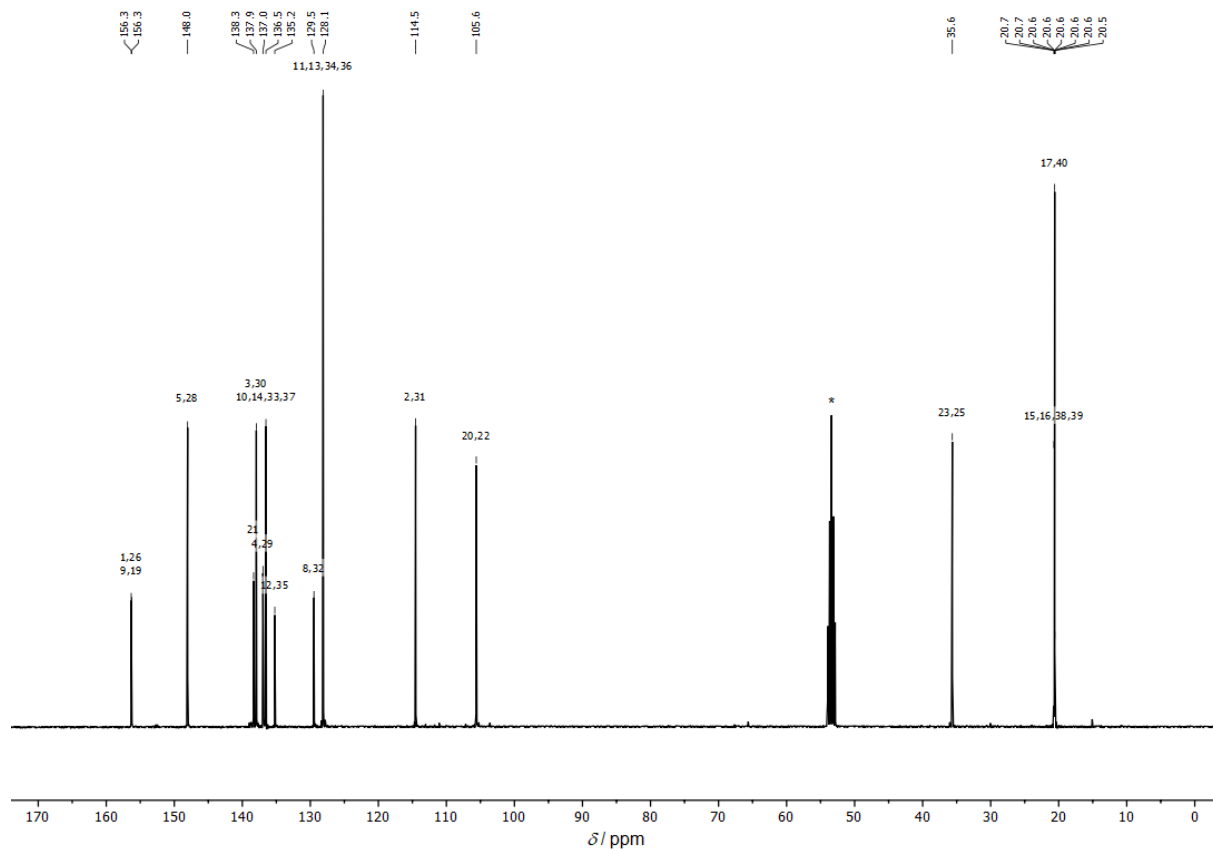


Figure S6. ¹³C{¹H} NMR spectrum of ddpd⁵Mes in CD₂Cl₂. * CHDCl₂.

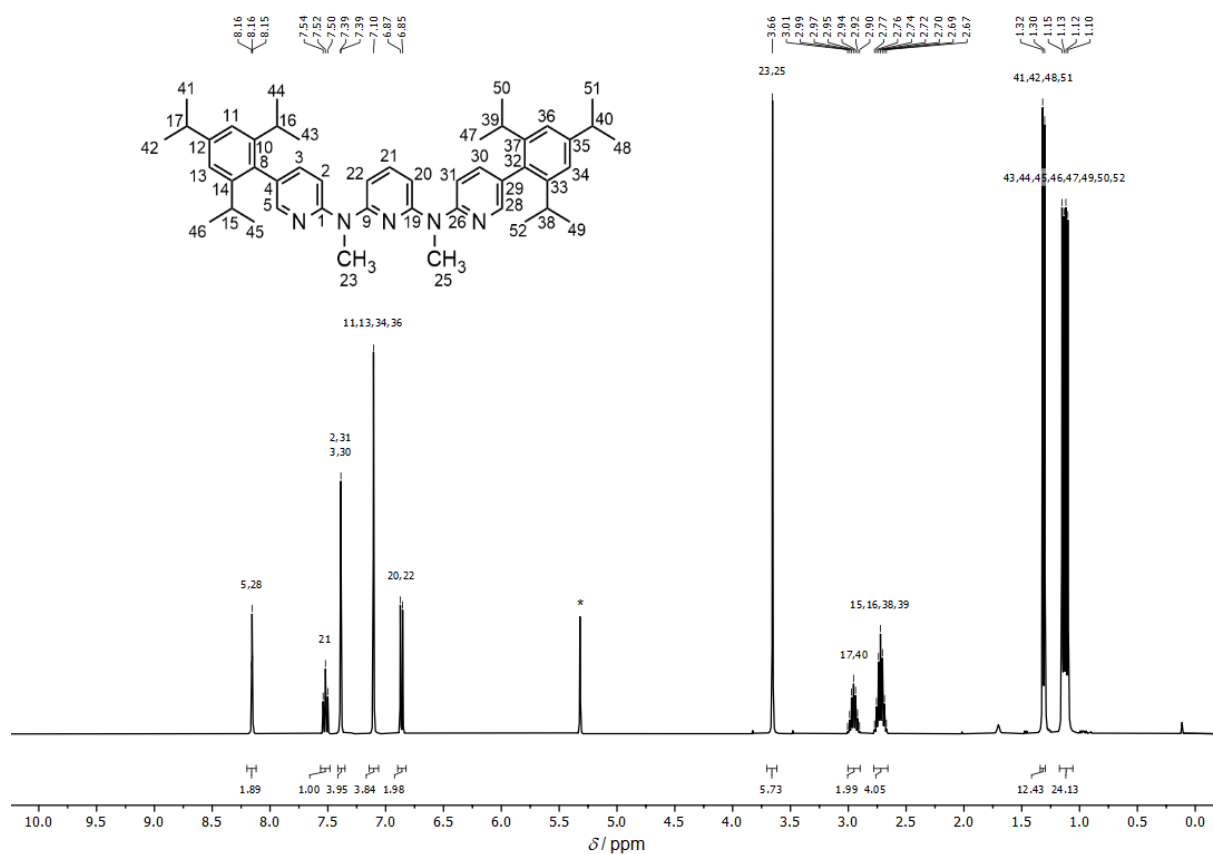


Figure S7. ^1H NMR spectrum of $\text{ddpd}^{5\text{Tripp}}$ in CD_2Cl_2 . * CHDCl_2 .

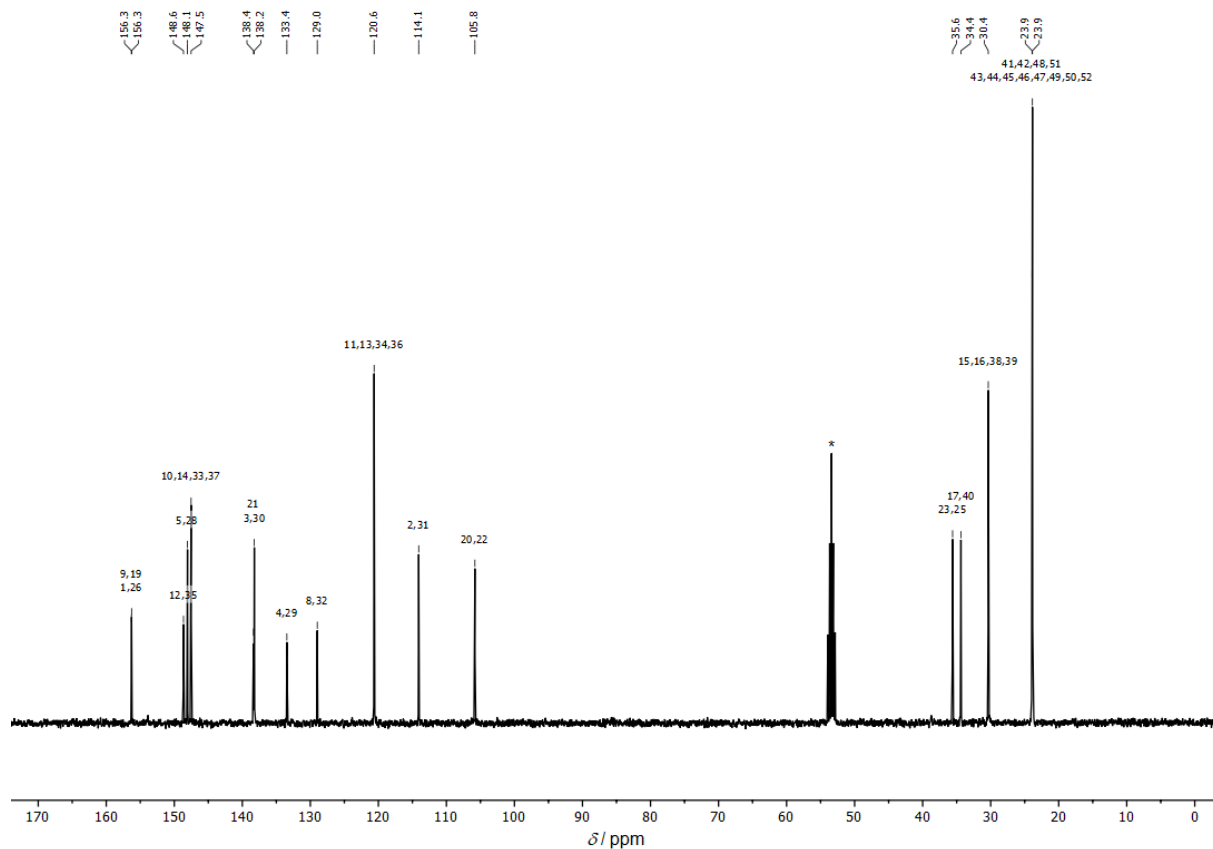


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{ddpd}^{5\text{Tripp}}$ in CD_2Cl_2 . * CHDCl_2 .

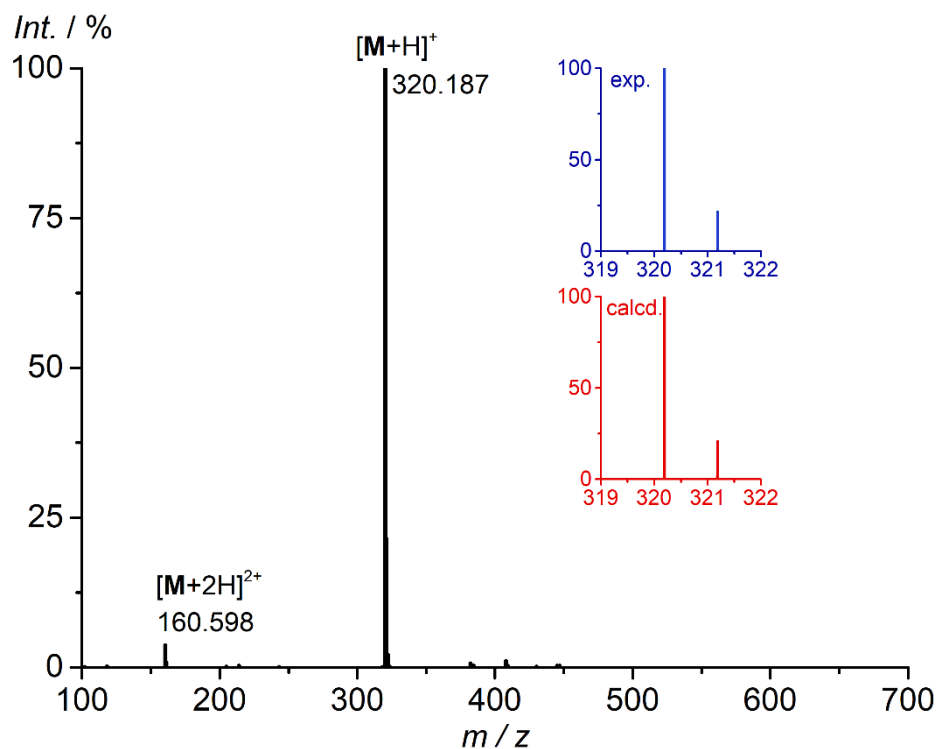


Figure S9. ESI⁺ mass spectrum of ddpd^{6Me} in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 320.

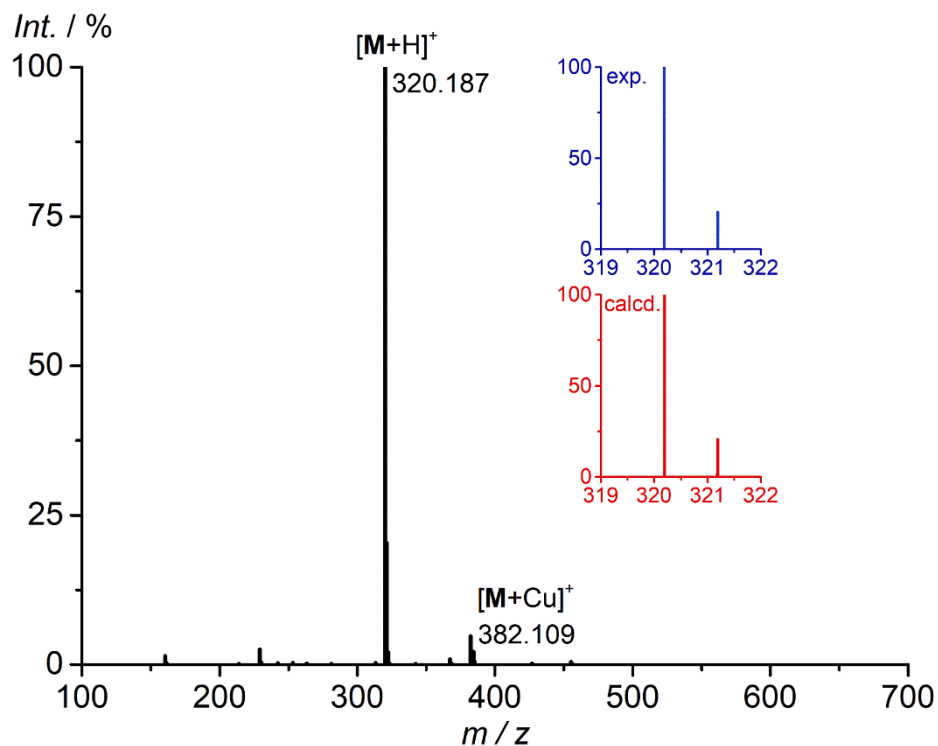


Figure S10. ESI⁺ mass spectrum of ddpd^{5Me} in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 320.

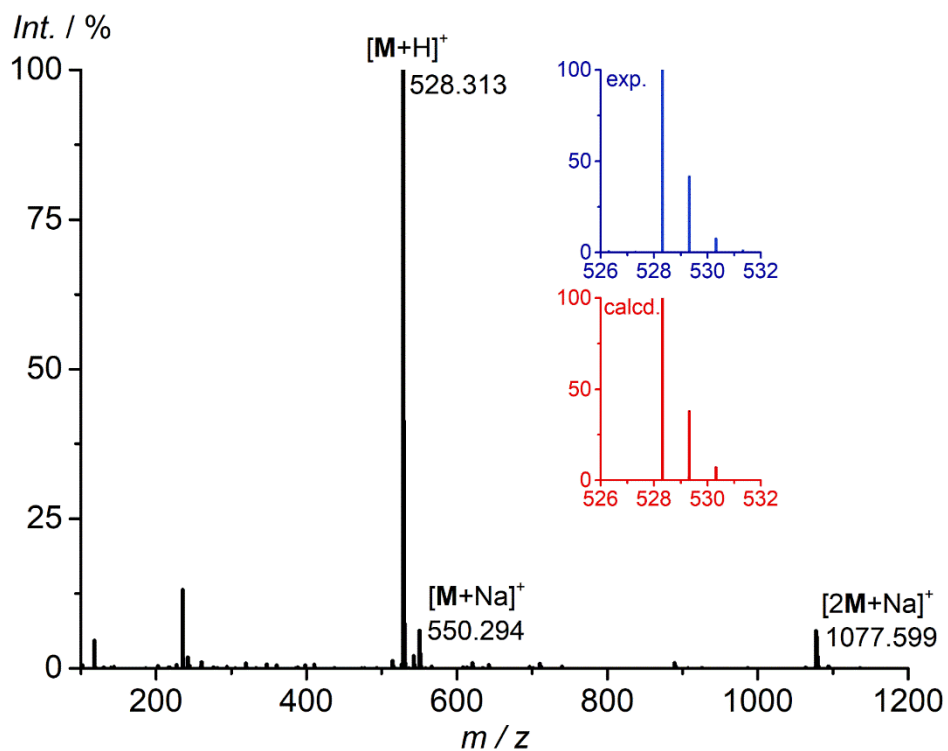


Figure S11. ESI⁺ mass spectrum of ddpd^{5Mes} in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 528.

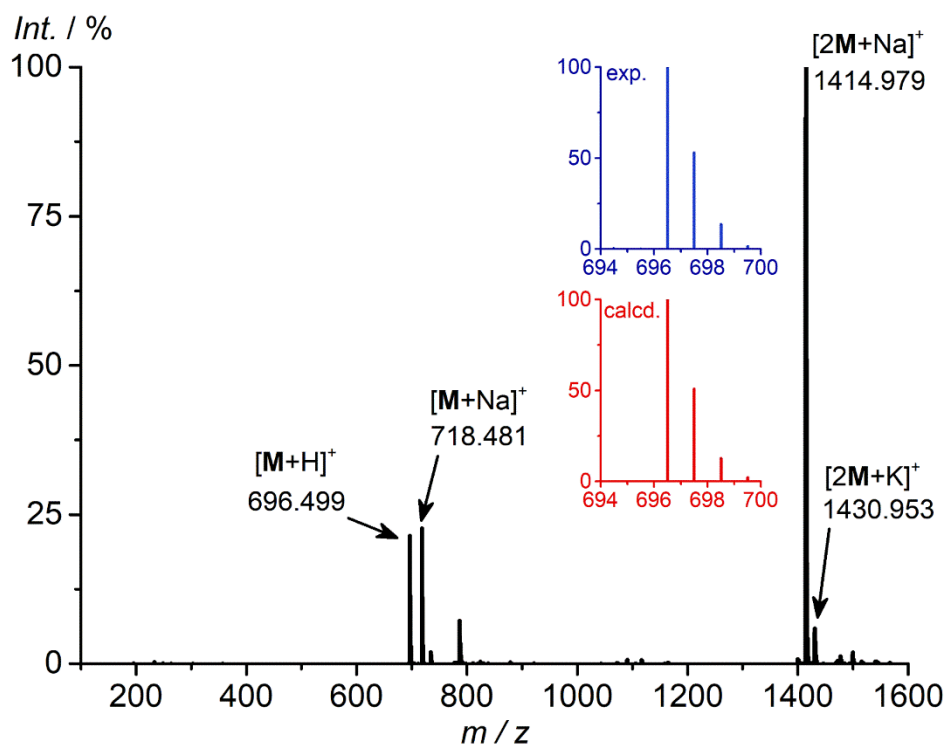


Figure S12. ESI⁺ mass spectrum of ddpd^{5Tripp} in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 696.

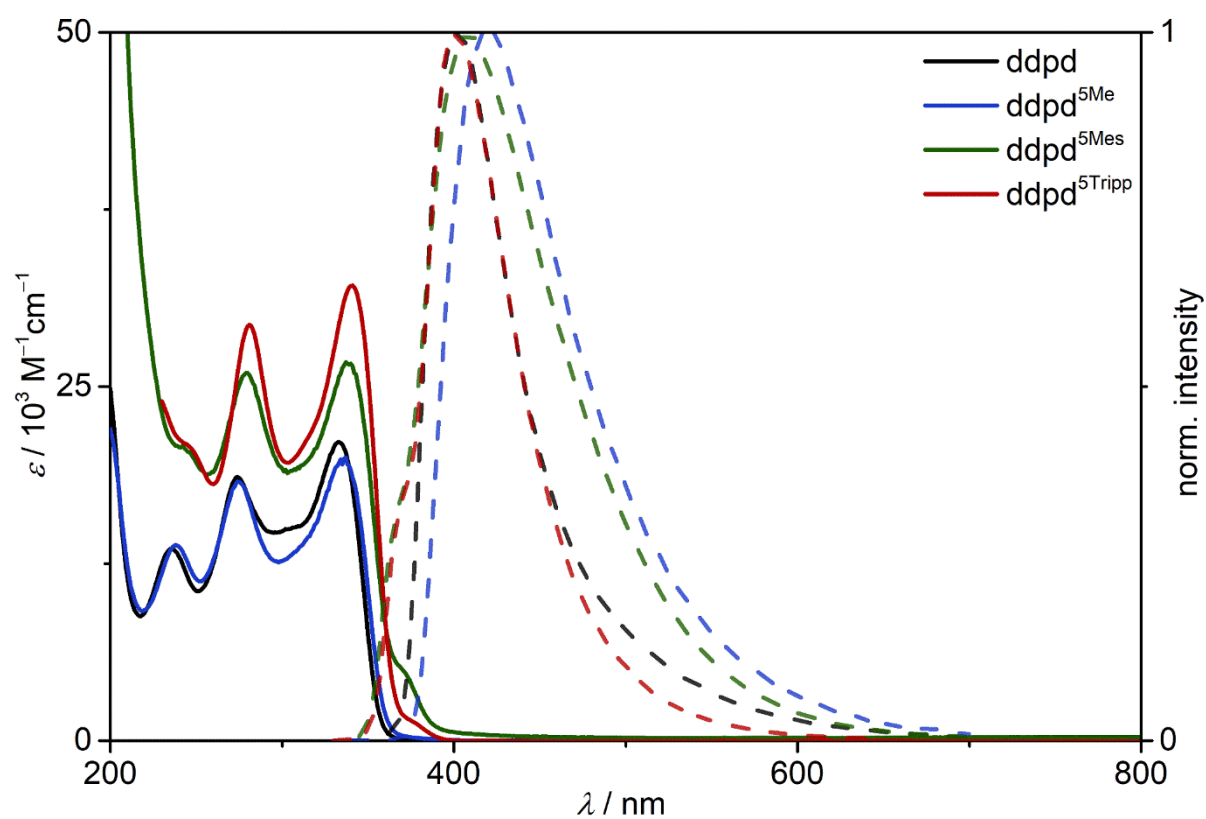


Figure S13. UV/Vis absorption (solid) and normalized emission spectra (dotted) of ligands ddpd ($\lambda_{\text{exc}} = 333 \text{ nm}$), ddpd^{5Me} ($\lambda_{\text{exc}} = 334 \text{ nm}$), ddpd^{5Mes} ($\lambda_{\text{exc}} = 337 \text{ nm}$), in acetonitrile and ddpd^{5Tripp} ($\lambda_{\text{exc}} = 320 \text{ nm}$) in dichloromethane at 293 K.

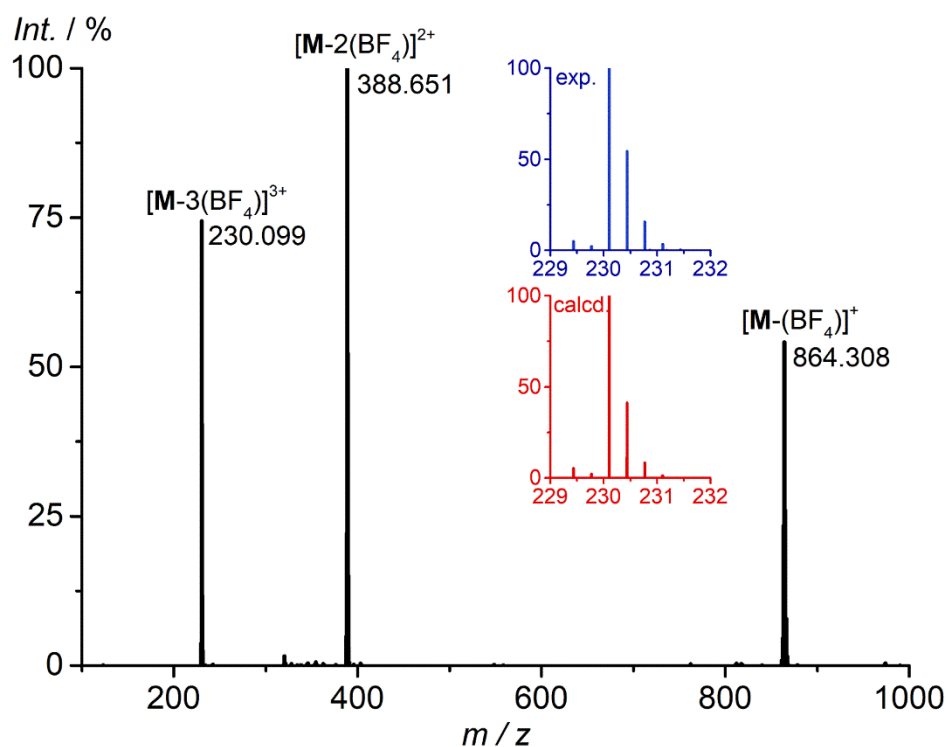


Figure S14. ESI⁺ mass spectrum of $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 230.

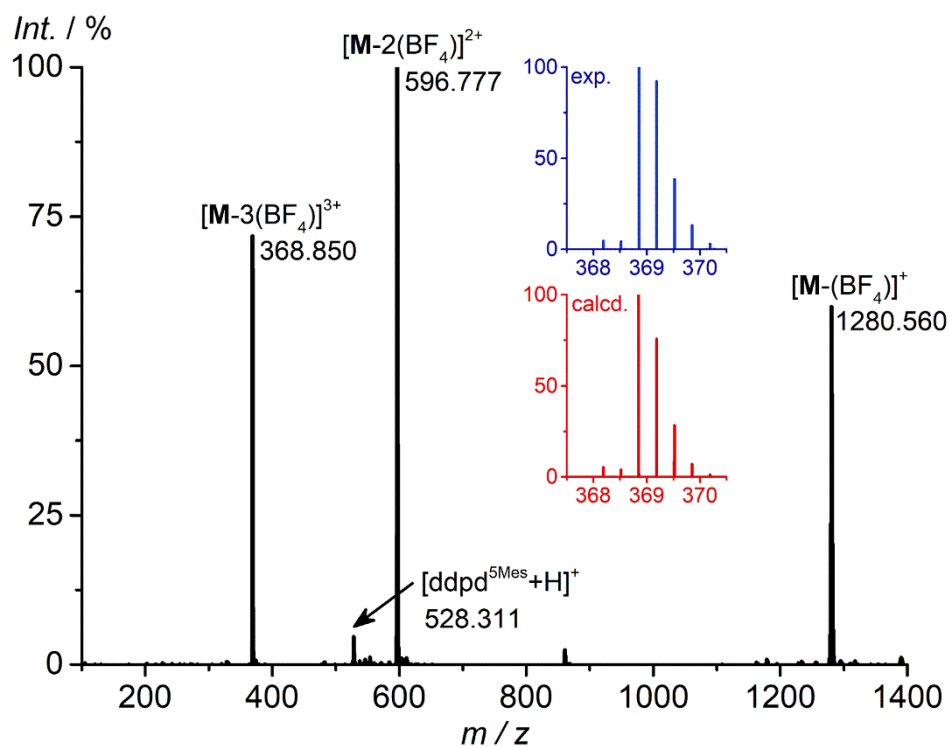


Figure S15. ESI⁺ mass spectrum of $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 369.

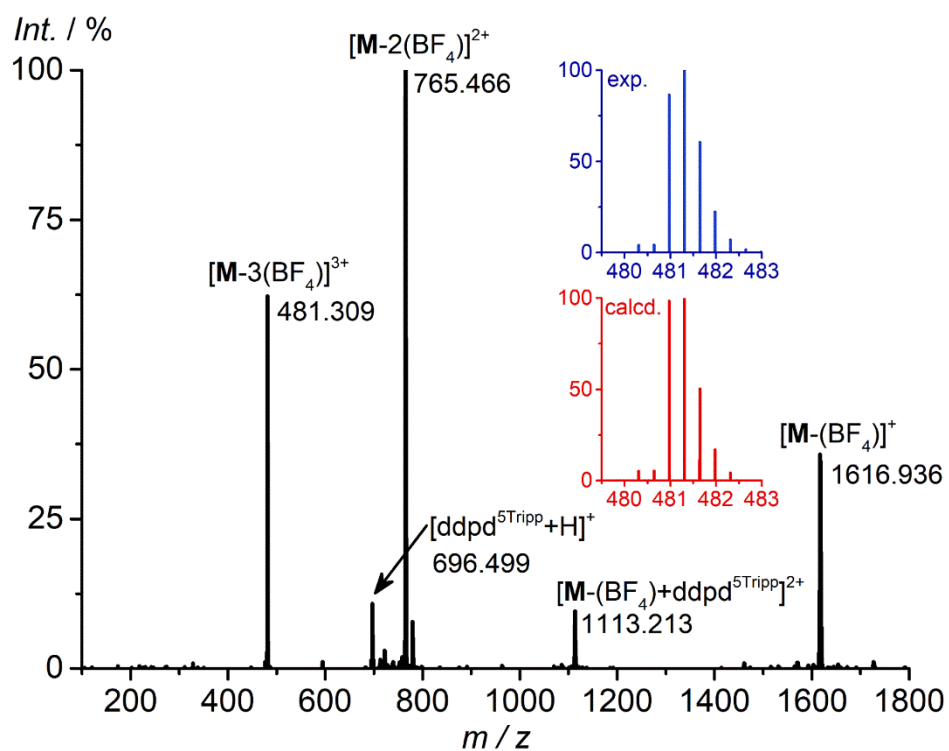


Figure S16. ESI⁺ mass spectrum of $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 481.

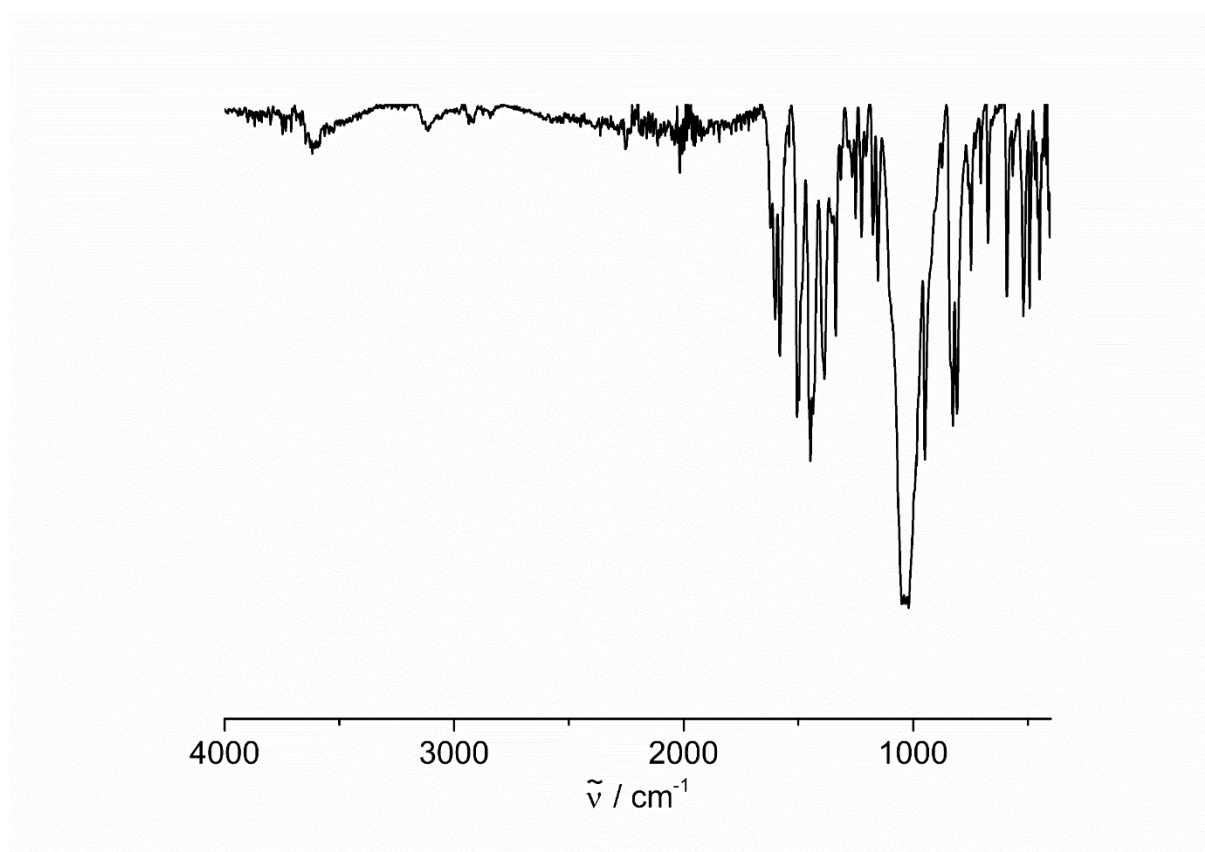


Figure S17. ATR-IR spectrum of $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$.

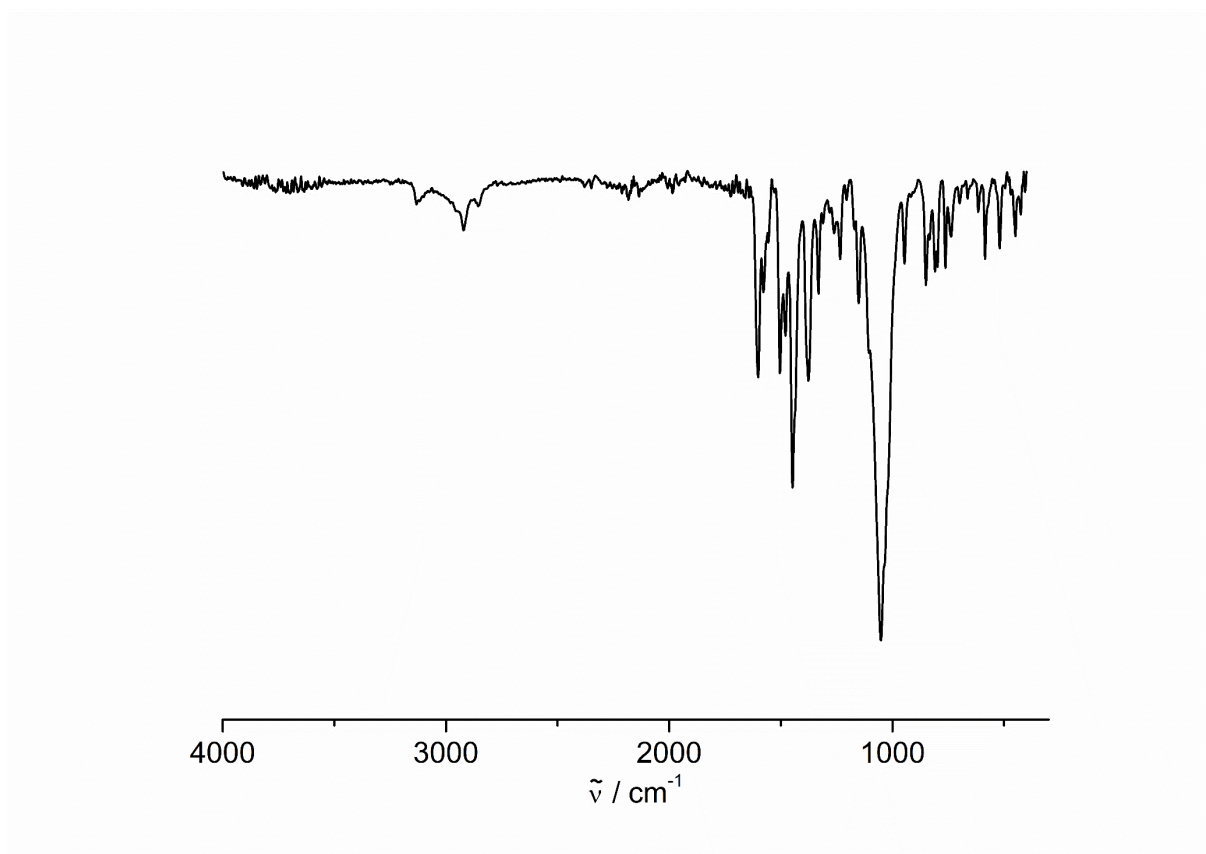


Figure S18. ATR-IR spectrum of $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$.

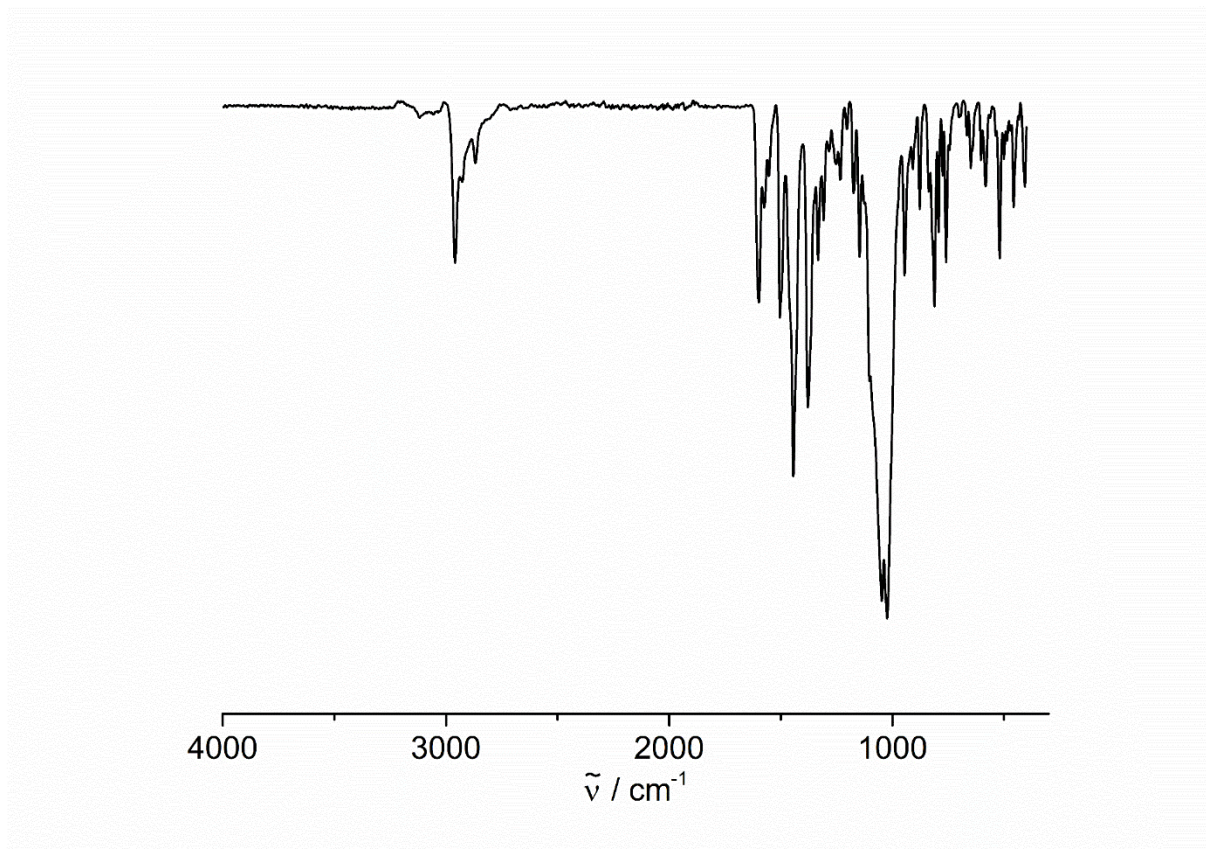


Figure S19. ATR-IR spectrum of $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$.

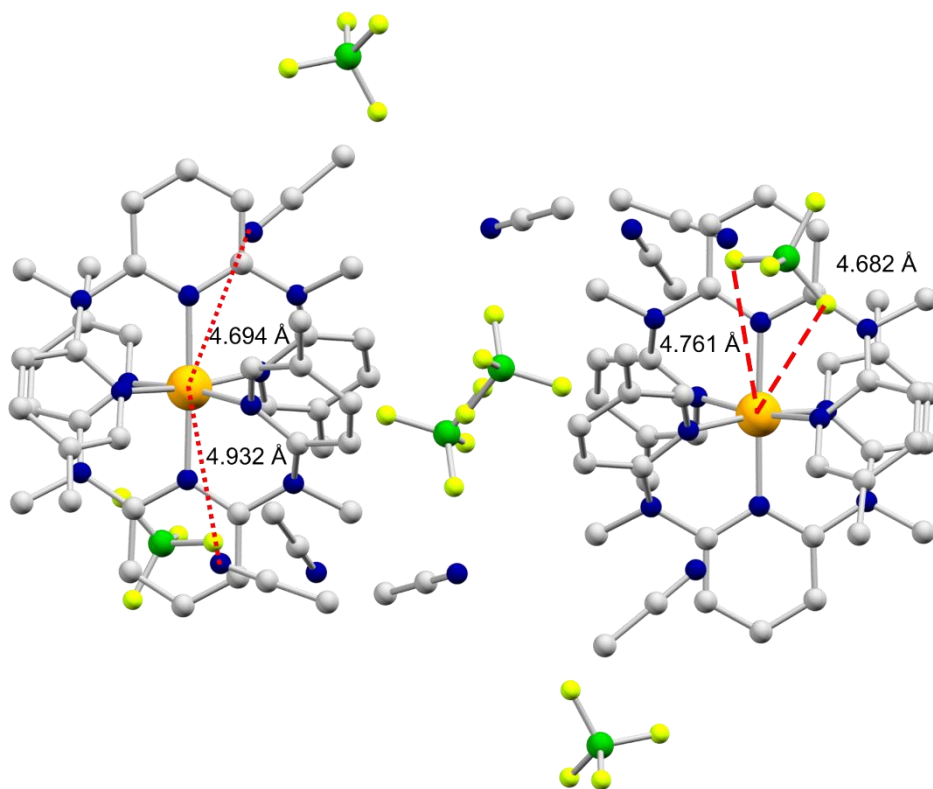


Figure S20. Packing of $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$ in the solid state with shortest $\text{Cr}\cdots\text{F}$ (dashed, BF_4^-) and $\text{Cr}\cdots\text{N}$ (dotted, MeCN) distances indicated in red. Hydrogen atoms are omitted for clarity.

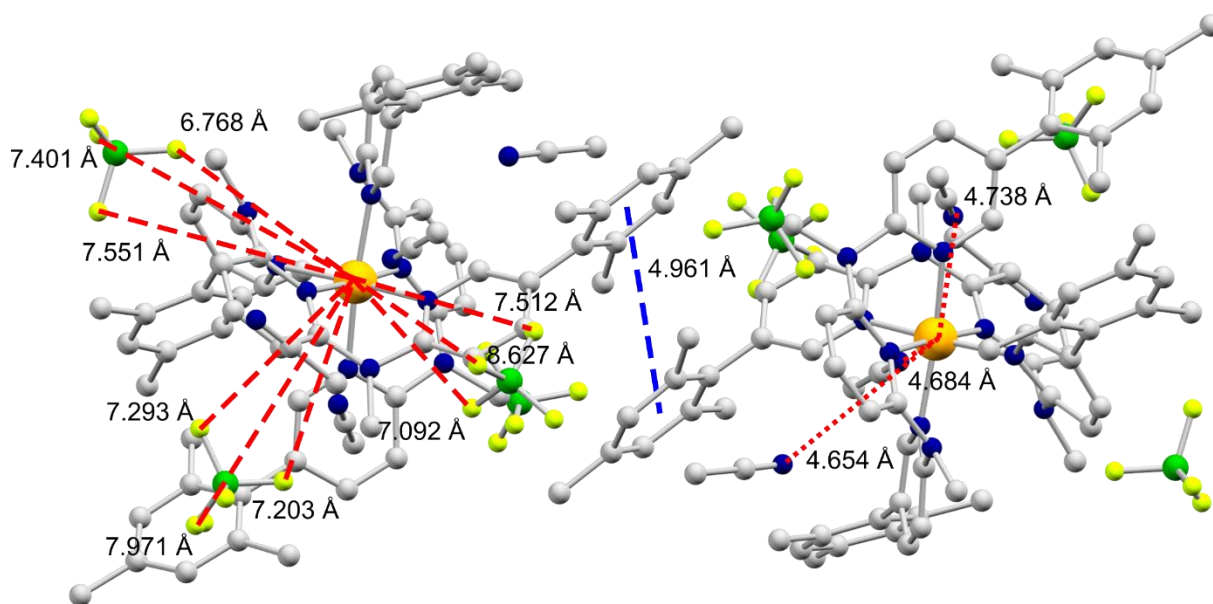


Figure S21. Packing of $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ in the solid state with intermolecular (blue dashed line) π - π stacking indicated. The π - π contact is denoted by the distance between ring centroids. Selected $\text{Cr}\cdots\text{F}$ (dashed, BF_4^-) and $\text{Cr}\cdots\text{N}$ (dotted, MeCN) distances are indicated in red. Hydrogen atoms are omitted for clarity.

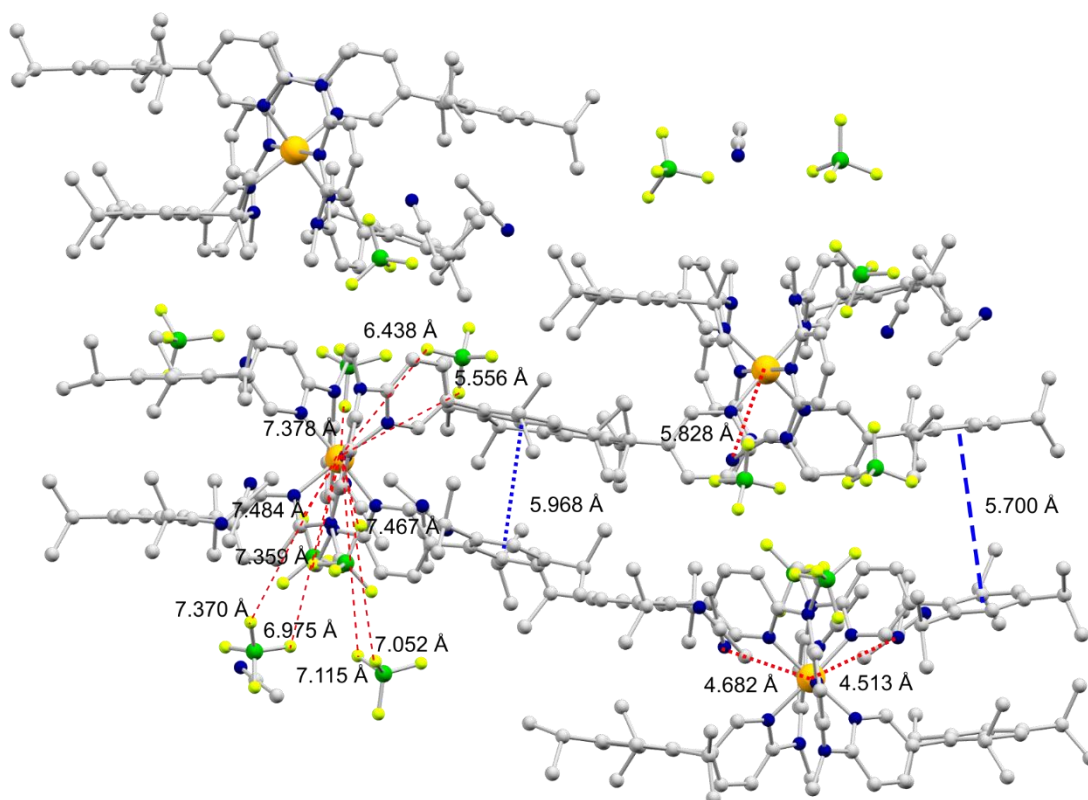


Figure S22. Packing of $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ in the solid state with average intramolecular (blue dotted lines) and intermolecular (blue dashed lines) π - π stacking indicated. The π - π contact is denoted by the distance between ring centroids. Selected Cr $\cdots$ F (dashed, BF_4^-) and Cr $\cdots$ N (dotted, MeCN) distances are indicated in red. Hydrogen atoms are omitted for clarity.

Table S1. Selected atom and centroid distances / Å and angles between planes / deg in $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$, $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ and $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ from XRD measurements.

	$[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$ ²⁰	$[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$	$[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$	$[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$
Intramol. centroids	-	-	-	5.968
Intermol. centroids	-	-	4.961	5.700
Shortest Cr $\cdots$ F (BF_4^-)	5.438 6.140 6.258 - - - - -	4.682 4.761 - - - - - -	6.768 7.401 7.551 7.203 7.293 7.971 7.092 7.512 8.627	5.556 6.438 7.378 6.975 7.370 7.052 7.115 7.467 7.378
Shortest Cr $\cdots$ N (MeCN)	4.613 4.815 -	4.694 4.932 -	4.654 4.684 4.738	4.513 4.682 5.828
Py _{central} -Cr-Py _{central}	13.8	15.2	19.1	9.8

Table S2. Bond lengths / Å and angles / deg of $[\text{Cr}^{\text{5H}}][\text{BF}_4]_3$, $^{20} [\text{Cr}^{\text{5Me}}][\text{BF}_4]_3$, $[\text{Cr}^{\text{5Mes}}][\text{BF}_4]_3$ and $[\text{Cr}^{\text{5Tripp}}][\text{BF}_4]_3$ from XRD measurements. Central pyridines, intraligand and interligand angles highlighted in purple, yellow and green, respectively.

	$[\text{Cr}^{\text{5H}}][\text{BF}_4]_3$ ²⁰	$[\text{Cr}^{\text{5Me}}][\text{BF}_4]_3$	$[\text{Cr}^{\text{5Mes}}][\text{BF}_4]_3$	$[\text{Cr}^{\text{5Tripp}}][\text{BF}_4]_3$
Cr1-N1	2.0485(18)	2.0448(14)	2.0577(17)	2.0523(14)
Cr1-N2	2.0393(18)	2.0294(14)	2.0268(17)	2.0222(14)
Cr1-N3	2.0394(19)	2.0471(14)	2.0623(18)	2.0561(14)
Cr1-N4	2.0446(17)	2.0492(13)	2.0579(18)	2.0576(14)
Cr1-N5	2.0444(18)	2.0300(14)	2.0215(17)	2.0238(14)
Cr1-N6	2.0485(18)	2.0403(13)	2.0549(18)	2.0449(14)
N1-Cr1-N2	85.13(8)	85.83(6)	87.63(7)	84.91(6)
N1-Cr1-N3	170.86(8)	172.00(5)	173.44(7)	170.02(6)
N1-Cr1-N4	91.06(87)	89.92(6)	88.71(7)	89.21(6)
N1-Cr1-N5	95.23(8)	93.47(6)	94.44(7)	95.40(6)
N1-Cr1-N6	89.49(7)	92.61(5)	91.25(7)	90.31(6)
N2-Cr1-N3	85.74(7)	86.18(6)	86.23(7)	85.26(6)
N2-Cr1-N4	95.10(7)	95.53(5)	91.65(7)	94.71(6)
N2-Cr1-N5	178.94(8)	178.31(5)	176.76(7)	179.13(6)
N2-Cr1-N6	94.02(7)	92.42(5)	95.71(7)	95.84(6)
N3-Cr1-N4	89.68(7)	90.31(6)	93.80(7)	93.29(5)
N3-Cr1-N5	89.68(7)	94.53(6)	91.79(7)	94.46(6)
N3-Cr1-N6	91.22(7)	88.26(5)	87.04(7)	89.00(6)
N4-Cr1-N5	85.89(7)	86.00(5)	85.91(7)	84.48(5)
N4-Cr1-N6	170.88(7)	171.81(5)	172.62(7)	169.35(6)
N5-Cr1-N6	84.99(7)	86.08(5)	86.74(7)	84.98(6)
Central pyridine, interligand trans, intraligand trans				

Table S3. Bond lengths / Å and angles / deg of $[\text{Cr}^{\text{5H}}]^{3+}$, $[\text{Cr}^{\text{6Me}}]^{3+}$, $[\text{Cr}^{\text{5Me}}]^{3+}$, $[\text{Cr}^{\text{5Mes}}]^{3+}$ and $[\text{Cr}^{\text{5Tripp}}]^{3+}$ from DFT calculations. Central pyridines, intraligand and interligand angles highlighted in purple, yellow and green, respectively.

	[Cr ^{5H}]3+	[Cr ^{6Me}]3+	[Cr ^{5Me}]3+	[Cr ^{5Mes}]3+	[Cr ^{5Tripp}]3+
Cr1-N1	2.059	2.150	2.056	2.062	2.064
Cr1-N2	2.046	2.045	2.048	2.038	2.041
Cr1-N3	2.059	2.162	2.056	2.057	2.060
Cr1-N4	2.059	2.155	2.055	2.068	2.062
Cr1-N5	2.046	2.039	2.047	2.045	2.044
Cr1-N6	2.059	2.156	2.055	2.059	2.060
N1-Cr1-N2	86.46	87.30	86.49	85.65	84.95
N1-Cr1-N3	172.92	174.12	172.91	172.49	170.06
N1-Cr1-N4	91.40	87.00	91.29	94.35	92.24
N1-Cr1-N5	93.54	93.45	93.51	92.52	95.12
N1-Cr1-N6	89.04	92.97	89.11	88.51	88.54
N2-Cr1-N3	86.46	86.83	86.42	86.97	85.11
N2-Cr1-N4	93.54	92.97	93.56	91.51	95.16
N2-Cr1-N5	180.00	179.21	179.98	176.84	179.76
N2-Cr1-N6	93.54	93.24	93.49	94.92	94.65
N3-Cr1-N4	89.04	93.26	89.14	87.22	88.57
N3-Cr1-N5	93.54	92.42	93.59	94.86	94.82
N3-Cr1-N6	91.40	87.41	91.33	90.76	92.34
N4-Cr1-N5	86.46	87.30	86.46	86.06	85.07
N4-Cr1-N6	172.92	173.78	172.95	173.13	170.20
N5-Cr1-N6	86.46	86.49	86.49	87.58	85.13
Central pyridine, interligand trans, intraligand trans					

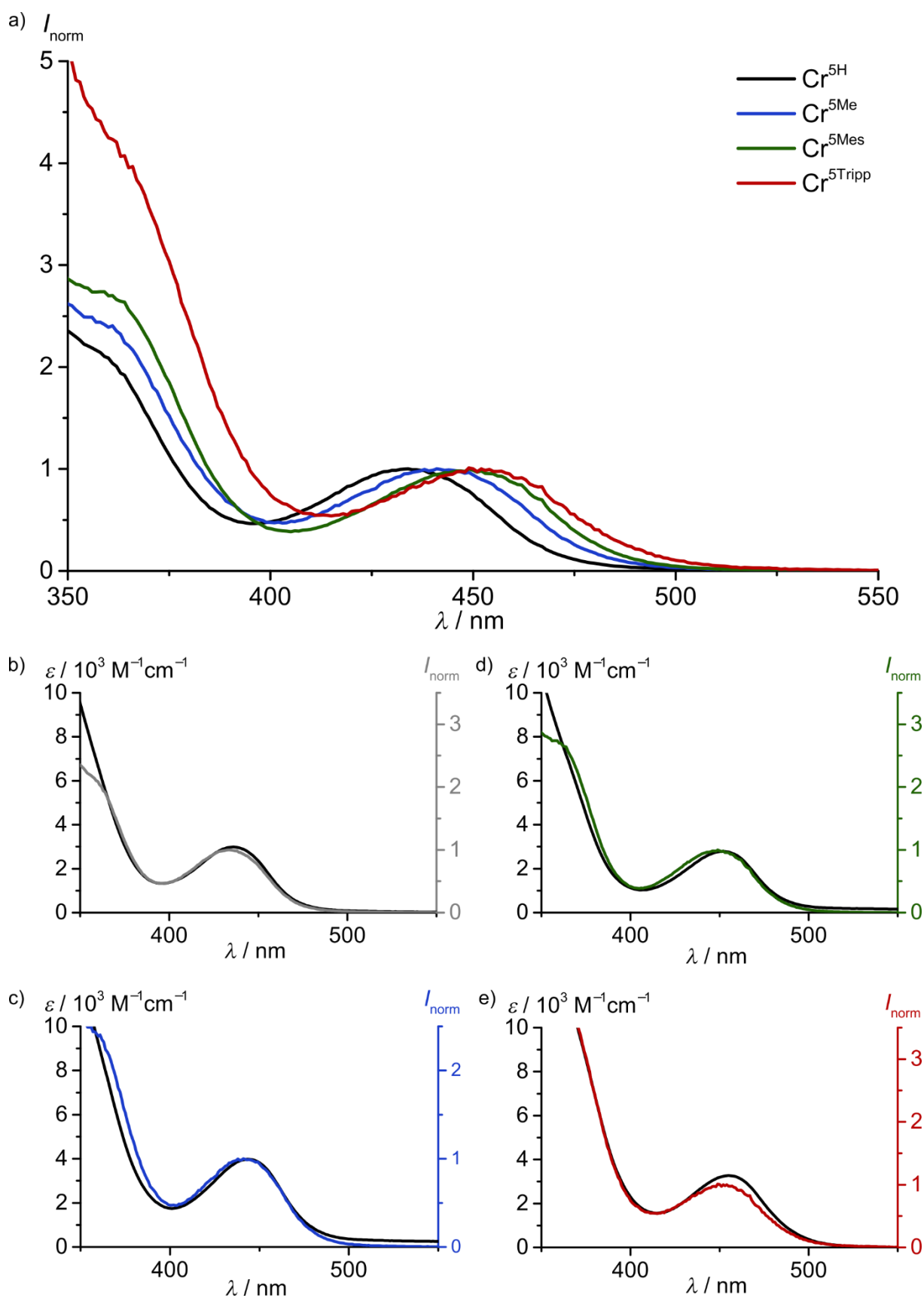


Figure S23. a) Normalized excitation spectra and superposition of absorption and excitation spectra of complexes b) $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$, c) $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$, d) $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ and e) $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ in acetonitrile at 293 K ($\lambda_{\text{em}} = 780 \text{ nm}$).

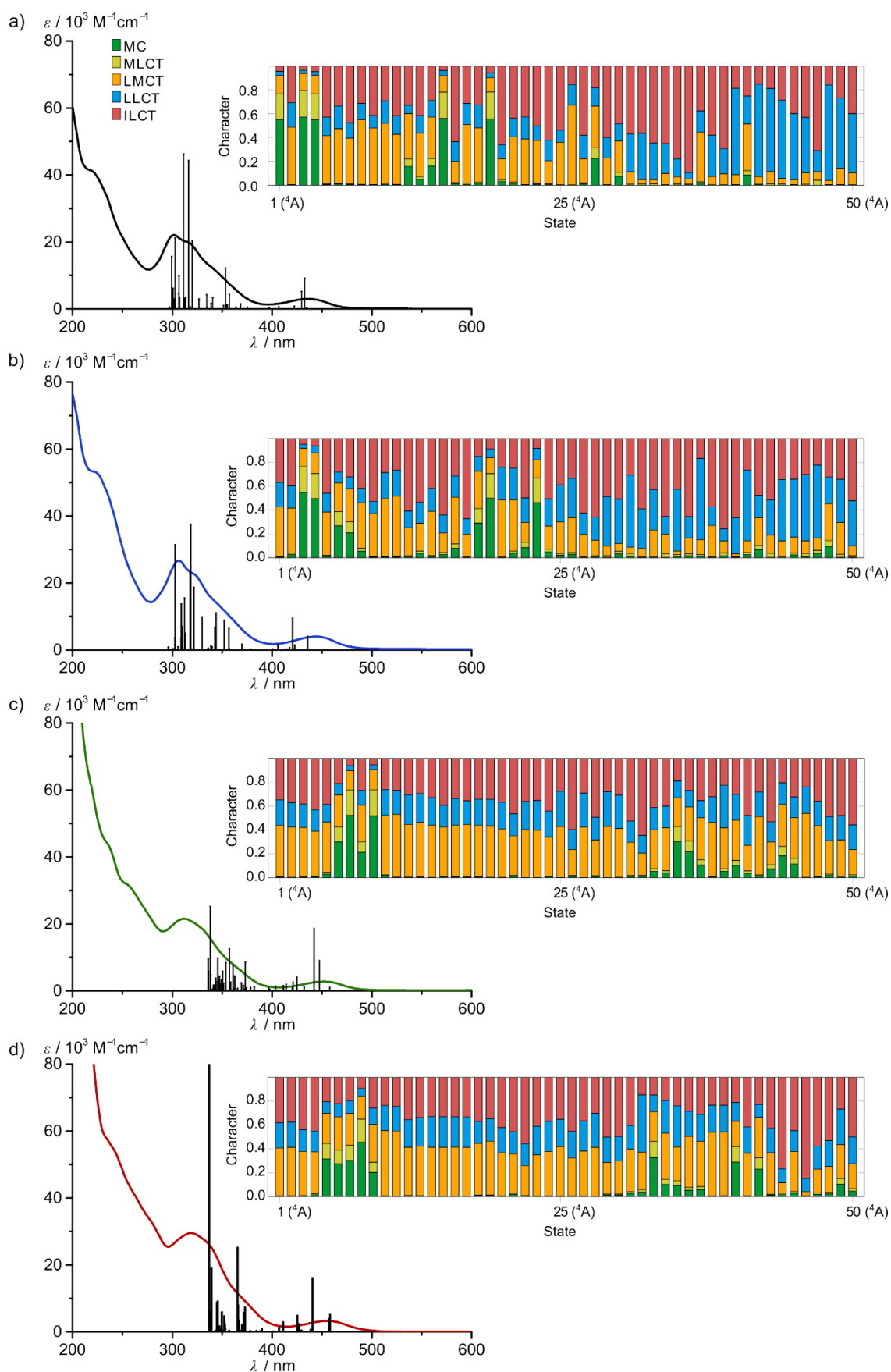


Figure S24. UV/Vis absorption spectra of a) $[\text{Cr}^{\text{VH}}][\text{BF}_4]_3$ b) $[\text{Cr}^{\text{5Me}}][\text{BF}_4]_3$, c) $[\text{Cr}^{\text{5Mes}}][\text{BF}_4]_3$ and d) $[\text{Cr}^{\text{5Tripp}}][\text{BF}_4]_3$ in acetonitrile at 293 K including the 50 lowest-energy spin-allowed TD-DFT calculated transitions (oscillator strengths). The color code indicates the character of the transition according to charge transfer number analysis (green: MC, yellow: MLCT, orange: LMCT, blue: LLCT, red: ILCT).^{9,10}

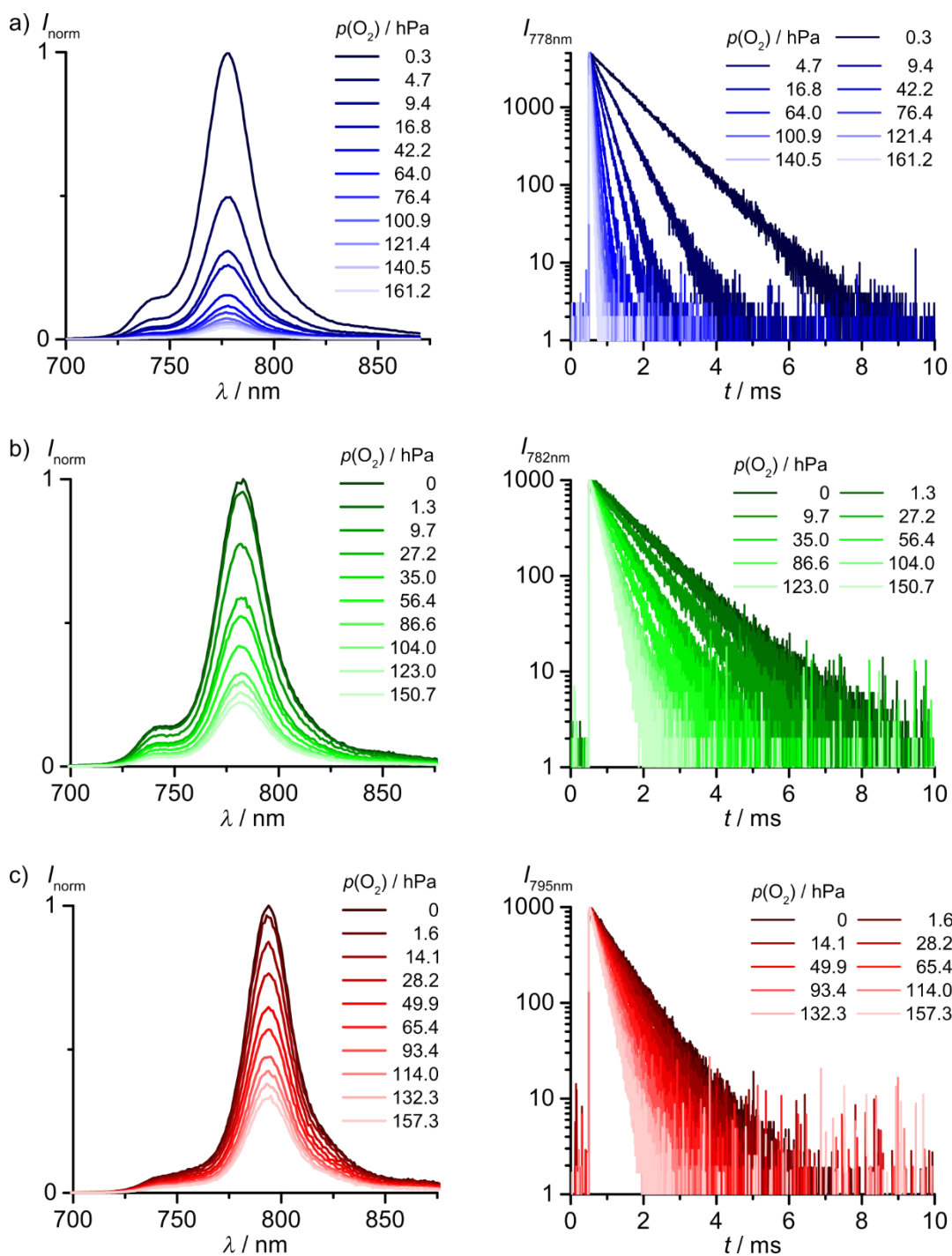


Figure S25. Oxygen quenching of luminescence intensity (left) and lifetime decay (right) of a) $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$, b) $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ and c) $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ in acetonitrile at 293 K.

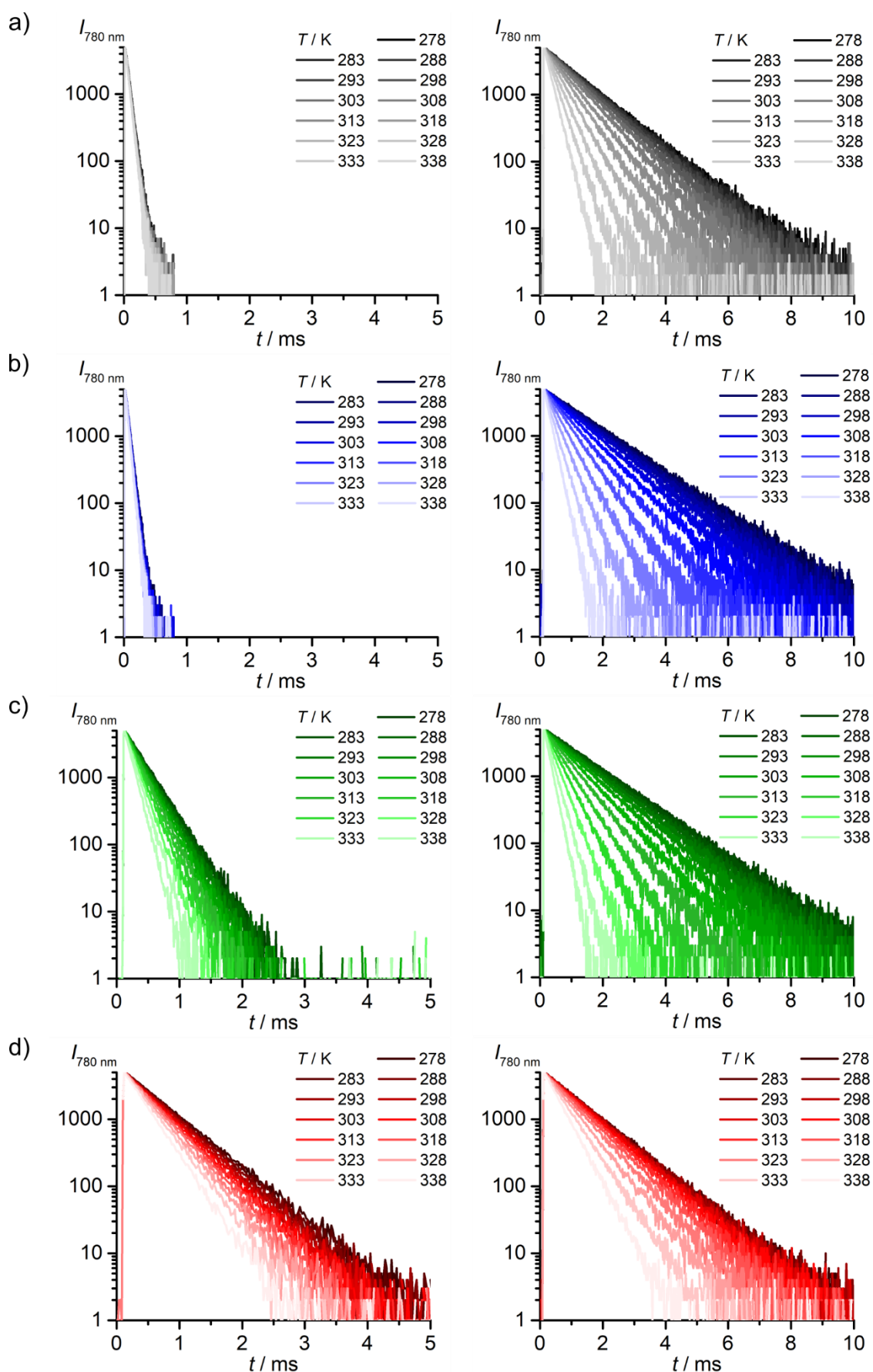


Figure S26. Temperature dependent luminescence decay of a) $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$, b) $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$, c) $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ and d) $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ in atmospheric (left) and under deoxygenated conditions (right) in acetonitrile.

Table S4. Emission lifetimes of $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$, $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$, $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ and $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ at variable temperatures in atmospheric and under deoxygenated conditions in acetonitrile.

T / K	$\tau_{\text{O}_2}(T) / \mu\text{s}$				$\tau_{\text{Ar}}(T) / \mu\text{s}$			
	$\text{Cr}^{5\text{H}}[\text{BF}_4]_3$		$\text{Cr}^{5\text{Me}}[\text{BF}_4]_3$		$\text{Cr}^{5\text{Mes}}[\text{BF}_4]_3$		$\text{Cr}^{5\text{Tripp}}[\text{BF}_4]_3$	
278	57	1153	55	1402	294	1342	569	1160
283	57	1128	54	1377	283	1305	562	1148
288	56	1115	53	1322	282	1250	541	1137
293	55	1058	53	1261	270	1190	527	1122
298	54	1003	51	1189	258	1101	506	1098
303	54	939	50	1072	244	999	488	1089
308	53	846	49	951	234	870	476	1051
313	53	747	48	795	219	729	461	1001
318	53	628	48	640	204	585	439	940
323	52	513	47	502	184	462	418	843
328	51	404	47	376	165	348	382	738
333	51	306	46	278	144	258	349	620
338	50	230	44	197	119	189	311	491

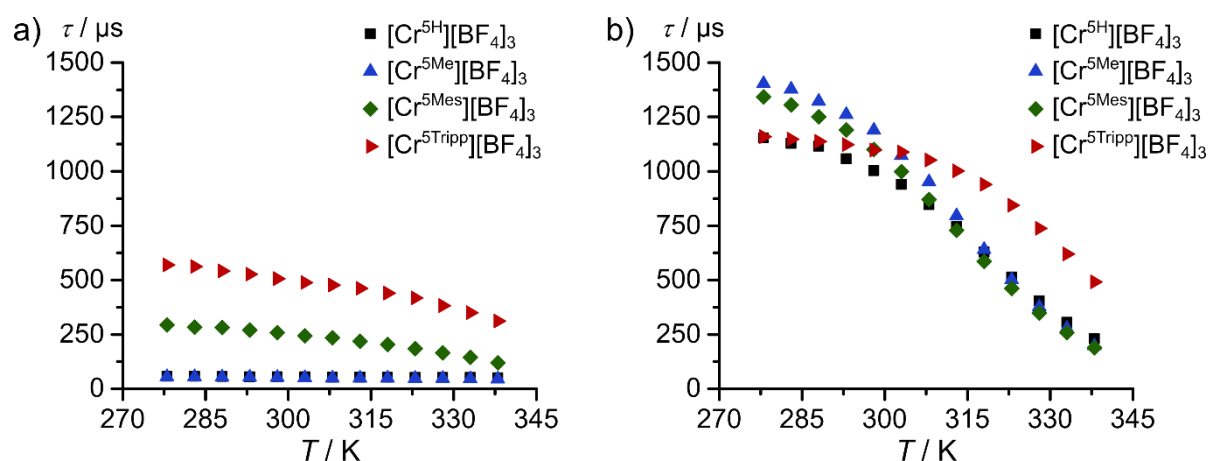


Figure S27. Plot of temperature dependent excited state lifetimes of $[\text{Cr}^{5\text{H}}][\text{BF}_4]_3$, $[\text{Cr}^{5\text{Me}}][\text{BF}_4]_3$, $[\text{Cr}^{5\text{Mes}}][\text{BF}_4]_3$ and $[\text{Cr}^{5\text{Tripp}}][\text{BF}_4]_3$ in a) atmospheric and under b) deoxygenated conditions in acetonitrile.

Table S5. Cartesian coordinates of the calculated ground state geometry of $[\text{Cr}^{\text{VH}}]^{3+}$ (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
24	0.000000	0.000000	0.000000
6	1.154209	2.726726	0.197888
6	1.180554	4.115108	0.198557
6	0.000108	4.806440	-0.000905
6	-1.180375	4.115091	-0.200089
6	-1.154102	2.726710	-0.198863
7	0.000035	2.045813	-0.000350
1	2.102258	4.641462	0.384612
1	-2.102053	4.641418	-0.386354
6	1.489211	-0.811393	2.438575
6	2.580962	-0.974575	3.252884
6	3.673329	-0.128995	3.064896
6	3.612947	0.863598	2.110309
6	2.457354	0.995242	1.330395
7	1.437725	0.127401	1.467847
1	4.559106	-0.229380	3.677786
1	0.626658	-1.453276	2.526980
1	2.581985	-1.749890	4.004488
1	4.432797	1.552395	1.990896
6	-2.457341	0.994868	-1.330706
6	-3.612958	0.862969	-2.110544
6	-3.673396	-0.129974	-3.064762
6	-2.581062	-0.975660	-3.252463
6	-1.489287	-0.812215	-2.438241
7	-1.437746	0.126938	-1.467861
1	-4.559192	-0.230557	-3.677590
1	-4.432787	1.551831	-1.991361
1	-2.582132	-1.751252	-4.003783
1	-0.626764	-1.454168	-2.526419
6	1.154173	-2.726739	-0.197967
6	1.180497	-4.115121	-0.198662
6	0.000050	-4.806440	0.000835
6	-1.180417	-4.115077	0.200071
6	-1.154123	-2.726696	0.198867
7	0.000018	-2.045812	0.000334
1	2.102186	-4.641485	-0.384765
1	-2.102097	-4.641393	0.386355
6	1.489148	0.811431	-2.438597
6	2.580878	0.974621	-3.252930
6	3.673234	0.129010	-3.065010
6	3.612862	-0.863614	-2.110456
6	2.457294	-0.995257	-1.330503
7	1.437674	-0.127396	-1.467898
1	4.558991	0.229402	-3.677926
1	0.626605	1.453335	-2.526950
1	2.581899	1.749960	-4.004509
1	4.432701	-1.552433	-1.991090
6	-2.457311	-0.994853	1.330767
6	-3.612902	-0.862951	2.110643
6	-3.673289	0.129967	3.064889
6	-2.580932	0.975628	3.252578
6	-1.489186	0.812183	2.438317
7	-1.437698	-0.126944	1.467908
1	-4.559061	0.230554	3.677752
1	-4.432745	-1.551800	1.991475
1	-2.581966	1.751195	4.003922
1	-0.626644	1.454113	2.526486
7	2.344554	-2.014881	-0.392565
6	3.585016	-2.662198	0.058369
1	3.984715	-3.362996	-0.676550
1	4.320278	-1.887509	0.259410
1	3.377073	-3.188034	0.985234
7	-2.344524	-2.014790	0.393176
6	-3.584959	-2.662275	-0.057586
1	-3.984679	-3.362824	0.677559
1	-4.320220	-1.887660	-0.258916
1	-3.376978	-3.188429	-0.984262
7	2.344587	2.014851	0.392442
7	-2.344517	2.014819	-0.393136
6	3.585039	2.662135	-0.058568
1	3.984793	3.362935	0.676319
1	4.320275	1.887427	-0.259637

1	3.377058	3.187961	-0.985430
6	-3.584934	2.662338	0.057629
1	-3.984647	3.362882	-0.677524
1	-4.320209	1.887742	0.258980
1	-3.376931	3.188504	0.984294
1	0.000138	5.888131	-0.001124
1	0.000064	-5.888131	0.001035

Table S6. Cartesian coordinates of the calculated ground state geometry of $[\text{Cr}^{\text{6Me}}]^{3+}$ (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
6	1.227555	2.647677	0.174218
6	1.266675	4.034804	0.199839
6	0.096838	4.742037	-0.006219
6	-1.086929	4.061481	-0.219113
6	-1.076782	2.672940	-0.205725
7	0.068166	1.978374	-0.017520
1	2.195181	4.546349	0.394017
1	-2.004010	4.594735	-0.408580
6	1.690870	-0.801265	2.580027
6	2.884848	-0.904818	3.269363
6	3.961627	-0.104395	2.925012
6	3.806565	0.829430	1.927858
6	2.581245	0.918993	1.263153
7	1.559827	0.063824	1.525006
1	4.901899	-0.183693	3.453921
1	4.606524	1.509893	1.693523
6	-2.455147	0.973934	-1.312999
6	-3.646972	0.967108	-2.036230
6	-3.822370	0.038427	-3.037537
6	-2.797871	-0.847879	-3.311682
6	-1.639022	-0.834356	-2.553985
7	-1.481413	0.048770	-1.521958
1	-4.734897	0.029918	-3.618359
1	-4.402233	1.710390	-1.848132
6	1.207007	-2.789118	-0.099133
6	1.232886	-4.177624	-0.069321
6	0.043532	-4.868285	0.063432
6	-1.146846	-4.172922	0.164859
6	-1.118547	-2.785970	0.129857
7	0.044136	-2.105022	-0.000095
1	2.165794	-4.705666	-0.176929
1	-2.081292	-4.692921	0.297759
6	1.845121	0.684250	-2.487551
6	3.028748	0.679439	-3.206774
6	4.037154	-0.210052	-2.888150
6	3.824094	-1.119021	-1.876332
6	2.611741	-1.103935	-1.188583
7	1.647508	-0.181462	-1.447414
1	4.966726	-0.218212	-3.441248
1	4.567424	-1.863609	-1.650074
6	-2.522344	-1.078294	1.179244
6	-3.743170	-1.070720	1.851938
6	-3.961847	-0.139828	2.842444
6	-2.950466	0.748102	3.155296
6	-1.757680	0.728101	2.451470
7	-1.553077	-0.160382	1.433200
1	-4.898614	-0.129043	3.383259
1	-4.489977	-1.813124	1.629821
7	2.401094	-2.076215	-0.206434
6	3.590719	-2.726178	0.366266
1	4.025845	-3.474070	-0.298501
1	4.330522	-1.960756	0.580198
1	3.300185	-3.198132	1.299742
7	-2.310680	-2.065626	0.212872
6	-3.497779	-2.716868	-0.362684
1	-3.952994	-3.442803	0.312820
1	-4.224579	-1.948089	-0.608978
1	-3.198454	-3.218332	-1.277892
7	2.414003	1.923591	0.313717
7	-2.273586	1.970870	-0.351705
6	3.624167	2.560517	-0.229985
1	4.081576	3.260756	0.470521
1	4.338919	1.782706	-0.483032

1	3.350964	3.088232	-1.138257
6	-3.478782	2.636386	0.167851
1	-3.898487	3.359623	-0.533020
1	-4.221244	1.875293	0.390050
1	-3.215377	3.143956	1.090631
1	0.108163	5.823571	-0.001030
1	0.044434	-5.949634	0.088987
24	0.043376	-0.060445	-0.002839
1	-2.884107	-1.566726	-4.113430
1	3.146002	1.385973	-4.015445
1	-3.071684	1.472267	3.947651
1	2.960276	-1.614430	4.079465
6	0.827197	1.701135	-2.909075
1	0.870440	1.801886	-3.992206
1	-0.182998	1.451129	-2.631699
1	1.070872	2.679492	-2.491138
6	0.544276	-1.621184	3.085478
1	-0.016852	-2.125628	2.313230
1	0.924389	-2.372132	3.773023
1	-0.149150	-0.987018	3.639322
6	-0.599470	-1.849001	-2.924810
1	-0.853644	-2.825708	-2.509298
1	-0.597293	-1.958219	-4.008031
1	0.396786	-1.590812	-2.607214
6	-0.736332	1.743694	2.869389
1	-0.775745	1.843865	3.952909
1	0.272518	1.493639	2.586966
1	-0.980228	2.722612	2.453538

Table S7. Cartesian coordinates of the calculated ground state geometry of $[\text{Cr}^{\text{5Me}}]^{3+}$ (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
6	1.22197	2.660232	0.200775
6	1.261177	4.048657	0.191003
6	0.090814	4.749211	-0.034648
6	-1.092028	4.067366	-0.251902
6	-1.077986	2.678412	-0.244814
7	0.065784	1.988576	-0.017678
1	2.183893	4.567687	0.392305
1	-2.005296	4.600463	-0.459366
6	1.468932	-0.874154	2.465253
6	2.535667	-1.070962	3.310864
6	3.636319	-0.22289	3.133406
6	3.610896	0.772575	2.182934
6	2.477709	0.920155	1.373461
7	1.449522	0.065835	1.493676
1	4.510309	-0.332895	3.763438
1	0.59394	-1.502618	2.532062
1	4.443835	1.449468	2.085458
6	-2.36377	0.946522	-1.39677
6	-3.496722	0.812383	-2.208845
6	-3.539865	-0.194747	-3.146287
6	-2.457038	-1.068556	-3.307837
6	-1.389334	-0.882982	-2.460914
7	-1.353428	0.069389	-1.501923
1	-4.413574	-0.294563	-3.778397
1	-4.315334	1.508104	-2.123379
1	-0.527605	-1.530559	-2.51597
6	1.180199	-2.799209	-0.148906
6	1.194031	-4.188083	-0.13336
6	0.001304	-4.866726	0.034387
6	-1.178735	-4.163362	0.190258
6	-1.139088	-2.775005	0.182317
7	0.026878	-2.106495	0.011269
1	2.116208	-4.724381	-0.285827
1	-2.110725	-4.67968	0.35186
6	1.600605	0.728236	-2.404107
6	2.708336	0.898195	-3.201703
6	3.779769	0.024647	-2.975558
6	3.689259	-0.967534	-2.025923
6	2.519452	-1.085168	-1.265513
7	1.516872	-0.208731	-1.432692
1	4.682342	0.112456	-3.567592
1	0.743134	1.374915	-2.511955

1	4.500088	-1.664485	-1.891407
6	-2.447293	-1.019842	1.270365
6	-3.616779	-0.865104	2.024708
6	-3.687485	0.141169	2.961116
6	-2.597159	0.992985	3.179753
6	-1.491669	0.788111	2.387312
7	-1.426122	-0.163269	1.428689
1	-4.58977	0.257049	3.548777
1	-4.443283	-1.544712	1.896621
1	-0.620952	1.418072	2.487914
7	2.378887	-2.098511	-0.321416
6	3.604652	-2.74789	0.16274
1	4.014897	-3.461707	-0.55395
1	4.341668	-1.975813	0.367339
1	3.375248	-3.259479	1.092749
7	-2.324852	-2.04944	0.341821
6	-3.56149	-2.68304	-0.135065
1	-3.987072	-3.376885	0.592191
1	-4.283266	-1.900616	-0.354322
1	-3.339694	-3.214498	-1.055728
7	2.39901	1.938569	0.428263
7	-2.267567	1.975342	-0.464287
6	3.656431	2.565605	-0.000879
1	4.050796	3.266413	0.737189
1	4.385556	1.780091	-0.181514
1	3.475405	3.08803	-0.935523
6	-3.51427	2.630626	-0.045982
1	-3.893466	3.330148	-0.793169
1	-4.258131	1.86065	0.141187
1	-3.326343	3.160203	0.883289
1	0.100615	5.830887	-0.041171
1	-0.008652	-5.948376	0.043711
24	0.046441	-0.058776	-0.002875
6	2.76668	1.97681	-4.240973
1	3.579374	2.673065	-4.023398
1	2.954264	1.551518	-5.228879
1	1.833888	2.538303	-4.277466
6	1.22197	2.660232	0.200775
6	1.261177	4.048657	0.191003
6	0.090814	4.749211	-0.034648
6	-1.092028	4.067366	-0.251902
6	-1.077986	2.678412	-0.244814
7	0.065784	1.988576	-0.017678
1	2.183893	4.567687	0.392305
1	-2.005296	4.600463	-0.459366
6	1.468932	-0.874154	2.465253
6	2.535667	-1.070962	3.310864
6	3.636319	-0.22289	3.133406
6	3.610896	0.772575	2.182934

Table S8. Cartesian coordinates of the calculated ground state geometry of $[\text{Cr}^{5\text{Mes}}]^{3+}$ (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
24	8.926913	9.429243	8.465156
7	7.734977	10.739418	7.415496
7	8.106973	12.377064	9.079042
7	10.06575	11.038023	9.010373
7	11.98582	9.638553	8.913485
7	10.195834	8.308991	9.653338
7	10.018037	9.125668	6.741729
7	9.920281	6.809635	7.134349
7	7.88654	7.765601	7.914506
7	5.9059	8.78993	8.721076
7	7.670319	9.544198	10.08938
6	7.154787	10.347907	6.261301
1	7.434197	9.370372	5.902089
6	6.247021	11.116493	5.561355
6	5.671864	10.642064	4.278193
6	6.528875	10.328738	3.205172
6	8.023745	10.496235	3.293453
1	8.451835	10.571059	2.295385
1	8.49681	9.643651	3.785293
1	8.307058	11.38766	3.853285
6	5.978478	9.876258	2.009456

1	6.642376	9.651672	1.182072
6	4.605011	9.716544	1.843797
6	4.039661	9.184751	0.555499
1	4.612741	9.538722	-0.302822
1	2.998838	9.483186	0.426994
1	4.074102	8.09141	0.541067
6	3.775503	10.050077	2.90915
1	2.70201	9.945264	2.798119
6	4.27969	10.520651	4.120579
6	3.302191	10.894733	5.205198
1	3.036103	11.953482	5.14223
1	3.700487	10.723179	6.202436
1	2.381659	10.321138	5.099018
6	5.922738	12.357716	6.121387
1	5.227341	13.014042	5.616454
6	6.51351	12.773833	7.293198
1	6.287188	13.748287	7.693304
6	7.452975	11.951349	7.922377
6	7.440454	13.428588	9.859899
1	7.536884	14.416683	9.406206
1	7.87637	13.445716	10.851605
1	6.388394	13.170411	9.948126
6	9.488006	12.239677	9.249692
6	10.244249	13.328925	9.668361
1	9.777736	14.285719	9.833457
6	11.608094	13.175289	9.825612
1	12.212295	14.013147	10.146329
6	12.20252	11.952569	9.570661
1	13.26174	11.814838	9.713022
6	11.405005	10.892501	9.165732
6	13.387797	9.624143	8.477929
1	13.573375	8.684772	7.963522
1	14.089541	9.729394	9.307438
1	13.540408	10.435572	7.77478
6	11.522266	8.504038	9.578082
6	12.401865	7.596876	10.175817
1	13.467926	7.716311	10.07414
6	11.891851	6.592843	10.97008
1	12.570025	5.919083	11.476765
6	10.511894	6.476596	11.174234
6	9.928151	5.561489	12.189915
6	9.105211	4.485736	11.823395
6	8.818082	4.170295	10.379772
1	8.230861	4.955101	9.899553
1	8.258738	3.239577	10.294777
1	9.742532	4.065547	9.809561
6	8.558142	3.683882	12.822857
1	7.928309	2.849237	12.536044
6	8.804099	3.92102	14.1728
6	8.168279	3.067983	15.236052
1	7.184087	3.461564	15.507285
1	8.774207	3.048496	16.142566
1	8.025534	2.043582	14.889499
6	9.62416	4.992846	14.512426
1	9.815773	5.20399	15.5583
6	10.185547	5.824172	13.547207
6	11.010667	7.008086	13.981549
1	12.065778	6.885064	13.72825
24	8.926913	9.429243	8.465156
7	7.734977	10.739418	7.415496
7	8.106973	12.377064	9.079042
7	10.06575	11.038023	9.010373
7	11.98582	9.638553	8.913485
7	10.195834	8.308991	9.653338
7	10.018037	9.125668	6.741729
7	9.920281	6.809635	7.134349
7	7.88654	7.765601	7.914506
7	5.9059	8.78993	8.721076
7	7.670319	9.544198	10.08938
6	7.154787	10.347907	6.261301
1	7.434197	9.370372	5.902089
6	6.247021	11.116493	5.561355
6	5.671864	10.642064	4.278193
6	6.528875	10.328738	3.205172
6	8.023745	10.496235	3.293453
1	8.451835	10.571059	2.295385
1	8.49681	9.643651	3.785293

1	8.307058	11.38766	3.853285
6	5.978478	9.876258	2.009456
1	6.642376	9.651672	1.182072
6	4.605011	9.716544	1.843797
6	4.039661	9.184751	0.555499
1	4.612741	9.538722	-0.302822
1	2.998838	9.483186	0.426994
1	4.074102	8.09141	0.541067
6	3.775503	10.050077	2.90915
1	2.70201	9.945264	2.798119
6	4.27969	10.520651	4.120579
6	3.302191	10.894733	5.205198
1	3.036103	11.953482	5.14223
1	3.700487	10.723179	6.202436
1	2.381659	10.321138	5.099018
6	5.922738	12.357716	6.121387
1	5.227341	13.014042	5.616454
6	6.51351	12.773833	7.293198
1	6.287188	13.748287	7.693304
6	7.452975	11.951349	7.922377
6	7.440454	13.428588	9.859899
1	7.536884	14.416683	9.406206
1	7.87637	13.445716	10.851605
1	6.388394	13.170411	9.948126
6	9.488006	12.239677	9.249692
6	10.244249	13.328925	9.668361
1	9.777736	14.285719	9.833457
6	11.608094	13.175289	9.825612
1	12.212295	14.013147	10.146329
6	12.20252	11.952569	9.570661
1	13.26174	11.814838	9.713022
6	11.405005	10.892501	9.165732
6	13.387797	9.624143	8.477929
1	13.573375	8.684772	7.963522
1	14.089541	9.729394	9.307438
1	13.540408	10.435572	7.77478
6	11.522266	8.504038	9.578082
6	12.401865	7.596876	10.175817
1	13.467926	7.716311	10.07414
6	11.891851	6.592843	10.97008
1	12.570025	5.919083	11.476765
6	10.511894	6.476596	11.174234
6	9.928151	5.561489	12.189915
6	9.105211	4.485736	11.823395
6	8.818082	4.170295	10.379772
1	8.230861	4.955101	9.899553
1	8.258738	3.239577	10.294777
1	9.742532	4.065547	9.809561
6	8.558142	3.683882	12.822857
1	7.928309	2.849237	12.536044
6	8.804099	3.92102	14.1728
6	8.168279	3.067983	15.236052
1	7.184087	3.461564	15.507285
1	8.774207	3.048496	16.142566
1	8.025534	2.043582	14.889499
6	9.62416	4.992846	14.512426
1	9.815773	5.20399	15.5583

Table S9. Cartesian coordinates of the calculated ground state geometry of $[\text{Cr}^{\text{5Tripp}}]^{3+}$ (CPCM(MeCN)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVP).

Atom	x	y	z
24	0.158588	-0.02335	0.02619
7	1.483885	-1.599333	-0.040323
7	2.370841	-0.881765	2.020611
7	0.041139	-0.433338	2.024911
7	-2.284598	0.024106	1.929483
7	-1.190457	1.481051	0.436786
7	-1.342024	-1.331068	-0.518483
7	-2.082216	0.253566	-2.094728
7	0.283226	0.381912	-1.970504
7	2.642298	0.498898	-1.74864
7	1.676591	1.355073	0.221214
6	1.435299	-2.506704	-1.039067
1	0.584421	-2.43753	-1.697047

6	2.386903	-3.487593	-1.218947
6	2.206202	-4.610821	-2.175825
6	2.066944	-4.398059	-3.558455
6	2.002175	-3.013987	-4.1775
1	2.173898	-2.282056	-3.391405
6	3.090546	-2.791691	-5.232766
1	4.082497	-2.968782	-4.812765
1	3.051154	-1.763068	-5.597707
1	2.959742	-3.456829	-6.088087
6	0.604695	-2.750968	-4.754305
1	-0.159588	-2.801141	-3.975764
1	0.355586	-3.489226	-5.518617
1	0.560589	-1.762885	-5.21127
6	1.961055	-5.503462	-4.401971
1	1.863251	-5.344611	-5.469083
6	1.974981	-6.805956	-3.922781
6	1.876941	-7.983181	-4.870289
1	1.832868	-7.575079	-5.884067
6	0.595778	-8.793151	-4.636706
1	0.580597	-9.219353	-3.631113
1	0.529841	-9.61579	-5.352191
1	-0.290275	-8.167181	-4.749918
6	3.11736	-8.880455	-4.779507
1	3.200892	-9.331465	-3.788176
1	4.028873	-8.310494	-4.969682
1	3.057719	-9.687744	-5.512629
6	2.065569	-6.99281	-2.546976
1	2.036229	-7.999023	-2.148824
6	2.171141	-5.927111	-1.66062
6	0.871872	-6.924228	0.253798
1	0.871173	-7.096473	1.331855
1	0.74987	-7.88964	-0.239611
1	0.003967	-6.312073	0.010319
6	2.175014	-6.235951	-0.169457
1	2.217506	-5.299548	0.382674
6	3.397856	-7.065342	0.239698
1	3.398816	-7.229595	1.319397
1	4.327207	-6.560705	-0.031257
1	3.391391	-8.04182	-0.24869
6	3.506717	-3.418167	-0.37806
1	4.321455	-4.116774	-0.512447
6	3.555253	-2.51952	0.664314
1	4.388149	-2.530289	1.347671
6	2.470174	-1.663648	0.871621
6	3.60169	-0.667274	2.792813
1	3.908557	-1.555407	3.348296
1	3.438219	0.151079	3.485576
1	4.390038	-0.380243	2.102061
6	1.155236	-0.780123	2.712133
6	1.10466	-1.041154	4.074599
1	1.995239	-1.326783	4.609208
6	-0.118445	-0.986207	4.716784
1	-0.181147	-1.20408	5.774308
6	-1.262199	-0.655906	4.013405
1	-2.214273	-0.586808	4.51305
6	-1.151836	-0.360762	2.661621
6	-3.587323	-0.459099	2.405736
1	-3.984418	0.144082	3.224397
1	-3.475078	-1.485602	2.737569
1	-4.283105	-0.443052	1.571004
6	-2.27809	1.19452	1.174123
6	-3.363323	2.074917	1.185777
1	-4.268861	1.827055	1.714092
6	-3.23077	3.306274	0.584287
1	-4.051998	4.008881	0.629959
6	-2.024209	3.687315	-0.020208
6	-1.060189	2.706523	-0.114991
1	-0.133675	2.893838	-0.632869
6	-1.783727	5.09009	-0.449522
6	-1.877845	6.11324	0.521804
6	-2.076592	5.834047	2.005531
1	-2.180882	4.761233	2.151013
6	-3.349801	6.49167	2.549644
1	-3.490157	6.228595	3.600252
1	-4.230885	6.164819	1.993785
1	-3.292849	7.579793	2.480873
6	-0.843438	6.256572	2.813298

1	-0.980179	6.00593	3.866901
1	-0.667913	7.331743	2.743955
1	0.053366	5.748467	2.45993
6	-1.712126	7.434981	0.124074
1	-1.777414	8.214164	0.872721
6	-1.442443	7.783762	-1.195619
6	-1.275165	9.231554	-1.608284
1	-1.093285	9.237355	-2.686763
6	-0.062626	9.877028	-0.926538
1	-0.188079	9.893462	0.158511
1	0.061916	10.907245	-1.267199
1	0.852109	9.326935	-1.150788
6	-2.548869	10.043177	-1.342859
1	-2.767196	10.087426	-0.27358
1	-3.409898	9.598935	-1.846048
1	-2.430677	11.067065	-1.704181
6	-1.308882	6.759899	-2.123178
1	-1.07091	7.016478	-3.148391
6	-1.463859	5.417422	-1.779168
6	-1.247217	4.371201	-2.857504
1	-1.479729	3.3961	-2.436007
6	-2.176221	4.562785	-4.060588
1	-3.22262	4.56193	-3.749141
1	-2.03185	3.750932	-4.776725
1	-1.976692	5.503785	-4.576262
6	0.224987	4.346419	-3.289578
1	0.881594	4.122251	-2.446239
1	0.523589	5.312868	-3.699985
1	0.385204	3.589896	-4.057201
6	-1.443845	-2.556378	0.040154
1	-0.594707	-2.880471	0.618663
6	-2.541134	-3.374794	-0.120494
6	-2.560964	-4.794185	0.320929
6	-2.76321	-5.794262	-0.657625
6	-2.799541	-5.498296	-2.150876
1	-2.704632	-4.425101	-2.29916
6	-1.599512	-6.13796	-2.859905
1	-1.615608	-7.225015	-2.767901
1	-0.657696	-5.780939	-2.442857
1	-1.613757	-5.890774	-3.923387
6	-4.122208	-5.932201	-2.792883
1	-4.973	-5.449588	-2.307866
1	-4.261505	-7.01258	-2.71948
1	-4.13381	-5.663864	-3.851427
6	-2.856982	-7.121109	-0.254173
1	-3.006614	-7.884413	-1.006988
6	-2.740616	-7.49937	1.079485
6	-2.85171	-8.951152	1.495587
1	-2.757275	-8.980513	2.584856
6	-1.71354	-9.792892	0.904684
1	-1.789372	-10.828114	1.244523
1	-0.740509	-9.402358	1.205533
1	-1.754267	-9.792058	-0.186857
6	-4.21884	-9.540633	1.127942
1	-5.029454	-8.95672	1.568249
1	-4.300453	-10.568044	1.489378
1	-4.360728	-9.553479	0.044983
6	-2.48924	-6.506785	2.016635
1	-2.361732	-6.793494	3.053457
6	-2.385261	-5.161096	1.667382
6	-2.028914	-4.161632	2.752391
1	-2.115665	-3.161078	2.334263
6	-2.973963	-4.22166	3.956398
1	-2.71608	-3.437345	4.670881
1	-2.903561	-5.180113	4.473128
1	-4.010835	-4.076463	3.647389
6	-0.568476	-4.358524	3.183721
1	-0.422515	-5.358991	3.595382
1	-0.292844	-3.63226	3.94768
1	0.113689	-4.244076	2.338566
6	-3.62941	-2.813425	-0.804788
1	-4.547696	-3.376799	-0.901821
6	-3.524038	-1.585646	-1.418185
1	-4.341801	-1.20502	-2.007306
6	-2.31516	-0.888473	-1.334859
6	-3.251799	0.916802	-2.685334
1	-4.006756	1.030049	-1.911703

1	-3.668798	0.359381	-3.526004
1	-2.957315	1.90507	-3.021293
6	-0.843114	0.462798	-2.717481
6	-0.784805	0.742346	-4.075713
1	-1.686876	0.786893	-4.663353
6	0.453704	0.909932	-4.667339
1	0.520663	1.116962	-5.726748
6	1.606701	0.81444	-3.910414
1	2.573882	0.973645	-4.357714
6	1.493335	0.562969	-2.549684
6	3.89361	0.093501	-2.402335
1	4.55988	-0.308195	-1.643404
1	4.382892	0.921268	-2.919006
1	3.670796	-0.694684	-3.11356
6	2.747249	1.258799	-0.586988
6	3.928764	1.930123	-0.260009
1	4.816967	1.80598	-0.856927
6	3.920386	2.823808	0.787186
1	4.819261	3.380798	1.014813
6	2.745959	3.076247	1.510964
6	1.671247	2.26464	1.21901
1	0.755387	2.339896	1.781693
6	2.655756	4.213623	2.463313
6	2.899945	5.513994	1.972456
6	3.099882	5.819497	0.494392
1	3.063561	4.886755	-0.063711
6	1.955734	6.687042	-0.04396
1	1.933304	7.663484	0.442463
1	0.988257	6.211894	0.115879
1	2.080155	6.849524	-1.116397
6	4.462354	6.464734	0.217708
1	5.278482	5.831473	0.571135
1	4.547268	7.432832	0.715239
1	4.593114	6.625509	-0.854556
6	2.884663	6.582406	2.866298
1	3.067285	7.583177	2.4936
6	2.618402	6.414069	4.218542
6	2.623485	7.596401	5.164788
1	2.865984	8.481338	4.569657
6	3.70396	7.44399	6.243039
1	3.500969	6.576587	6.875136
1	3.732368	8.328353	6.883313
1	4.69058	7.312914	5.794408
6	1.245564	7.82158	5.798853
1	1.264085	8.702126	6.444745
1	0.951221	6.964181	6.408184
1	0.481194	7.971065	5.035024
6	2.328979	5.130832	4.670097
1	2.085741	4.98305	5.714413
6	2.332327	4.028037	3.822038
6	1.93964	2.68025	4.399343
1	2.088864	1.923518	3.632679
6	0.448755	2.677563	4.764218
1	0.233745	3.440076	5.51525
1	0.156227	1.709958	5.171214
1	-0.173329	2.884651	3.890879
6	2.804439	2.272773	5.5964
1	2.521031	1.275341	5.938967
1	2.680336	2.961643	6.433649
1	3.861843	2.25427	5.325623

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6.2 Supporting Information: Ligand Functionalization: Docking Molecular Rubies to Substrates

Ligand Functionalization: Docking Molecular Rubies to Substrates

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Supporting Information

Author contributions:

L. S. performed the synthesis, characterization, DFT, UV-VIS, steady-state and time-resolved luminescence experiments, visualized the data and wrote the original draft. E. M. helped with the ligand syntheses. K. H. supervised the project.

M. S. performed the click reaction of chromium complexes with azide-functionalized ligands to alkyne-functionalized oligo peptides, under the supervision of A. H..

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1. Materials and Methods

General procedures. All reagents were used as received from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer, Sigma-Aldrich and TCI). Air and/or moisture-sensitive reactions were performed in dried glassware under an inert gas atmosphere (argon, quality 4.6). THF was refluxed over potassium and distilled under argon prior to use in moisture-sensitive reactions. Other dry solvents (acetonitrile, dichloromethane) were obtained from Acros Organics and degassed by purging with argon for 20 min. A glovebox (UniLab/MBraun, Ar 4.8, O₂ < 1 ppm, H₂O < 1 ppm) was used for storage and weighing of sensitive compounds.

NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400.1 MHz (¹H), 100.7 MHz (¹³C{¹H}). All resonances are reported in ppm versus the solvent signal as internal. ^[1] (s) = singlet, (d) = doublet, (t) = triplet, (m) = multiplet.

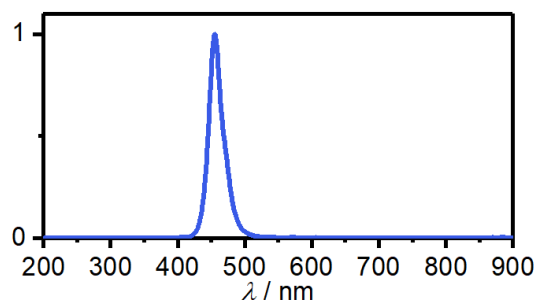
ESI⁺ mass spectra were recorded on an Agilent 6545 QTOF-MS spectrometer with analyte solutions in acetonitrile.

ATR-IR spectra were recorded with a Bruker Alpha II FT-IR spectrometer with a Platinum Di-ATR unit.

UV/Vis absorption spectra were recorded on a Jasco V770 spectrometer using 1.0 cm quartz cells. For measurements under oxygen-free conditions 1.0 cm quartz cells with a PTFE capping or with a Schott valve were used.

Emission and excitation spectra were recorded on an Edinburgh Instruments spectrometer (FLS 1000) equipped with the photomultiplier detector PMT-980, covering the spectral range between 200 nm and 980 nm. A xenon arc lamp Xe2 (450 W) was used for excitation. **Luminescence decay curves** were recorded in the multi-channel scaling mode (MCS, FLS1000) employing the VPL450 LASER ($\lambda_{\text{exc}} = 451.3$ nm) from Edinburgh Instruments as excitation source.

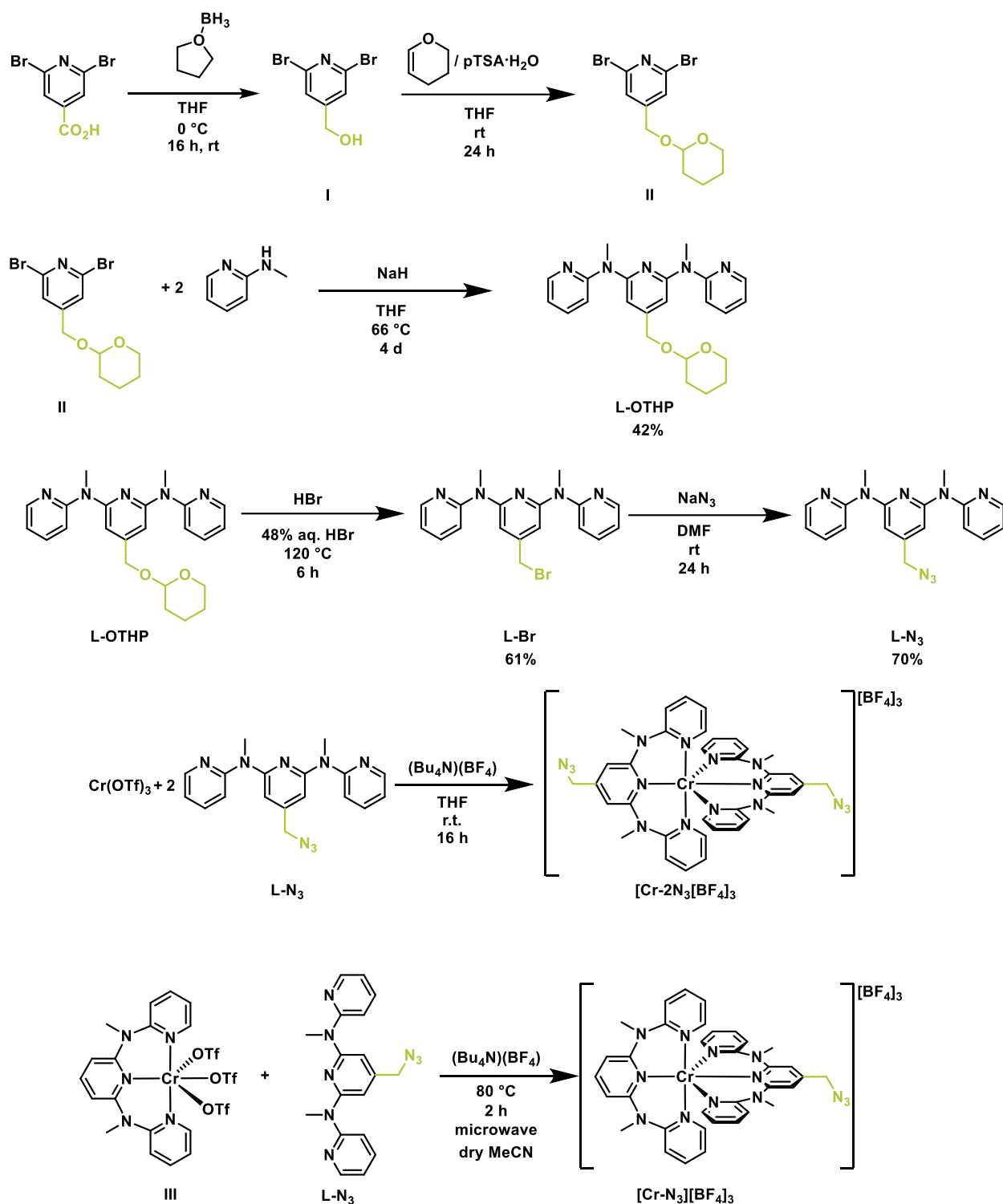
Irradiation experiments were carried out focusing blue light of an LED (Prismatix UHP-T-460-DI, 3.5 W, focus spot diameter ca. 0.8 cm) on to the sample solutions under stirring in a temperature controlled Peltier-holder (Agilent Cary dual-cell holder).



Normalized emission spectrum of the Prismatix UHP-T-460-DI LED ($\lambda_{\text{max}} = 456$ nm, $\lambda_{\text{centroid}} = 460$ nm).

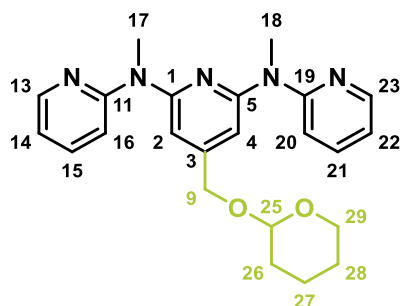
The samples for spectroscopy and irradiation were prepared in long-neck cuvettes with a Schott valve. For measurements in the absence of oxygen, solutions were purged with argon using a cannula for 15 minutes prior to use.

2. Synthetic Procedures



(2,6-Dibromopyridine-4-yl)methanol (**I**),^[2] (2,6-dibromo-4-(tetrahydropyran-2-yloxymethyl)-pyridine) (**II**),^[3] ddpd^[4] and $\text{Cr}(\text{ddpd})(\text{OTf})_3$ (**III**)^[5] were synthesized according to literature procedures.

Synthesis of Ligand $\text{ddpd}^{\text{CH}_2\text{OTHP}}$ (**L-OTHP**):



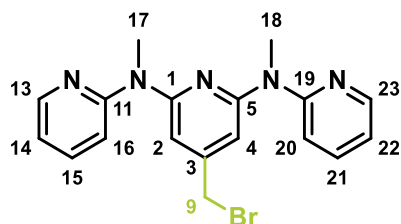
2-Aminopyridine (3.98 g, 39.79 mmol, 2.1 eq) was added via syringe to a suspension of NaH (1.44 g of 60 wt%, 35.91 mmol, 2.1 eq) in dry THF (50 mL). After stirring for 30 min, (2,6-dibromo-4-(tetrahydropyran-2-yloxymethyl)-pyridine) (**II**, 6.15 g, 17.52 mmol, 1.0 eq) was added. The solution was refluxed for 3 days and water was added (10 mL). After solvent evaporation, the residue was taken up in Et₂O (50 mL) and extracted twice with saturated aqueous Na₂CO₃ solution (2 x 25 mL). The organic phase was dried over MgSO₄ and concentrated under reduced pressure. The crude product was subjected to column chromatography on Alox (5:1 cyclohexane/EA, + 2% NEt₃). $\text{ddpd}^{\text{CH}_2\text{OTHP}}$ was obtained as a yellow oil. Yield: 3.00 g, 7.40 mmol, 42%.

¹H NMR (400 MHz, CD₂Cl₂, 296 K): δ /ppm = 8.32 (ddd, J = 5.0, 2.1, 0.9 Hz, 2H, H^{13,23}), 7.52 (ddd, J = 8.4, 7.2, 2.0 Hz, 2H, H^{15,21}), 7.27 (dt, J = 8.4, 1.0 Hz, 2H, H^{16,20}), 6.85 (ddd, J = 7.1, 4.9, 1.0 Hz, 2H, H^{14,22}), 6.72 (s, 2H, H^{2,4}), 4.65 (m, 1H, H²⁵), 4.65 and 4.40 (both d, J = 13.1, both 1H, H⁹), 3.83 and 3.49 (both m, both 1H, H²⁹) 3.56 (s, 6H, H^{17,18}), 1.88 – 1.43 (m, 5H, H²⁶⁻²⁸).

¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 296 K): δ /ppm = 157.8 (C^{11,19}), 156.4 (C^{1,5}), 150.5 (C³), 147.9 (C^{13,23}), 136.6 (C^{15,21}), 116.6 (C^{14,22}), 115.2 (C^{16,20}), 104.1 (C^{2,4}), 97.9 (C²⁵), 67.5 (C⁹), 62.0 (C²⁹), 35.7 (C^{17,18}), 30.5, 25.44 and 19.27 (C²⁶⁻²⁸).

MS (ESI⁺, MeCN): Calcd. for C₂₃H₂₈N₅O₂⁺: m/z = 406.223. Found: m/z (%) = 406.223 (100, [$\text{ddpd}^{\text{CH}_2\text{OTHP}} + \text{H}$]⁺).

Synthesis of Ligand $\text{ddpd}^{\text{CH}_2\text{Br}}$ (**L-Br**):



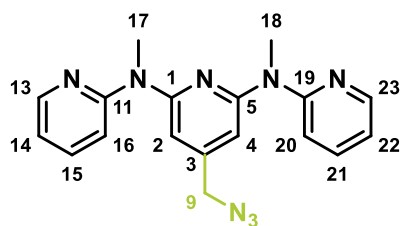
L-OTHP (2.10 g, 5.18 mmol, 1.0 eq.) was refluxed in aqueous HBr (48%, 50 mL) for 6 hours. After cooling to room temperature, the solution was brought to pH 8 with saturated aqueous Na₂CO₃ solution and extracted with ethylacetate (3 x 50 mL). The combined organic fractions were dried over Na₂SO₄ and concentrated under reduced pressure. $\text{ddpd}^{\text{CH}_2\text{Br}}$ was obtained as a yellow to brown oil. Yield: 1.22 g, 3.17 mmol, 61%.

¹H NMR (400 MHz, CD₂Cl₂, 296 K): δ /ppm = 8.34 (ddd, J = 4.9, 2.0, 0.9 Hz, 2H, H^{13,23}), 7.56 (ddd, J = 8.4, 7.2, 2.0 Hz, 2H, H^{15,21}), 7.28 (dt, J = 8.4, 1.0 Hz, 2H, H^{16,20}), 6.90 (ddd, J = 7.2, 4.9, 1.0 Hz, 2H, H^{14,22}), 6.69 (s, 2H, H^{2,4}), 4.29 (s, 2H, H⁹), 3.55 (s, 6H, H^{17,18}).

¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 296 K): δ /ppm = 157.6 (C^{11,19}), 156.5 (C^{1,5}), 148.6 (C³), 148.0 (C^{13,23}), 136.8 (C^{15,21}), 117.9 (C^{14,22}), 115.8 (C^{16,20}), 104.6 (C^{2,4}), 35.7 (C⁹), 32.0 (C^{17,18}).

MS (ESI⁺, MeCN): Calcd. for C₁₈H₁₉BrN₅⁺: m/z = 384.081, 386.079. Found: m/z (%) = 384.082 (100, [$\text{ddpd}^{\text{CH}_2\text{Br}} + \text{H}$]⁺), 386.080 (99, [$\text{ddpd}^{\text{CH}_2\text{Br}} + \text{H}$]⁺).

Synthesis of Ligand $\text{ddpd}^{\text{CH}_2\text{N}_3}$ (**L-N₃**):



L-Br (1.22 g, 3.17 mmol, 1.0 eq.) was dissolved in DMF (50 mL). NaN_3 (0.35 mg, 5.40 mmol, 1.7 eq) was added as a solid. Stirring at room temperature was continued for 24 h. The solution was concentrated to half of its volume. Water (50 mL) and saturated aqueous NaHCO_3 solution (10 mL) were added (aqueous phase pH 8). The pale yellow emulsion was extracted with ethyl acetate (3 x 50 mL). The combined organic fractions were dried over MgSO_4 and concentrated under reduced pressure. The crude product was subjected to flash column chromatography (SiO_2 , 1:3 acetone/DCM). $\text{ddpd}^{\text{CH}_2\text{N}_3}$ was obtained as a yellow oil. Yield: 425 mg, 1.23 mmol, 70%.

^1H NMR (400 MHz, CD_2Cl_2 , 296 K): δ / ppm = 8.35 (ddd, J = 4.9, 2.0, 0.9 Hz, 2H, $\text{H}^{13,23}$), 7.56 (ddd, J = 8.4, 7.2, 2.0 Hz, 2H, $\text{H}^{15,21}$), 7.30 (dt, J = 8.4, 1.0 Hz, 2H, $\text{H}^{16,20}$), 6.90 (ddd, J = 7.2, 4.9, 1.0 Hz, 2H, $\text{H}^{14,22}$), 6.63 (s, 2H, $\text{H}^{2,4}$), 4.24 (s, 2H, H^9), 3.57 (s, 6H, $\text{H}^{17,18}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2 , 296 K): δ / ppm = 158.0 ($\text{C}^{11,19}$), 157.1 ($\text{C}^{1,5}$), 148.4 ($\text{C}^{13,23}$), 147.2 (C^3), 137.2 ($\text{C}^{15,21}$), 117.6 ($\text{C}^{14,22}$), 116.2 ($\text{C}^{16,20}$), 104.0 ($\text{C}^{2,4}$), 54.3 (C^9), 36.1 ($\text{C}^{17,18}$).

MS (ESI^+ , MeCN): Calcd. for $\text{C}_{18}\text{H}_{19}\text{N}_8^+$: m/z = 347.172. Found: m/z (%) = 347.173 (100, $[\text{ddpd}^{\text{CH}_2\text{N}_3} + \text{H}]^+$).

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2098 (s), 1590 (s), 1558 (s), 1472 (s), 1411 (vs), 1338 (m), 1293 (m), 1258 (vw), 1237 (w), 1155 (m), 1107 (m), 988 (w), 777 (m), 740 (w), 423 (w).

UV/Vis (MeCN): λ_{max} / nm (ϵ / $10^3 \text{ M}^{-1}\text{cm}^{-1}$): 390 (1.3), 336 (13.2), 300 sh (14.2), 275 (17.0), 234 (13.4, $\pi\pi^*$).

Emission (MeCN): λ_{em} / nm (λ_{exc} / nm): 393 sh, 460 (336).

Synthesis of complex $[\text{Cr}(\text{ddpd}^{\text{CH}_2\text{N}_3})_2][\text{BF}_4]_3$ ($[\text{Cr}(\text{L-N}_3)_2][\text{BF}_4]_3$):

L-N₃ (100 mg, 0.29 mmol, 1.9 eq) was dissolved in THF (10 mL) yielding a yellow solution. A blue solution of $\text{Cr}(\text{OTf})_3$ (75 mg, 0.15 mmol, 1.0 eq) in THF was added, resulting in an orange colored solution and precipitate. After stirring overnight under inert conditions at room temperature, the solid was filtered and washed with THF. The residue was dissolved in MeCN (10 mL) and $(\text{Bu}_4\text{N})(\text{BF}_4)$ (1.0 g, 1.0 mmol, 6.7 eq.) was added.

Work-up: The reaction solution was dried in vacuo and the orange residue was washed with THF (3 x 5 mL). Then it was dissolved in water, filtered, dried and again washed with THF (3 x 5 mL). Dissolved in MeCN (5 mL), insoluble residues were filtered off and the orange solution was subjected to crystallization with Et_2O , resulting in orange needles.

Several further attempts to crystalize the samples failed. Because the complex could not be isolated in pure form, yield and molar absorption coefficients were not determined.

Analytical data is subject to change as the exact composition and purity of the complex could not be confirmed in the context of this work.

MS (ESI⁺, MeCN): Calcd. for $\text{C}_{36}\text{H}_{36}\text{CrN}_{16}^{3+}$: $m/z = 248.09$. Found: m/z (%) = 250.77 (3), 419.66 (3), 926.32 (2).

IR (ATR): $\tilde{\nu} / \text{cm}^{-1} = 2108$ (m), 1608 (s), 1577 (s), 1497 (s), 1476 (m), 1374 (w), 1334 (vw), 1286 (vw), 1258 (vw), 1234 (w), 1180 (w), 1142 (w), 1049 (vs), 833 (w), 783 (s), 757 (w), 660 (w), 522 (w), 445 (w).

UV/Vis (H_2O): $\lambda_{\text{max}} / \text{nm}$: 432, 318 sh, 301.

Emission (H_2O): $\lambda_{\text{em}} / \text{nm}$ ($\lambda_{\text{exc}} / \text{nm}$): 740, 778 (435).

Synthesis of complex $[\text{Cr}(\text{ddpd})(\text{ddpd}^{\text{CH}_2\text{N}_3})][\text{BF}_4]_3$ ($[\text{Cr}(\text{ddpd})(\text{L-N}_3)][\text{BF}_4]_3$) adapted from a literature procedure: [5,6]

$\text{Cr Br}_3(\text{ddpd})$ (168 mg, 0.29 mmol, 1.0 eq), AgCF_3SO_3 (222 mg, 0.86 mmol, 3.0 eq) and dry MeCN (5 mL) were loaded into a vial which was then sealed and heated in the microwave at 70 °C for 30 min. Resulting yellow precipitates were removed by filtration. Filtration was repeated after standing overnight to ensure complete precipitation of yellow AgBr . The orange reaction solution was employed in the following step.

L-N₃ (100 mg, 0.29 mmol, 1.0 eq) was dissolved in dry MeCN (2 mL) and added to the vial. The reaction mixture was sealed in a vial and heated in the microwave at 80 °C for 2 h. To the resulting orange solution an acetonitrile solution of $(\text{Bu}_4\text{N})(\text{BF}_4)$ (1.9 g, 5.8 mmol, 20 eq. in 4 mL) was added. The work-up followed the steps described for $[\text{Cr}(\text{L-N}_3)_2][\text{BF}_4]_3$.

Several attempts to crystalize the samples failed. Because the complex could not be isolated in pure form, yield and molar absorption coefficients were not determined.

Analytical data is subject to change as the exact composition and purity of the complex could not be confirmed in the context of this work.

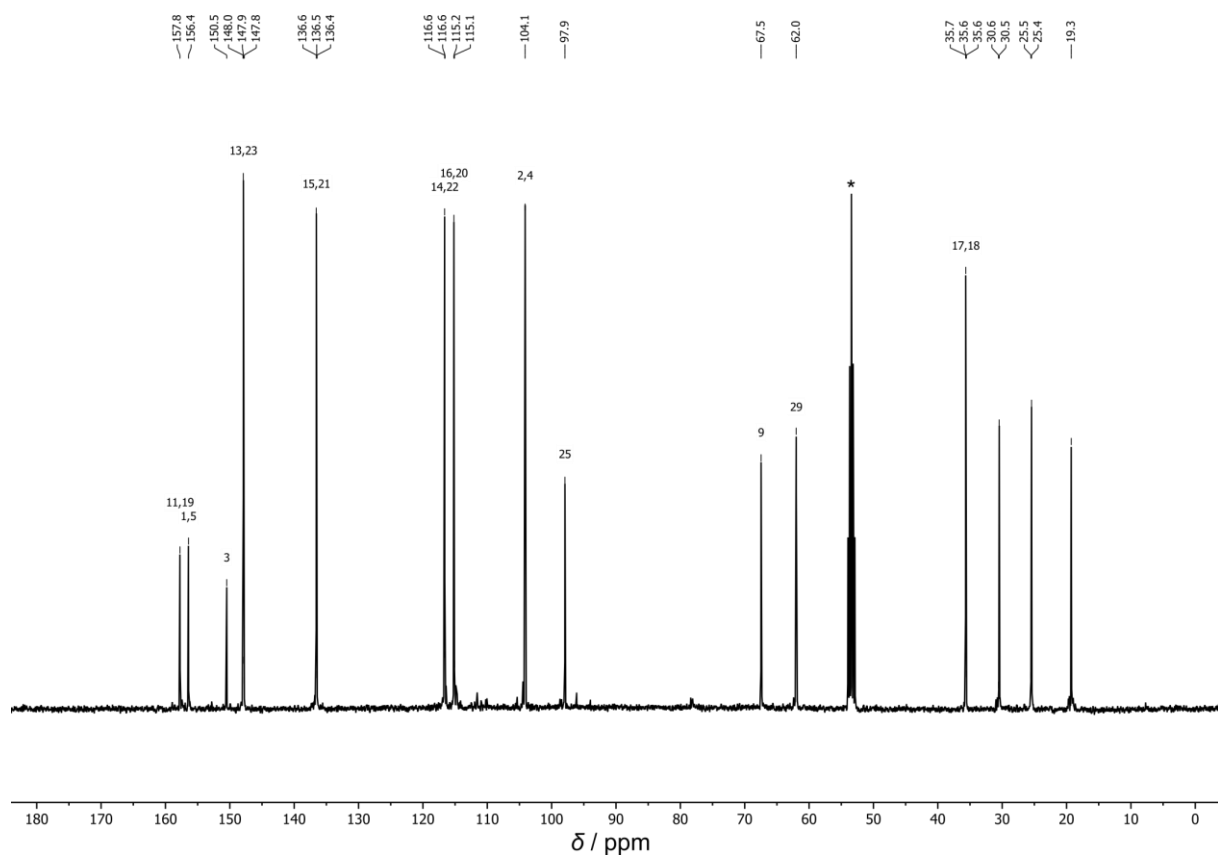
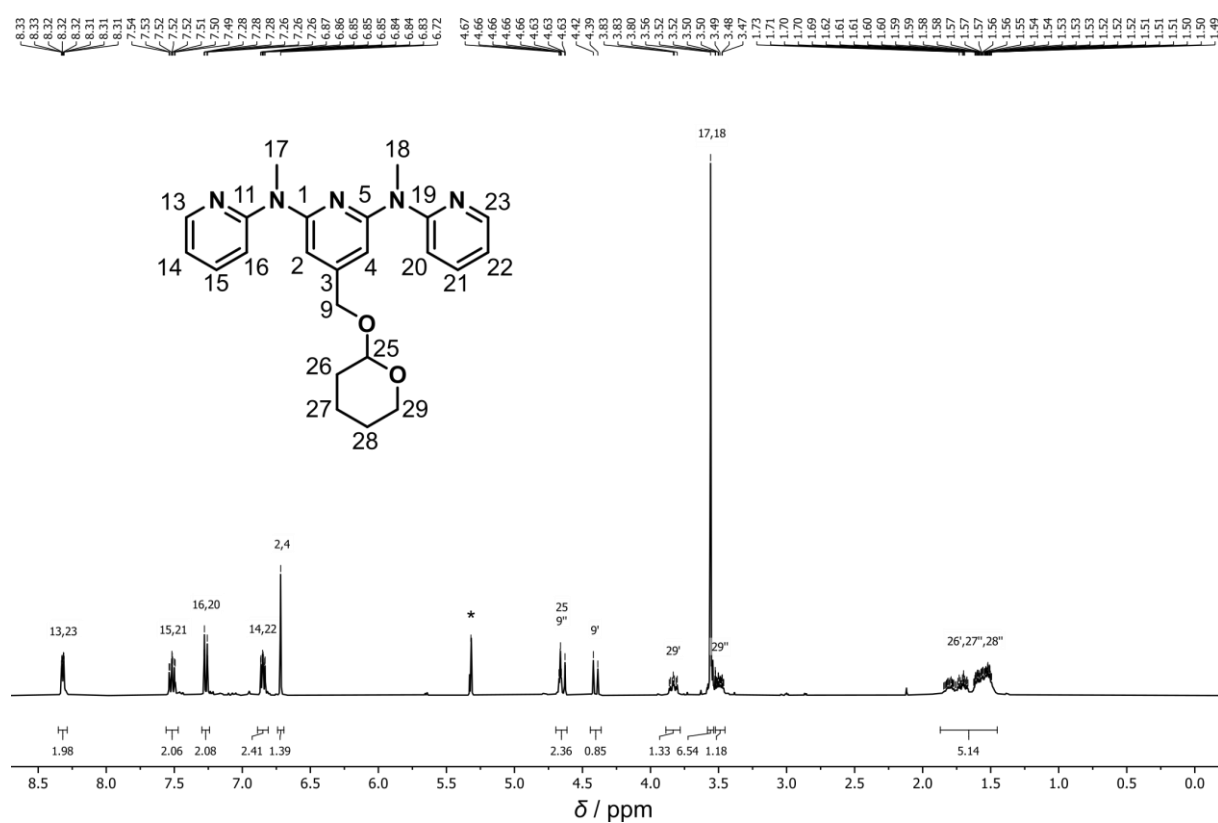
MS (ESI⁺, MeCN): Calcd. for $\text{C}_{35}\text{H}_{35}\text{CrN}_{13}^{3+}$: m/z (%) = 229.751. Found: m/z (%) = 231.09 (40), 390.14 (70), 867.28 (20).

IR (ATR): $\tilde{\nu} / \text{cm}^{-1} = 2110$ (m), 1608 (s), 1577 (s), 1497 (s), 1433 (vs), 1372 (w), 1344 (w), 1239 (w), 1178 (w), 1141 (w), 1055 (vs), 949 (w), 867 (vw), 779 (s), 753 (w), 669 (m), 583 (vw), 520 (w), 444 (w).

UV/Vis (H_2O): $\lambda_{\text{max}} / \text{nm}$: 434, 318 sh, 301.

Emission (H_2O): $\lambda_{\text{em}} / \text{nm}$ ($\lambda_{\text{exc}} / \text{nm}$): 738, 778 (435).

3. NMR spectroscopy



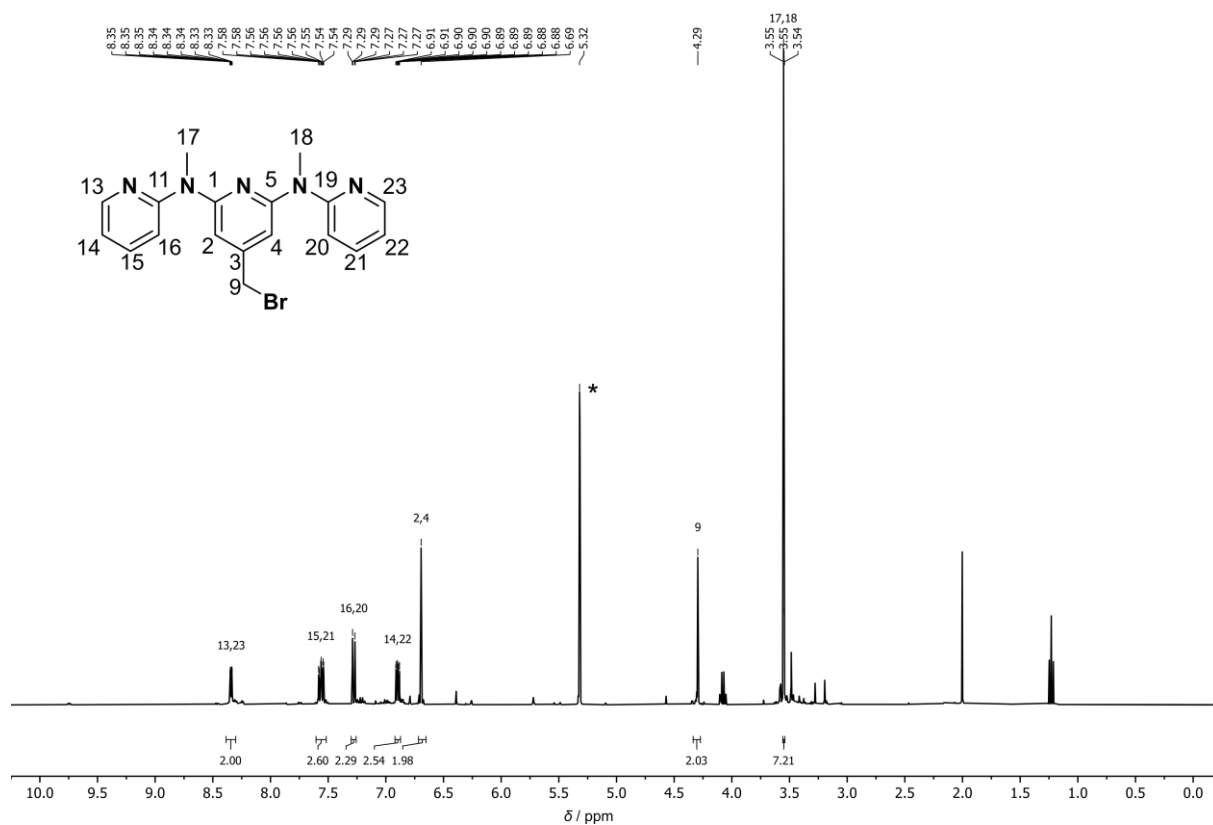


Figure S3. ^1H NMR spectrum of L-Br in CD_2Cl_2 . * CHDCl_2 .

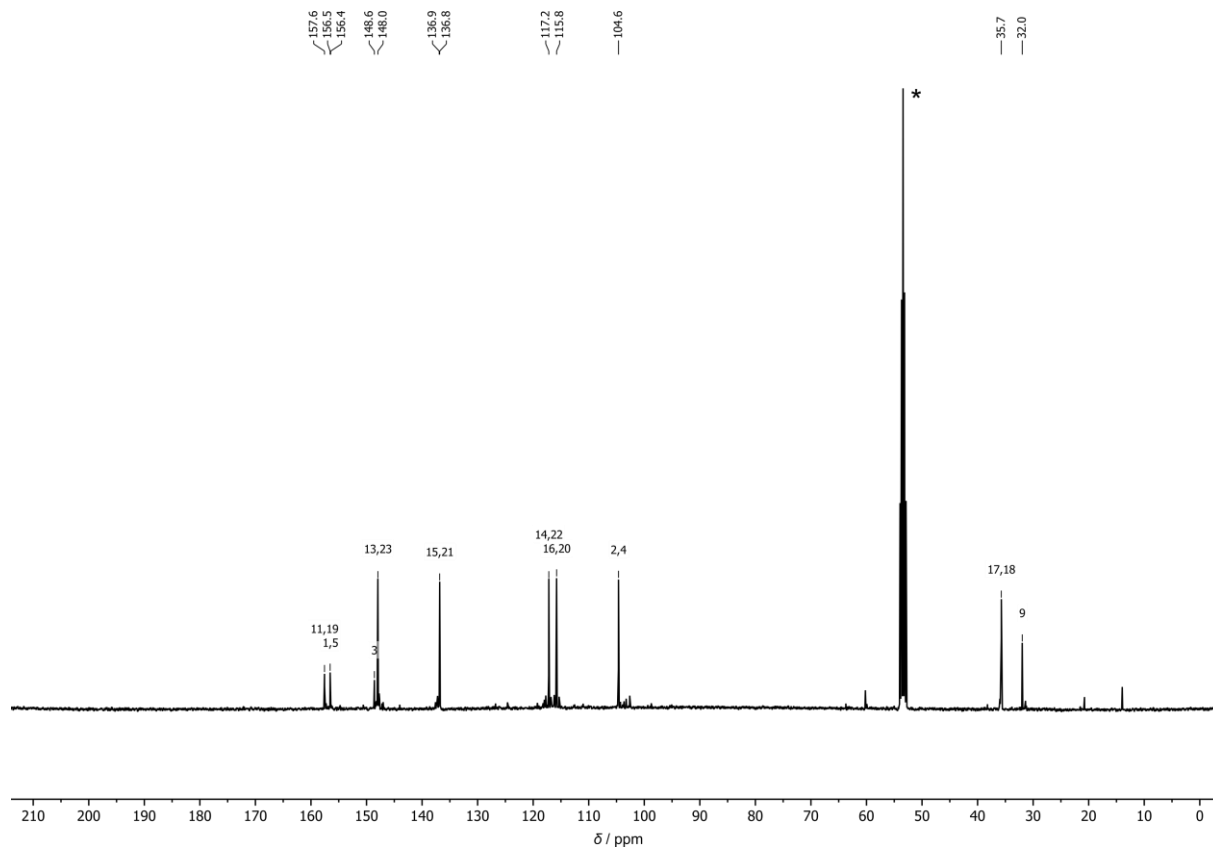


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of L-Br in CD_2Cl_2 . * CHDCl_2 .

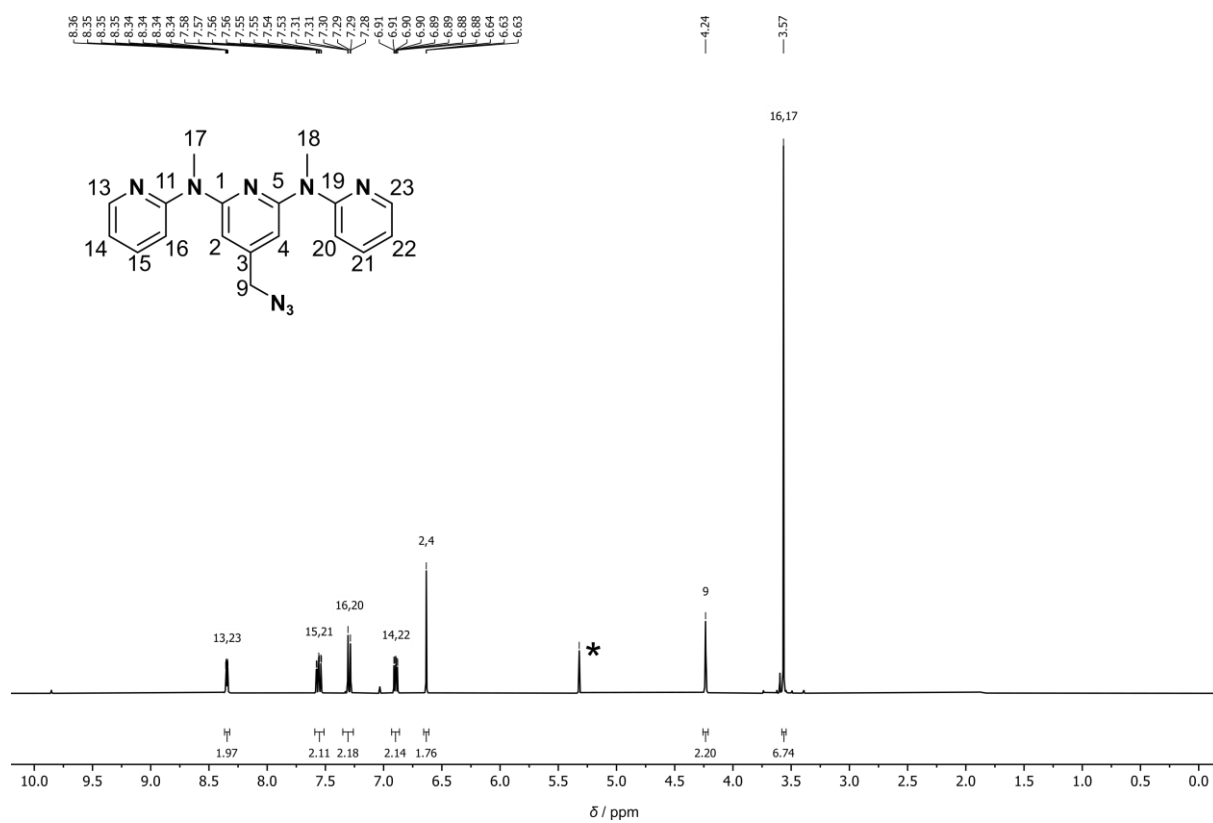


Figure S5. ¹H NMR spectrum of **L-N₃** in CD₂Cl₂. *CHDCl₂.

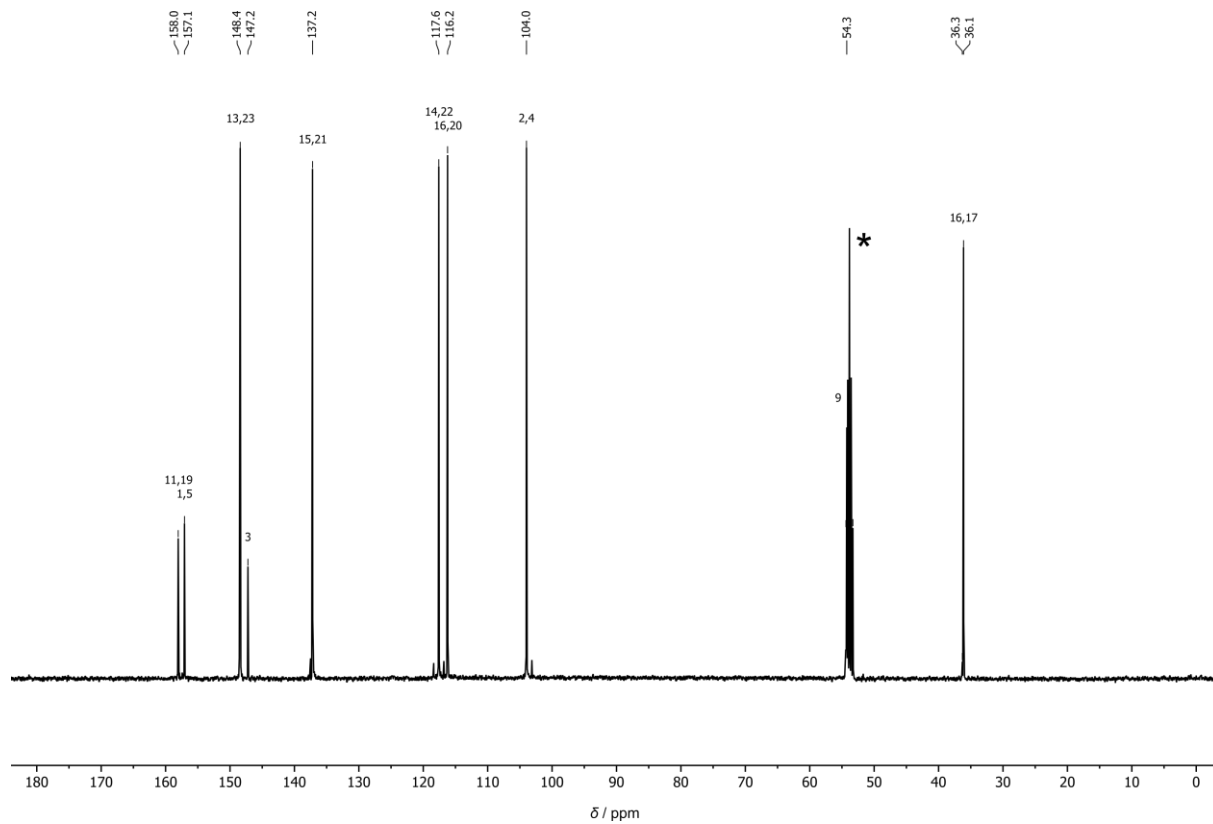


Figure S6. ¹³C{¹H} NMR spectrum of **L-N₃** in CD₂Cl₂. *CHDCl₂.

4. ESI⁺ mass spectra

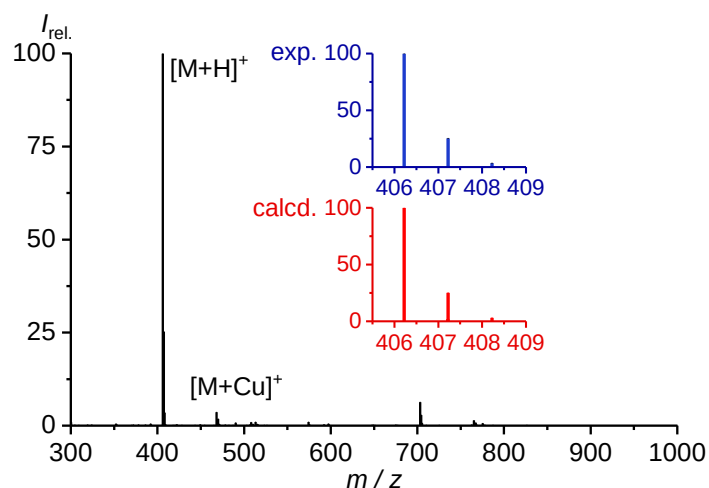


Figure S7. ESI⁺ mass spectrum of **L-OTHP** in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 406.

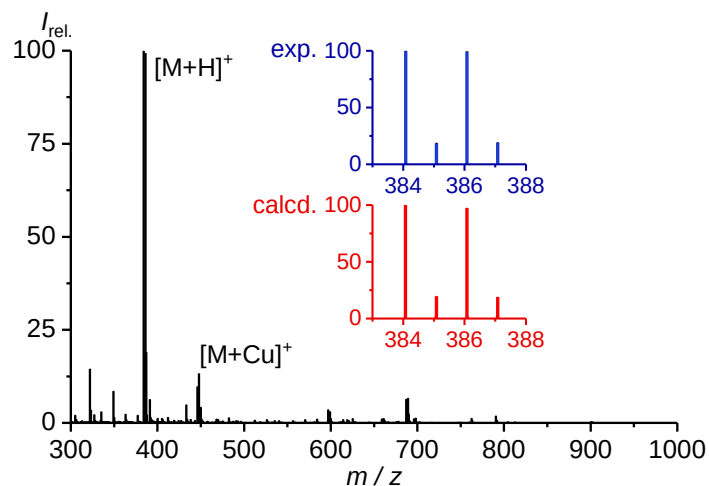


Figure S8. ESI⁺ mass spectrum of **L-Br** in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 383.

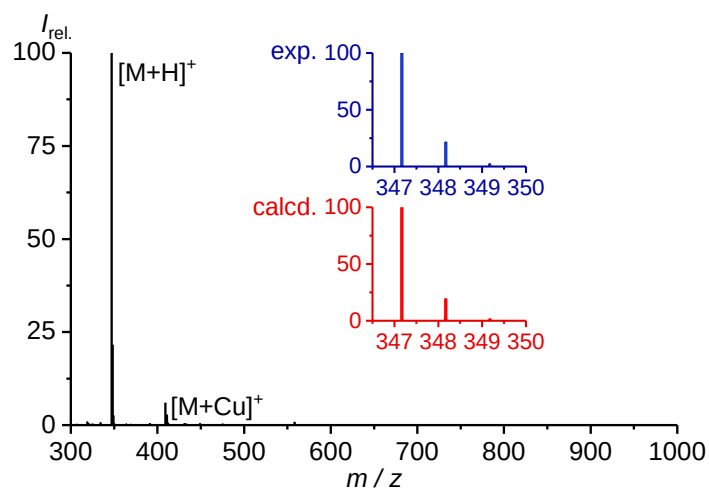


Figure S9. ESI⁺ mass spectrum of **L-N₃** in MeCN. The insets depict the experimental (blue) and calculated (red) isotopic pattern of the peak at m/z 347.

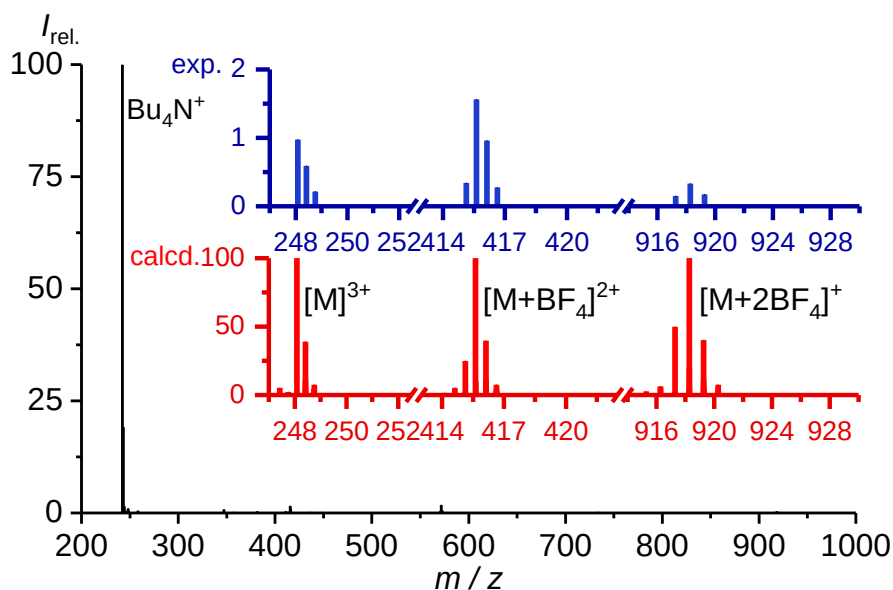


Figure S10. ESI⁺ mass spectrum of $[\text{Cr}(\text{L-N}_3)_2][\text{BF}_4]_3$ in H_2O . The red insets depict the calculated isotopic pattern of the peaks for $\{[\text{Cr}(\text{ddpd}^{\text{CH}_2\text{N}_3})_2][\text{BF}_4]_2\}^+$, $\{[\text{Cr}(\text{ddpd}^{\text{CH}_2\text{N}_3})_2][\text{BF}_4]\}^{2+}$ and $[\text{Cr}(\text{ddpd}^{\text{CH}_2\text{N}_3})_2]^{3+}$. The blue insets depict the experimental pattern isotopic pattern.

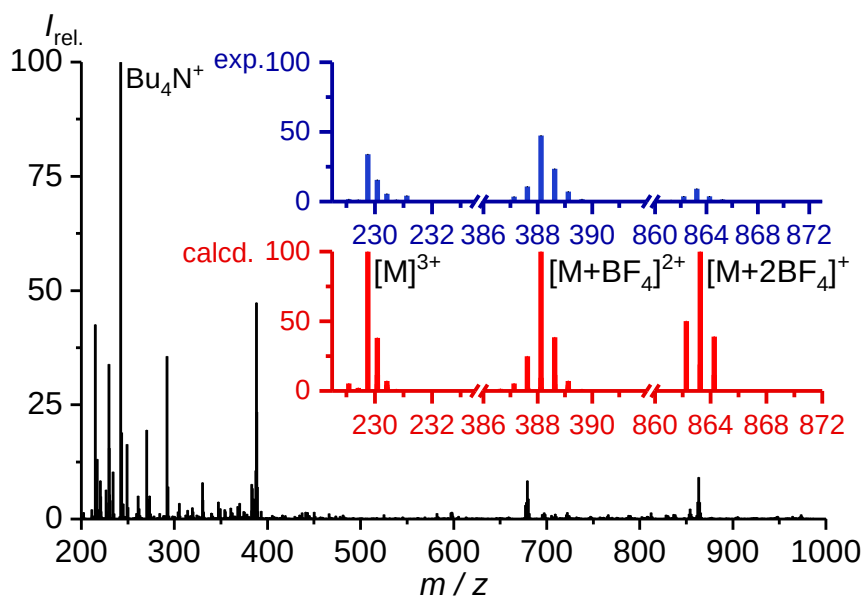


Figure S11. ESI⁺ mass spectrum of $[\text{Cr}(\text{ddpd})(\text{L-N}_3)][\text{BF}_4]_3$ in H_2O . The red insets depict the calculated isotopic pattern of the peaks for $\{[\text{Cr}(\text{ddpd})(\text{ddpd}^{\text{CH}_2\text{N}_3})][\text{BF}_4]_2\}^+$, $\{[\text{Cr}(\text{ddpd})(\text{ddpd}^{\text{CH}_2\text{N}_3})][\text{BF}_4]\}^{2+}$ and $[\text{Cr}(\text{ddpd})(\text{ddpd}^{\text{CH}_2\text{N}_3})]^{3+}$. The blue insets depict the experimental pattern isotopic pattern.

5. IR spectra

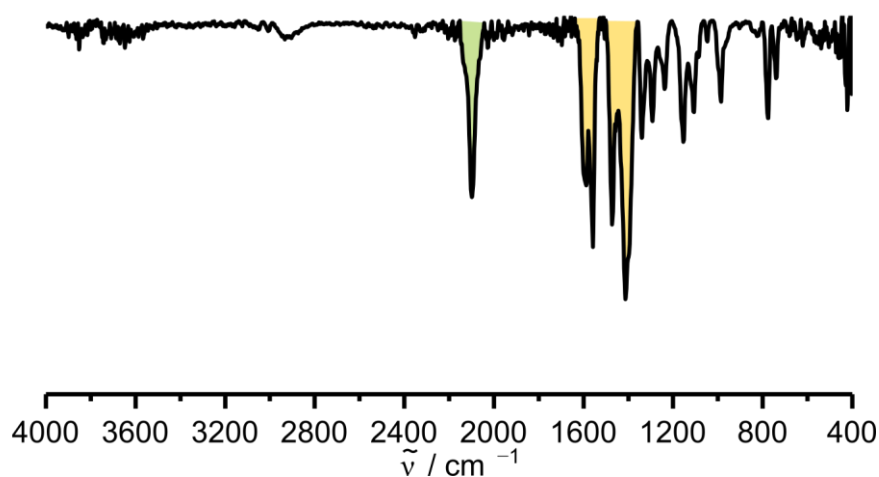


Figure S12. ATR-IR spectrum of **L-N₃**. Characteristic bands highlighted in green and yellow.

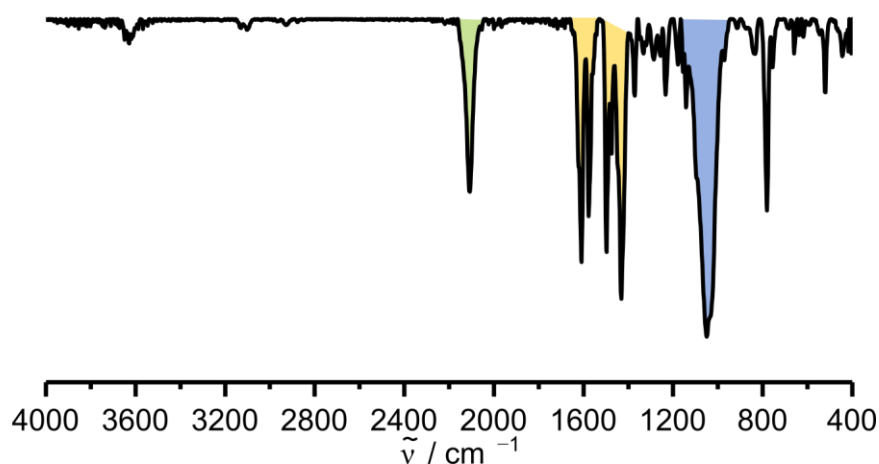


Figure S13. ATR-IR spectrum of **[Cr(L-N₃)₂][BF₄]₃**. Characteristic bands of L-N₃ highlighted in green (N₃ stretching) and yellow, BF₄ stretching highlighted in blue.

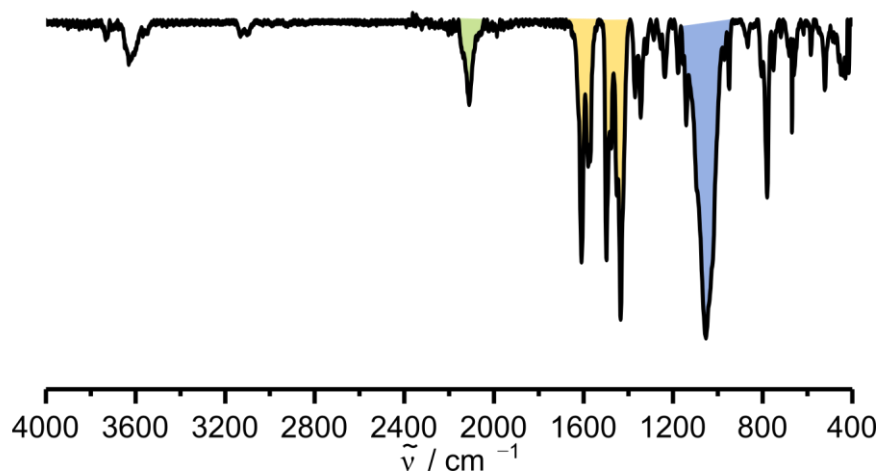


Figure S14. ATR-IR spectrum of **[Cr(ddpd)(L-N₃)] [BF₄]₃**. Characteristic bands of L-N₃ highlighted in green (N₃ stretching) and yellow, BF₄ stretching highlighted in blue.

6. Absorption and emission spectroscopy, luminescence lifetimes

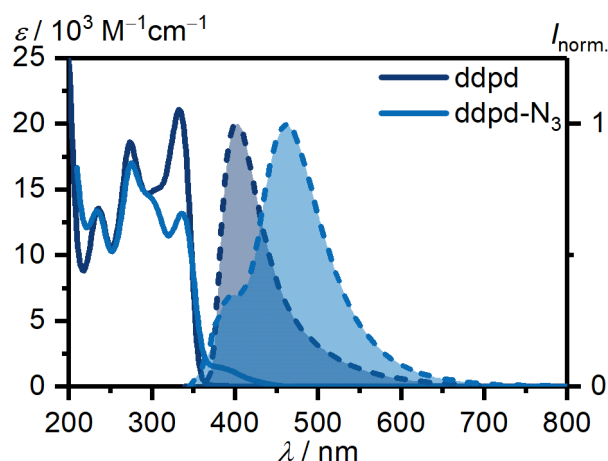


Figure S15. UV/Vis absorption (solid) and normalized emission spectra (dotted) of ligands ddpd ($\lambda_{\text{exc}} = 333 \text{ nm}$, $c = 7 \cdot 10^{-5} \text{ M}$), **L-N₃** ($\lambda_{\text{exc}} = 336 \text{ nm}$, $c = 3 \cdot 10^{-5} \text{ M}$), in acetonitrile at 293 K.

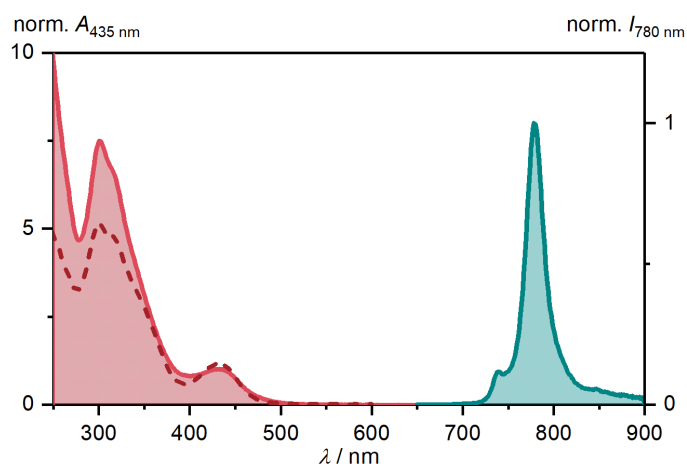


Figure S16. UV/Vis absorption (solid, red), normalized emission (solid, cyan; $\lambda_{\text{exc}} = 435 \text{ nm}$) and excitation spectra (dotted, red; $\lambda_{\text{em}} = 780 \text{ nm}$) of complex [Cr(L-N₃)₂][BF₄]₃ in water ($c = 1 \cdot 10^{-5} \text{ M}$) at 293 K.

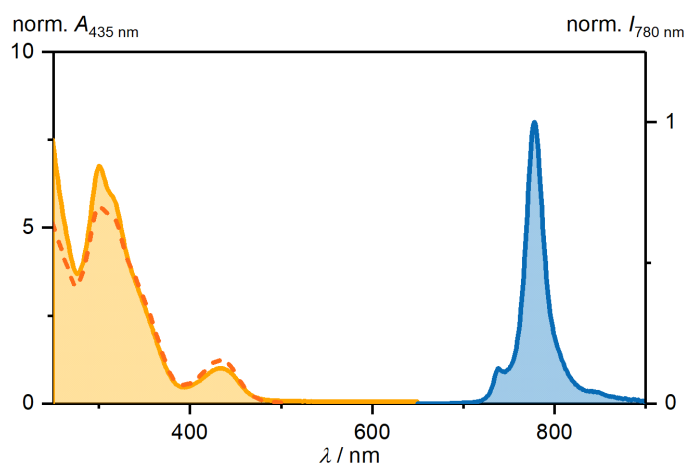


Figure S17. UV/Vis absorption (solid, orange), normalized emission (solid, blue; $\lambda_{\text{exc}} = 435 \text{ nm}$) and excitation spectra (dotted, orange; $\lambda_{\text{em}} = 778 \text{ nm}$) of complex [Cr(ddpd)(L-N₃)][BF₄]₃ in water ($c = 1 \cdot 10^{-5} \text{ M}$) at 293 K.

7. Irradiation experiments

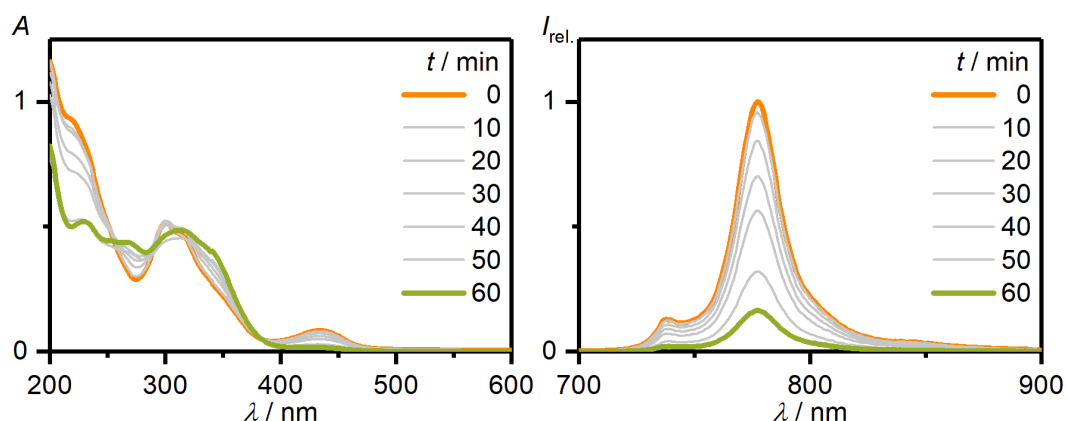


Figure S18. UV/Vis absorption (left) and emission spectra (right) of $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ ($c = 2 \cdot 10^{-5}$ M), after irradiation with the CW LASER ($\lambda_{\text{irr}} = 450$ nm), in deaerated water at 293 K.

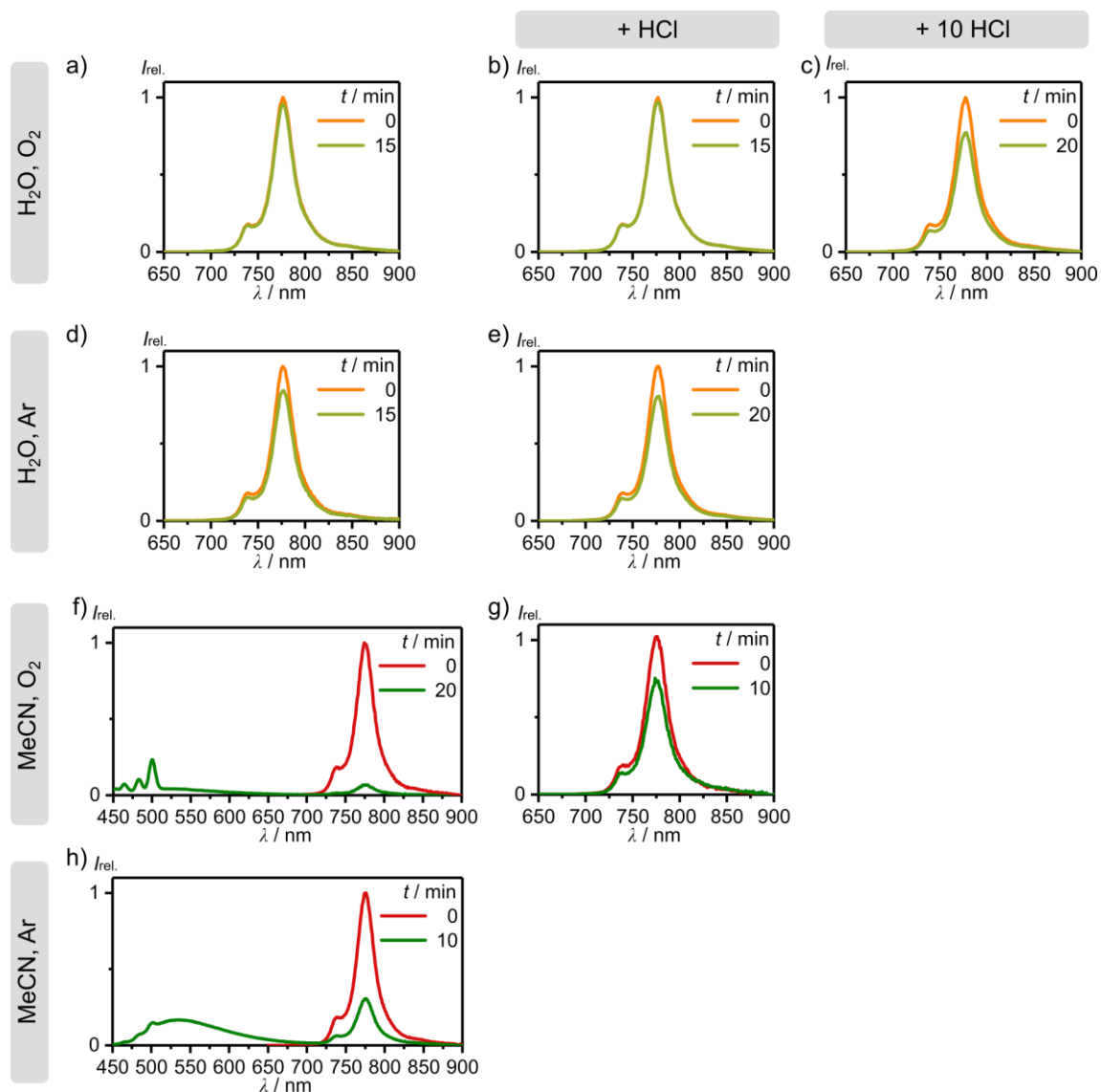


Figure S19. Emission spectra of complex $[\text{Cr}(\text{ddpd})_2][\text{Cl}]_3$, ($c = 2 \cdot 10^{-5}$ M) before and after irradiation with the CW LASER ($\lambda_{\text{irr}} = 450$ nm), in water (orange, light green) and acetonitrile (red, dark green) at 333 K.

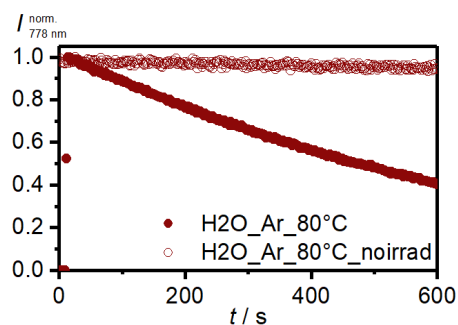


Figure S20. Intensity decay traces of $[\text{Cr}(\text{ddpd})_2][\text{Cl}]_3$ emission under irradiation with CW LASER (filled circles) and without irradiation (empty circles) at 80 °C in water.

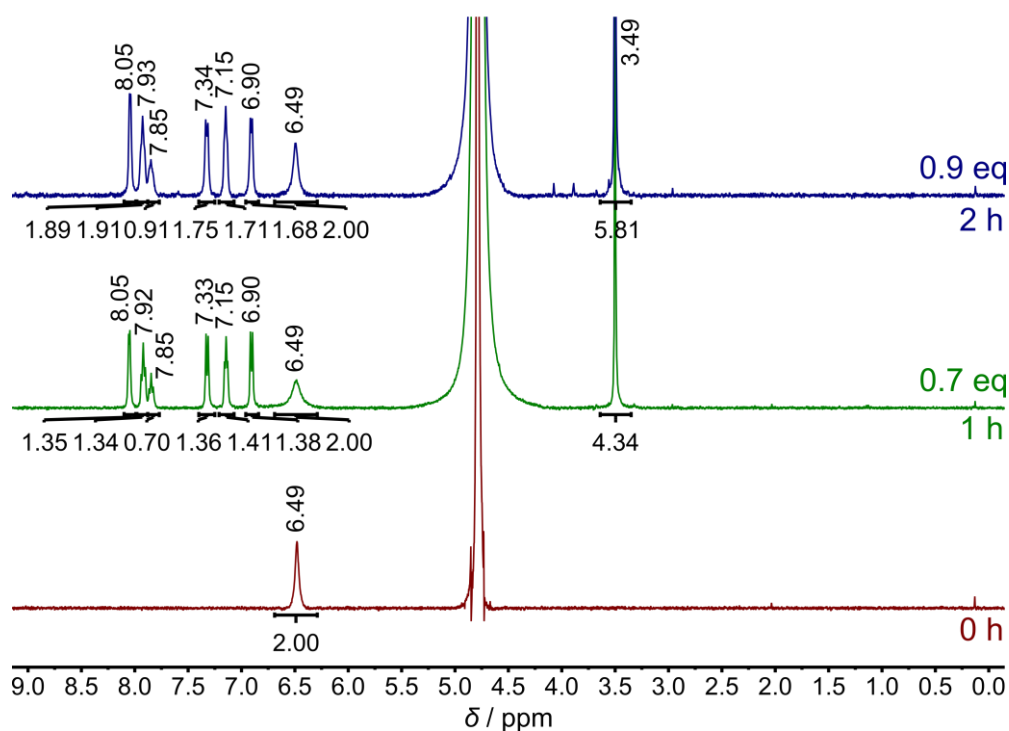


Figure S21. NMR spectra of $[\text{Cr}(\text{ddpd})_2][\text{BF}_4]_3$ in deuterated water before (red) and after irradiation (green and blue) with the UHP 460 LED ($\lambda_{\text{irr}} = 456 \text{ nm}$) at 293 K. Signal at 6.49 ppm from internal standard disodium fumarate.

8. Oligonucleotides

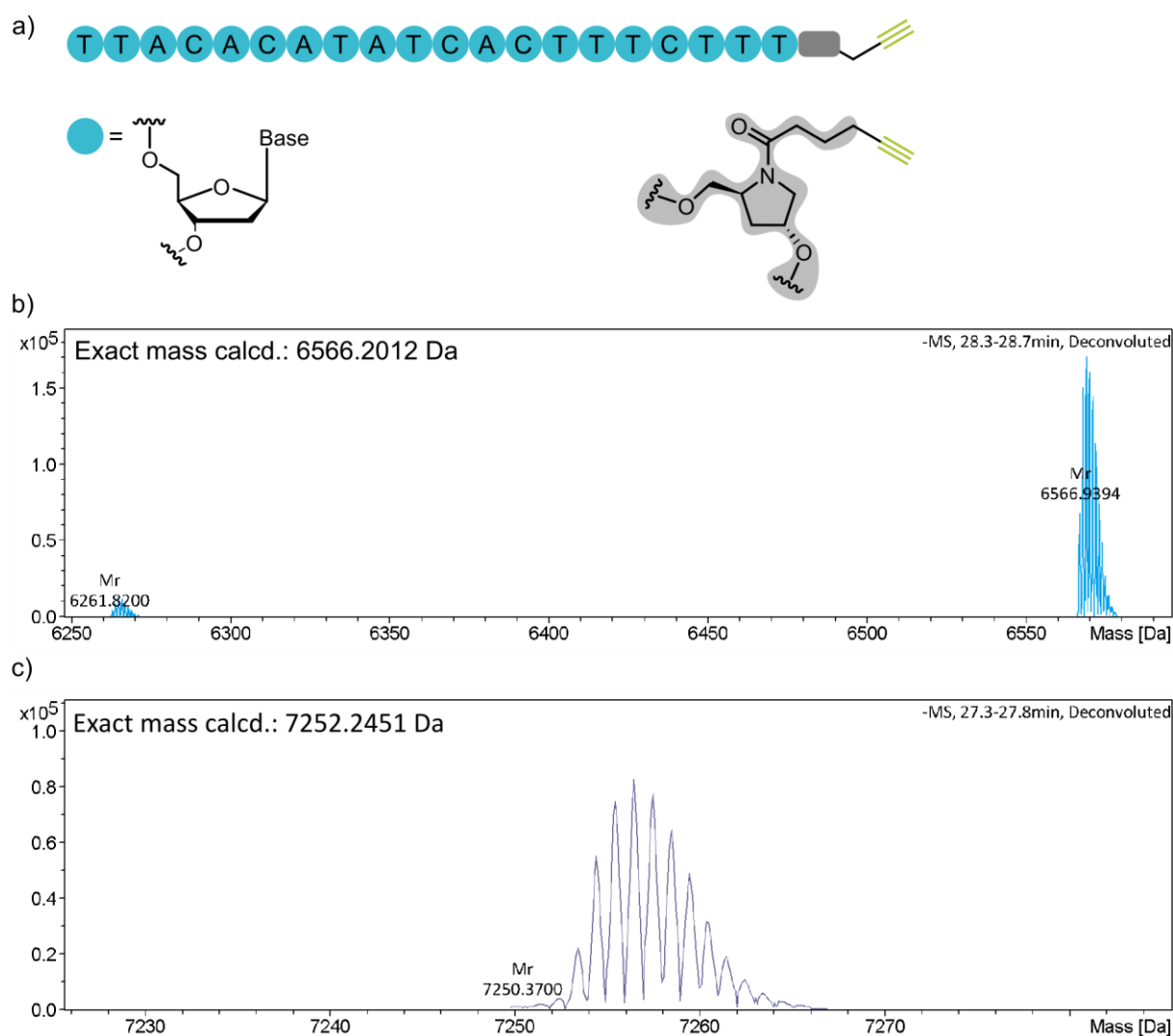


Figure S22. a) Schematic illustration of monofunctionalized oligonucleotide with b) corresponding MS spectrum and c) click product of monofunctionalized oligonucleotide and $[\text{Cr}(\text{ddpd})(\text{L-N}_3)]^{3+}$.

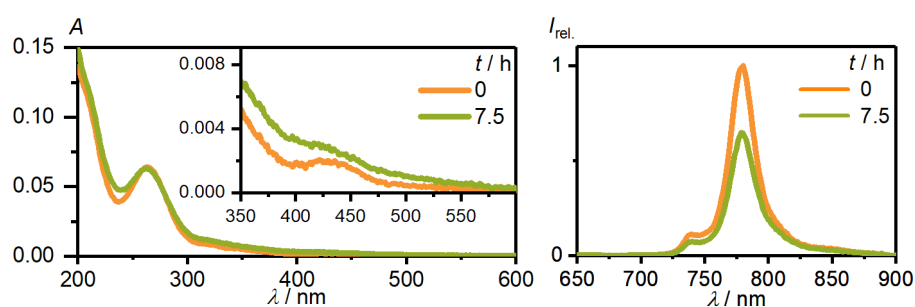


Figure S23. UV/Vis absorption (left) and emission spectra (right) of $[\text{Cr}(\text{ddpd})(\text{L-N}_3)]^{3+}$ -oligo (ca. $c = 2 \cdot 10^{-6}$ M) during irradiation with the UHP 460 LED ($\lambda_{\text{irr}} = 456$ nm), in water. Irradiation at 310 K, measurement at 293 K.

9. References

- [1] 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.
- [2] C. M. Amb, S. C. Rasmussen, *J. Org. Chem.* **2006**, *71*, 4696–4699.
- [3] J. Elhaïk, C. M. Pask, C. A. Kilner, M. A. Halcrow, *Tetrahedron* **2007**, *63*, 291–298.
- [4] A. Breivogel, C. Förster, K. Heinze, *Inorg. Chem.* **2010**, *49*, 7052–7056.
- [5] J.-R. Jiménez, B. Doistau, C. Besnard, C. Piguet, *Chem. Commun.* **2018**, *54*, 13228–13231.
- [6] J. Chong, C. Besnard, C. M. Cruz, C. Piguet, J.-R. Jiménez, *Dalton Trans.* **2022**, *51*, 4297–4309.

6.3 Supporting Information: The Overlooked NIR Luminescence of Cr(ppy)₃

The overlooked NIR luminescence of Cr(ppy)₃

Laura Stein, Pit Boden, Robert Naumann, Christoph Förster, Gereon Niedner-Schatteburg and Katja Heinze

Supplementary Information

General. All reagents were used as received from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer, Sigma-Aldrich and TCI). THF and toluene were refluxed over potassium and distilled under argon prior to use. Dichloromethane was dried and distilled from calcium hydride under argon prior to use. All reactions and measurements were performed under argon and waterfree atmosphere unless otherwise noted. A glovebox (UniLab/MBraun – Ar 4.8, O₂ < 1 ppm, H₂O < 0.1 ppm) was used to store and weigh sensitive compounds for synthesis as well as to prepare any sample that required absence of oxygen and water.

FD mass spectra were recorded on a *Thermo Fischer DFS* mass spectrometer.

IR spectra were recorded on a *Bruker Alpha II* FTIR spectrometer with an ATR unit containing a diamond crystal.

Elemental analyses were performed by the central analytic service of the department of chemistry of the University of Mainz using an *vario EL Cube* from *Elementar*.

Electrochemical experiments were carried out on a *BioLogic SP-200* voltammetric analyzer using platinum wires as counter and working electrodes and 0.01 M Ag/AgNO₃ as the reference electrode. The measurements were carried out at a scan rate of 100 mV s⁻¹ for cyclic voltammetry experiments using 0.1 M [nBu₄N][PF₆] as supporting electrolyte and 0.001 M of the sample in dichloromethane. Potentials are referenced relative to the ferrocene/ferrocenium couple.

UV/Vis absorption spectra in solution were recorded on a *Jasco V770* spectrometer using 1.0 cm quartz cells with a Schott valve to maintain an inert atmosphere.

Steady-state irradiation was carried out with an *Asahi-MAX-303* Xe lamp (300 W), together with 420±5 nm filters. The samples were prepared under inert conditions in 1.0 cm quartz cells with a Schott valve. UV/Vis spectra were recorded after the indicated time intervals.

Emission spectra and luminescence decay curves (solutions and powder samples) 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 whole 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 the µs-xenon-flashlamp *mF2* (pulse width ca. 2 µs) as excitation source. Measurements at low temperature were conducted using a liquid nitrogen cooled cryostat *Optistat* from *Edinburgh Instruments*. Absolute luminescence quantum yields Φ were determined using an integrating sphere from *Edinburgh Instruments*. Relative uncertainty of Φ is estimated to be ±20 %.

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 × 10 mm quartz cuvette) the beam was brought to a diameter of 1.2 cm using a beam expander. 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.

KBr pellets were prepared by mixing neat powder of the compound (0.7 – 1.6 mg, depending on the experiment) with dry KBr (180 – 300 mg, stored in a compartment dryer at 80 °C, purchased from Merck) and grinding to a homogenous mixture. This mixture was filled in an evacuable pellet die with a diameter of 13 mm and sintered at a pressure of 0.75 GPa. Please consider the respective sections for more details on the specific sample preparations.

UV/VIS absorption spectroscopy in the solid state (KBr pellets) was performed with a *Lambda 900* UV/VIS spectrometer equipped with a diffuse reflectance accessory (*Harrick Praying Mantis*). The powder samples were prepared by mixing neat powder of the compound with dry KBr in a ratio of ca. 1:100 and grinding to a homogenous mixture.

Temperature-dependent steady state NIR luminescence measurements (KBr pellets) were conducted on a *Horiba Jobin Yvon Fluorolog 3-22 τ* spectrometer equipped with a 450 W Xenon lamp and a *DSS – IGA020L* NIR detector (850 nm $\leq \lambda_{em} \leq$ 1550 nm). Spectral selection was realized with double and single grating monochromators in the excitation and emission paths, respectively (excitation: 1200 grooves/mm; near-IR emission 600 grooves/mm). A combination of two long-pass filters (*FELH0500 Thorlabs*, transmission $\geq$ 92% above 500 nm and *FELH0850 Thorlabs*, transmission $\geq$ 90% above 860 nm) was used in the emission channel to avoid higher order excitation light. All emission spectra presented were corrected for the wavelength-dependent sensitivity of the detector. KBr pellets were prepared as described in the section on the preparation of KBr pellets using 0.7 mg of sample and 180 mg of KBr. Temperature-dependent experiments between 5 K and 290 K were performed using a closed-cycle helium cryostat (*ColdEdge, 101J cryocooler*) to cool down the sample. The cryocooler was equipped with a pellet holder (copper) and CaF₂ windows.

NIR luminescence quantum yields (KBr pellets) were determined in analogy to the procedures described by Wrighton et al. and later Liu et al., who measured fluorescence quantum yields with a conventional fluorescence spectrometer.^{1,2} All spectra were recorded at room temperature on the *Horiba Jobin Yvon Fluorolog 3-22 τ* spectrometer (see the sections on static NIR luminescence spectroscopy for more details) with the KBr pellets being mounted in a solid state sample holder. The absorption of the complex was measured by considering the difference in area between the excitation light ($\lambda_{exc} = 350$ nm) scattered by a neat KBr pellet (J_0) and a pellet containing the complex (J). For the luminescence the area J_f under the emission curve was considered. The quantum yields were measured relative to the standard Yb(tta)₃(H₂O)₂ with $\phi_r(Yb) = 0.55$ % as PMMA film.³ The NIR photoluminescence quantum yield was calculated according to the following equation, where the abbreviation S stands for the investigated sample with unknown quantum yield and Yb represents the reference Yb(tta)₃(H₂O)₂:

$$\phi_{NIR} = \frac{J_0 - J(Yb)}{J_0 - J(S)} \cdot \frac{J_f(S)}{J_f(Yb)} \cdot \phi_r(Yb)$$

The error bars for the photoluminescence quantum yields are estimated to ± 25 % for the applied procedures according to the literature.¹

Time-resolved step-scan FTIR experiments (KBr pellets) were performed with the FTIR spectrometer *Bruker Vertex 80v*, operated in the step-scan mode. A liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector (*Kolmar Tech., Model KV100-1-B-7/190*) with a rise time of 25 ns, connected to a fast preamplifier and a 14-bit transient recorder board (*Spectrum Germany, M3I4142, 400 MS/s*), was used for signal detection and processing. The laser setup used for the measurements includes a

Q-switched Nd:YAG laser (*Innolas SpitLight Evo I*) generating pulses with a duration of about 6 ns at a repetition rate of 100 Hz. The third harmonic (355 nm) of the Nd:YAG laser was used directly for sample excitation. The UV pump beam was attenuated to about 2.0 mJ per shot at a diameter of 9 mm. The beam was directed onto the sample and adjusted to have a maximal overlap with the IR beam of the spectrometer. The sample chamber was equipped with anti-reflection-coated germanium filters to prevent the entrance of laser radiation into the detector and interferometer compartments.

The KBr pellets were prepared as described in the section on luminescence spectroscopy (ca. 0.7 mg of the complex and ca. 180 mg KBr). The strongest peak in the ground state spectrum showed an absorption of about 0.6 OD with the mentioned concentration. The measurements were performed at a constant temperature of 20 K using a closed-cycle helium cryostat (*ARS Model DE-202A*). The cryocooler was equipped with a pellet holder and CaF₂ windows.

The temporal resolution of the 14-bit transient recorder board was chosen to 50 ns and 10000 time slices were recorded to cover a time range of 500 μ s. The time when the laser pulse reached the sample was set as zero point in all spectra. The time delay between the start of the experiment and the laser pulse was controlled with a *Stanford Research Systems DG535* delay generator and set to 1.3 μ s before the laser excitation of the sample. The spectral region was limited by undersampling to 988 – 1975 cm⁻¹ with a spectral resolution of 4 cm⁻¹ resulting in 555 interferogram points. An IR broad band filter (850 – 1750 cm⁻¹) and the CaF₂ windows (no IR transmission < 1000 cm⁻¹) of the cryostat prevented problems when performing a Fourier transformation (i.e. no IR intensity outside the measured region should be observed). FTIR ground state spectra were recorded systematically to check if there is no sample degradation. The error for the excited state lifetime is estimated to ± 10 %.

Crystal Structure Determination. Intensity data for crystal structure determination of *fac*-Cr(ppy)₃ were collected with a STADIVARI diffractometer from STOE & CIE GmbH using Mo-K α radiation (λ = 0.71073 Å). The diffraction frames were integrated using the STOE X-Area software package⁴ and were corrected for absorption with STOE LANA^{5,6} of the STOE X-Area software package.⁴ The structures were solved with SHELXT⁷ and refined by the full-matrix method based on F^2 using SHELXL⁸ of the SHELX⁹ software package and the ShelXle¹⁰ 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-2124885.

Crystallographic Data of *fac*-Cr(ppy)₃. C₃₃H₂₄CrN₃ (514.55); tetragonal; $P\bar{4}2_1c$; a = 23.0243(3) Å, b = 23.0243(3) Å, c = 9.21690(10) Å, α = 90°, β = 90°, γ = 90°; V = 4886.05(14) Å³; Z = 8; density (calculated) 1.399 g cm⁻³, T = 120(2) K, μ = 0.497 mm⁻¹, $F(000)$ = 2136; crystal size 0.090 x 0.069 x 0.058 mm³; θ = 1.978 to 29.750 deg.; $-31 \leq h \leq 29$, $-31 \leq k \leq 32$, $-11 \leq l \leq 12$; rfln collected = 49789; rfln unique = 6346 [$R(\text{int})$ = 0.0241]; completeness to θ = 25.242 deg. = 99.4 %; semi empirical absorption correction from equivalents; max. and min. transmission 0.9697 and 0.4753; data 6346; restraints 0, parameters 334; goodness-of-fit on F^2 = 1.009, final indices [$I > 2\sigma(I)$] R_1 = 0.0263, wR_2 = 0.0647; R indices (all data) R_1 = 0.0300, wR_2 = 0.0652; largest diff. peak and hole 0.259 and -0.427 e Å⁻³.

Density functional theory and CASSCF-NEVPT2 calculations were carried out using the ORCA program package 5.0.1.¹¹

DFT calculations were performed using the B3LYP functional^{12,13} employing the RIJCOSX approximation.^{14,15} 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.¹⁶ 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.^{17,18} Geometry optimizations were performed using Ahlrichs' polarized valence triple- ζ basis set (def2-TZVPP).^{19,20} Atompairwise dispersion correction was performed with the Becke-Johnson damping scheme (D3BJ).^{21,22} 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 assignment of the state characters has been done dividing the molecule into four fragments (metal center and three ppy⁻ ligands) and calculating charge transfer (CT) numbers, as implemented in the TheoDore software package.^{23,24}

CASSCF(7,12)-FIC-NEVPT2 calculations were performed at the DFT-optimized ground state geometry using the complete-active-space self-consistent field method including spin-orbit coupling (SOC-CASSCF)^{25,26} in conjunction with the fully internally contracted N-electron valence perturbation theory to second order (FIC-NEVPT2)^{27,28} in order to recover missing dynamic electron correlation. All electronic states are classified by irreducible representations of the *O* point group, in spite of the lower actual symmetry of the considered complex. In order 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 shell²⁹ 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 *fac*-Cr(ppy)₃: The precursor CrPh₃(thf)₃ was prepared according to a literature procedure.³⁰ The red product was used without further purification. *fac*-Cr(ppy)₃ was prepared according to a reported procedure from CrPh₃(thf)₃.³¹ The product was isolated as an analytically pure yellow powder. Orange crystals suitable for single crystal X-ray crystallography were obtained from concentrating a CH₂Cl₂/toluene solution. Elemental analysis. calcd. (%) for C₃₃H₂₄CrN₃ (514.57): C, 77.03; H, 4.70; N, 8.17; found: C, 77.24; H, 5.01; N, 8.09. MS (FD): *m/z* (%) = 514.396; calcd. for C₃₃H₂₄CrN₃ *m/z* (%) = 514.138. IR (ATR): $\tilde{\nu}$ = 3043 (w), 1595 (s), 1561 (m), 1469 (s), 1426 (m), 1298 (w), 1259 (m), 1168 (m), 1098 (w), 1059 (w), 1022 (w), 999 (w), 936 (vw), 878 (vw), 800 (w), 748 (vs), 732 (vs), 711 (s), 659 (m), 631 (m), 554 (w), 474 (w), 412 (m) cm⁻¹. UV-Vis (CH₂Cl₂): λ_{max} (ϵ / 10³ M⁻¹cm⁻¹): 261 (50.5), 298 (31.5), 385 (5.7), 440 (3.0) nm. CV (CH₂Cl₂, 0.1 M [ⁿBu₄N][PF₆], vs. ferrocene, 293 K): *E*_p = +0.24 V.

Table S1. Bond lengths [Å] and angles [deg] of *fac*-Cr(ppy)₃ and [Cr(bpy)₃]³⁺ from XRD measurements and DFT calculations. Intraligand and interligand angles highlighted in yellow and green, respectively.

	<i>fac</i> -Cr(ppy) ₃				[Cr(bpy) ₃] ³⁺	
	XRD	DFT quartet ground state	DFT lowest doublet state		XRD ³²	DFT quartet ground state
Cr1–N1	2.145(2)	2.146	2.138	Cr1–N1	2.042(5)	2.057
Cr1–N2	2.149(2)	2.146	2.147	Cr1–N2	2.042(5)	2.054
Cr1–N3	2.140(2)	2.146	2.153	Cr1–N3	2.042(5)	2.055
Cr1–C1	2.059(2)	2.063	2.055	Cr1–N4	2.042(5)	2.053
Cr1–C2	2.061(2)	2.063	2.053	Cr1–N5	2.042(5)	2.056
Cr1–C3	2.058(2)	2.063	2.044	Cr1–N6	2.042(5)	2.051
N1–Cr–N2	92.86(6)	93.9	93.6	N1–Cr–N2	94.6(2)	94.45
N1–Cr–N3	94.50(6)	93.9	93.3	N1–Cr–N3	94.6(2)	96.50
N1–Cr–C1	171.25(7)	172.0	171.5	N1–Cr–N4	171.0(2)	173.8
N1–Cr–C2	79.26(7)	79.3	79.4	N1–Cr–N5	79.1(2)	79.6
N1–Cr–C3	93.60(7)	90.8	91.4	N1–Cr–N6	92.3(2)	90.0
N2–Cr–N3	90.39(6)	93.9	93.7	N2–Cr–N3	94.6(2)	95.4
N2–Cr–C1	93.05(7)	90.8	90.7	N2–Cr–N4	92.3(2)	90.7
N2–Cr–C2	167.52(7)	172.0	171.9	N2–Cr–N5	171.0(2)	172.7
N2–Cr–C3	79.28(7)	79.3	79.4	N2–Cr–N6	79.1(2)	79.7
N3–Cr–C1	79.03(7)	79.3	79.1	N3–Cr–N4	79.1(2)	79.5
N3–Cr–C2	99.81(7)	90.8	90.9	N3–Cr–N5	92.3(2)	89.6
N3–Cr–C3	167.17(7)	172.0	171.9	N3–Cr–N6	171.0(2)	172.2
C1–Cr–C2	95.93(8)	96.4	96.7	N4–Cr–N5	94.6(2)	95.5
C1–Cr–C3	93.83(7)	96.4	96.6	N4–Cr–N6	94.6(2)	94.4
C2–Cr–C3	91.47(8)	96.4	96.4	N5–Cr–N6	94.6(2)	95.9

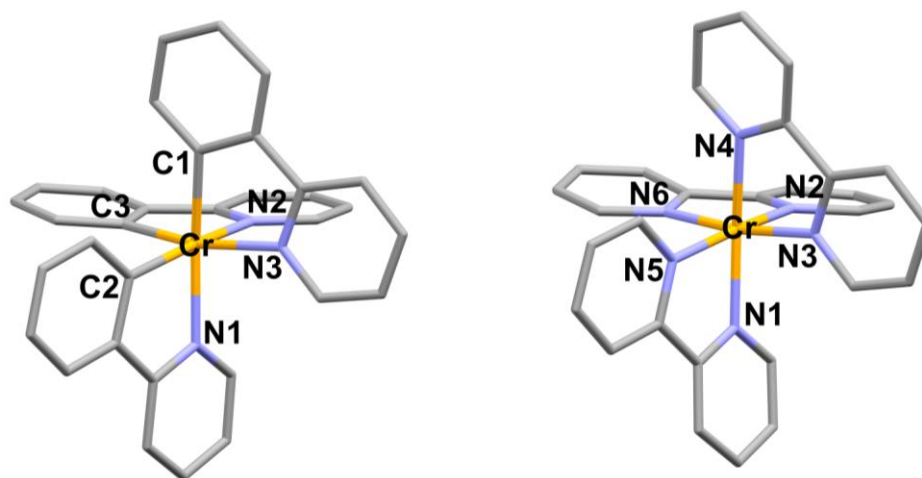


Figure S1. Molecular structures of *fac*-Cr(ppy)₃ and [Cr(bpy)₃]³⁺ ³² with atom numbering used in Table S1. Hydrogen atoms omitted for clarity.

Table S2. Shape parameters for octahedron $S(\text{OC-6})$ and trigonal prism $S(\text{TPR-6})$ of fac-Cr(ppy)_3 and $[\text{Cr(bpy)}_3]^{3+}$ from DFT calculated geometries and from XRD data.

	fac-Cr(ppy)_3		$[\text{Cr(bpy)}_3]^{3+}$	
	DFT	XRD	DFT	XRD ³²
$S(\text{OC-6})$	0.88	1.17	0.83	0.93
$S(\text{TPR-6})$	14.58	11.92	14.78	13.68

Table S3. Emission data of fac-Cr(ppy)_3 : Emission wavelength, corresponding quantum yields and excited state lifetimes at different temperatures and in different physical states. Excitation was at 420 nm, if not stated otherwise.

State/solvent	T / K	$\lambda_{\text{em}} / \text{nm}$	$\Phi / \%$	$\tau / \mu\text{s}$
2-MeTHF, Ar	293	910	-	9.5
2-MeTHF, Ar	77	890, 910 (sh), 1020 (sh)	-	48
CH_2Cl_2, Ar^a	293	910	0.03	9.3
Powder	293	905	0.02	10 (76 %); $\tau_2 = 3$ (24 %)
KBr pellet	298	925	0.3 ^b	-
KBr pellet	20	922	-	9.8 ^c

^a Excitation at 473 nm.

^b Relative to $\text{Yb(tta)}_2(\text{H}_2\text{O})_2$.

^c Excitation at 355 nm, from step-scan FTIR experiments.

Table S4. Emission data of $[\text{Cr(bpy)}_3][\text{PF}_6]_3$: Emission wavelength, corresponding quantum yields and excited state lifetimes.

Solvent	$\lambda_{\text{em}} / \text{nm}$	$\tau_{\text{RT}} (\tau_{\text{RT,deox}}) / \mu\text{s}$	$\tau_{\text{LT}} (\tau_{\text{LT,deox}}) / \mu\text{s}$	$\Phi_{\text{deox}} / \%$	reference
H_2O	730	52 (74)	6500 ^a	0.089	33,34
1 M HCl(aq)	729	– (69)	–	0.25 %	35

^a Aq. HClO_4 (pH = 3.1)/MeOH 1:1 v/v at 77 K.

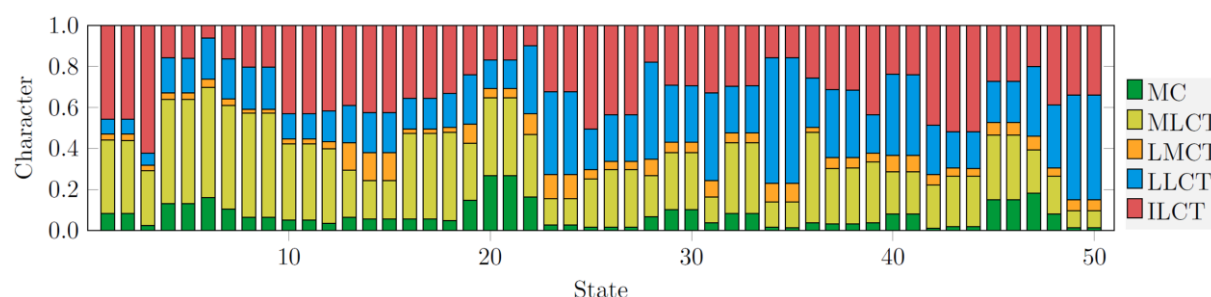
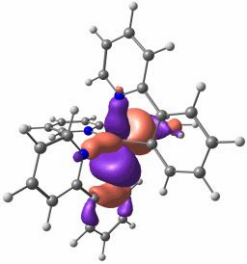
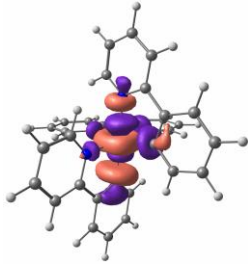
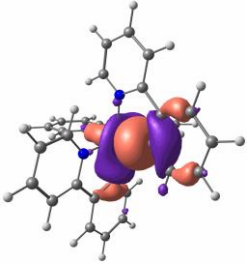
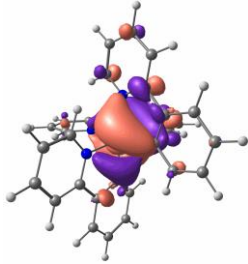
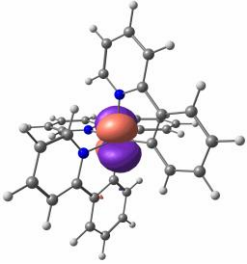
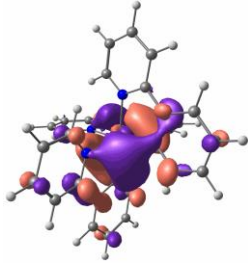
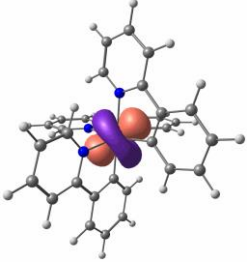
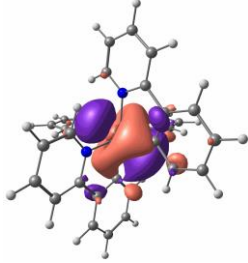
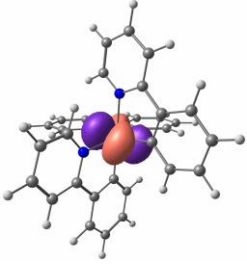
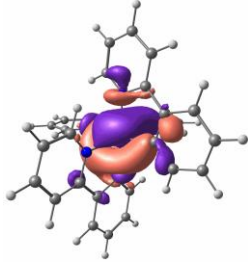
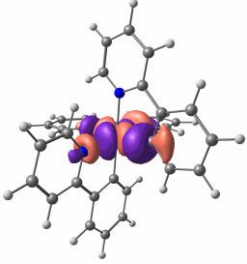
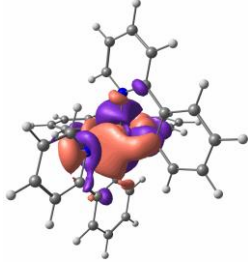


Figure S2. TD-DFT-UKS charge transfer numbers of fac-Cr(ppy)_3 defined from 0 to 1 of the lowest-lying 50 quartet states using the TheoDore software package.^{23,24}

Table S5. Orbital energies/Hartree of the canonical orbitals used in the active space of the CASSCF(7,12)-FIC-NEVPT2 calculation, depicted at a contour value of 0.03 a.u..

#	E / H	orbital	#	E / H	orbital
130	-0.373584		136	+0.257474	
131	-0.372416		137	+0.544860	
132	-0.044505		138	+0.564580	
133	-0.039633		139	+0.792775	
134	-0.019034		140	+0.963221	
135	+0.240689		141	+1.026967	

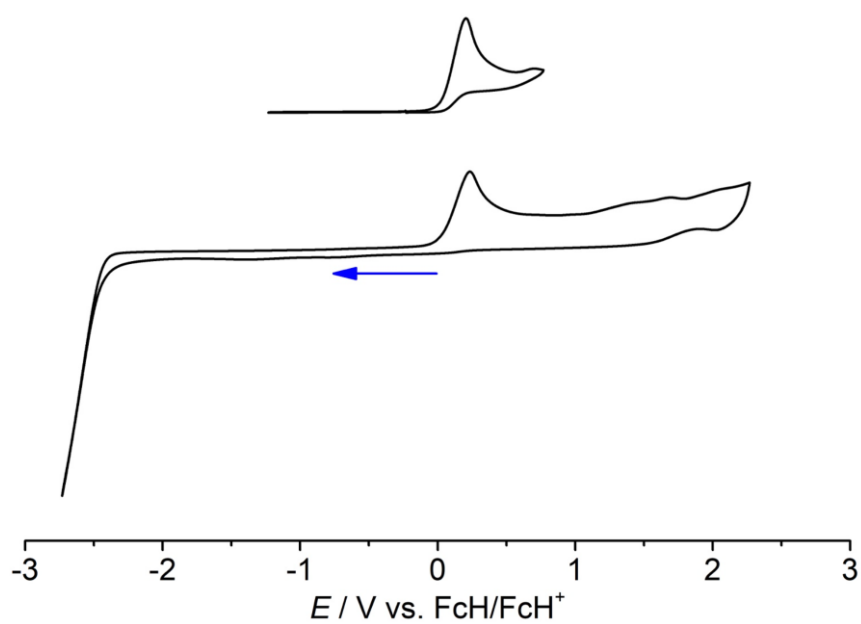


Figure S3. Cyclic voltammograms of *fac*-Cr(ppy)₃ in CH₂Cl₂/[ⁿBu₄N][PF₆]; *E* vs. ferrocene.

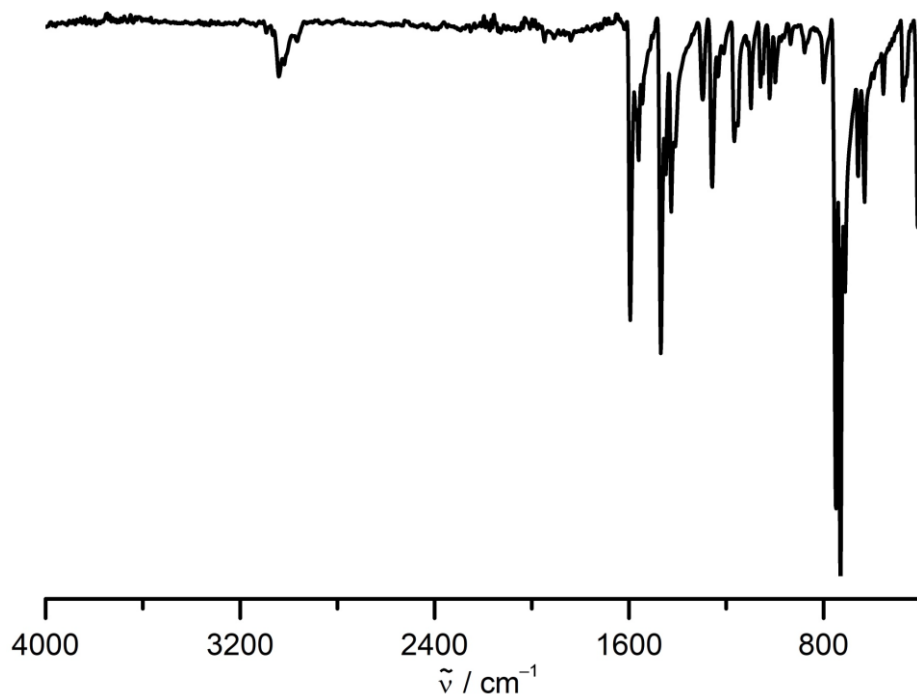


Figure S4. ATR-IR spectrum of solid *fac*-Cr(ppy)₃.

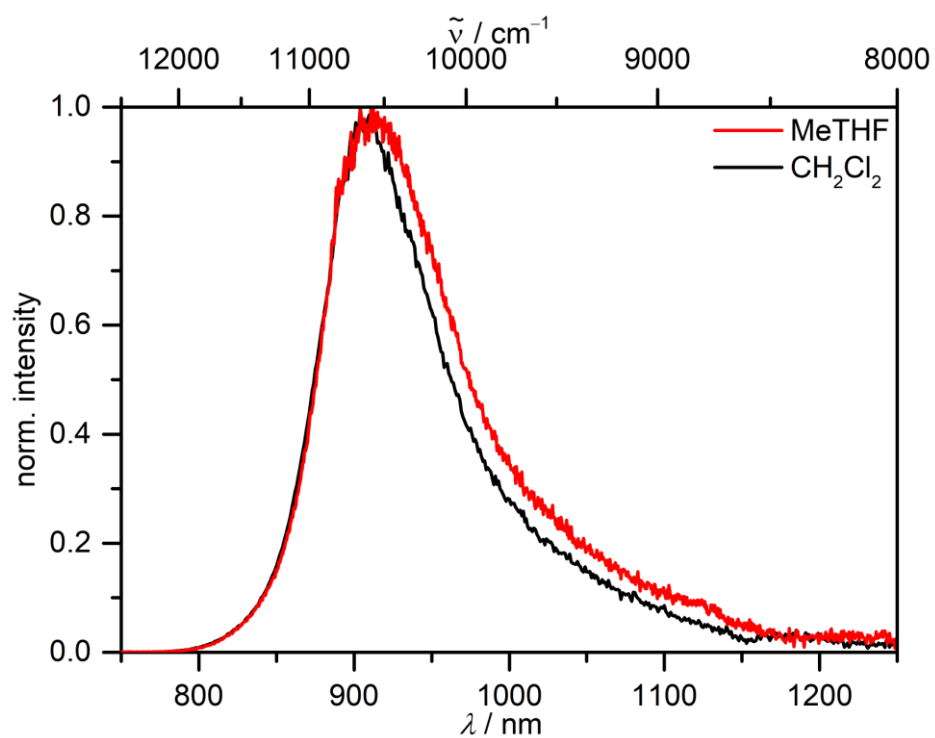


Figure S5. Emission spectra of *fac*-Cr(ppy)₃ in 2-MeTHF (red, λ_{exc} = 420 nm, scan slit width 10 nm) and CH₂Cl₂ (black, λ_{exc} = 473 nm, scan slit width 5 nm) at 293 K.

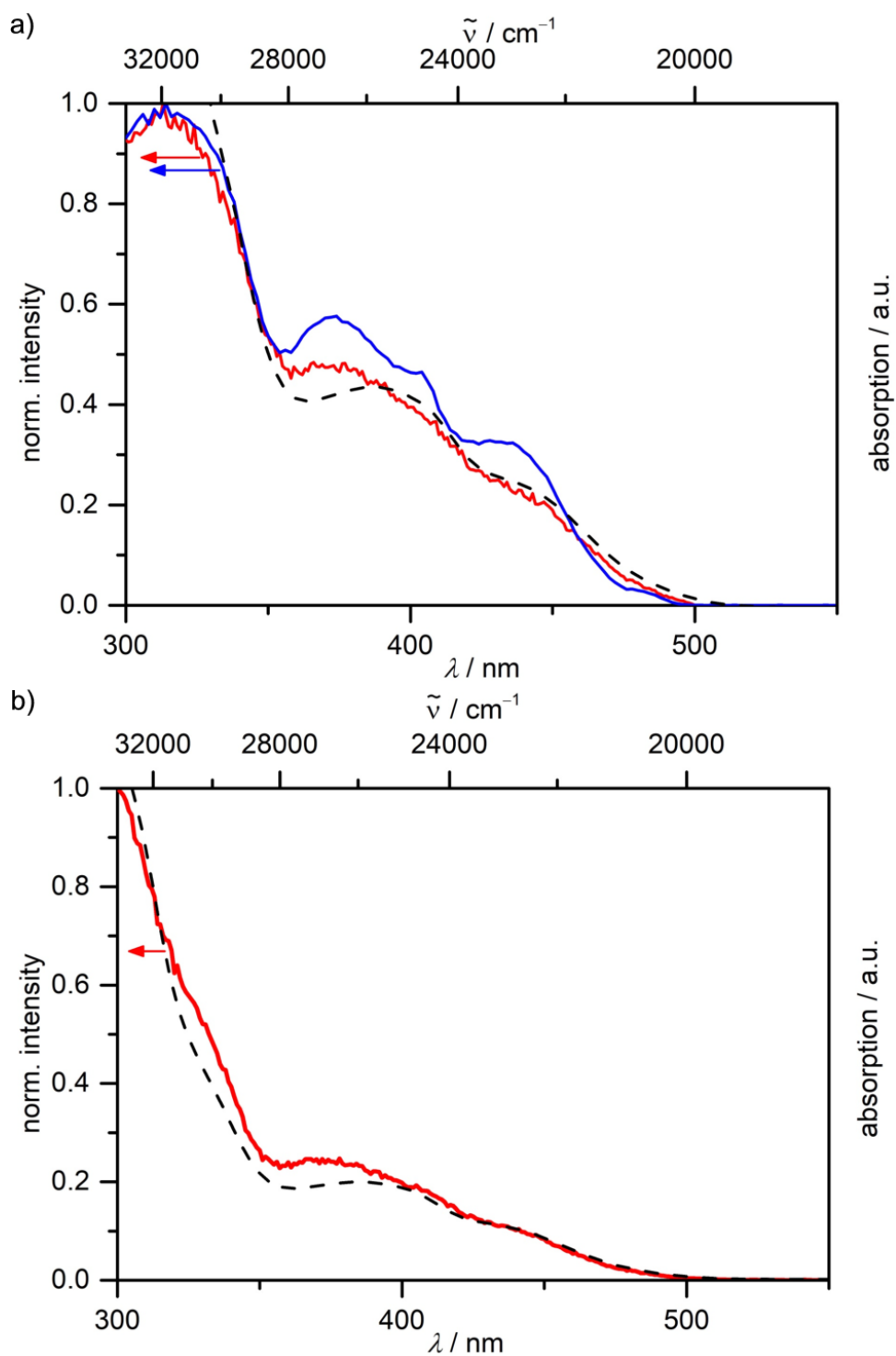


Figure S6. a) Absorption (black dotted line) and excitation spectra of *fac*-Cr(ppy)₃ in 2-MeTHF at 293 K (red, $\lambda_{em} = 880$ nm) and 77 K (blue, $\lambda_{em} = 890$ nm) and b) absorption (black dotted line) and excitation spectrum of *fac*-Cr(ppy)₃ in CH₂Cl₂ at 293 K (red, $\lambda_{em} = 870$ nm).

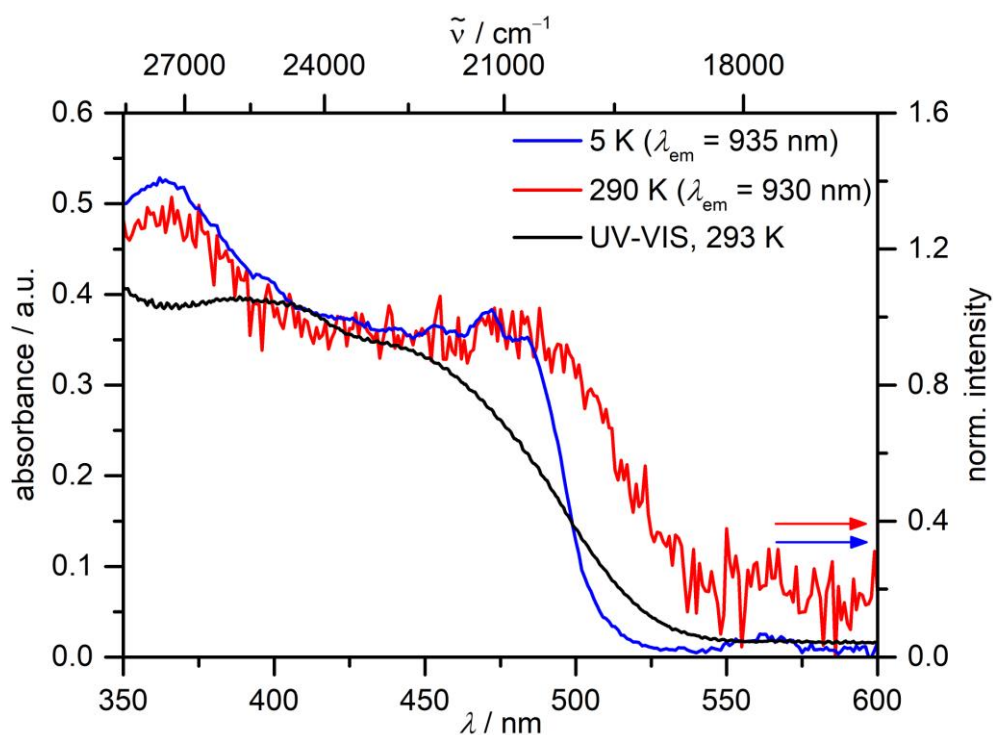


Figure S7. Absorption spectrum of *fac*-Cr(ppy)₃ as powder at 293 K (black) and excitation spectra of *fac*-Cr(ppy)₃ in a KBr pellet at 290 K (red, $\lambda_{\text{em}} = 930$ nm) and at 5 K (blue, $\lambda_{\text{em}} = 935$ nm).

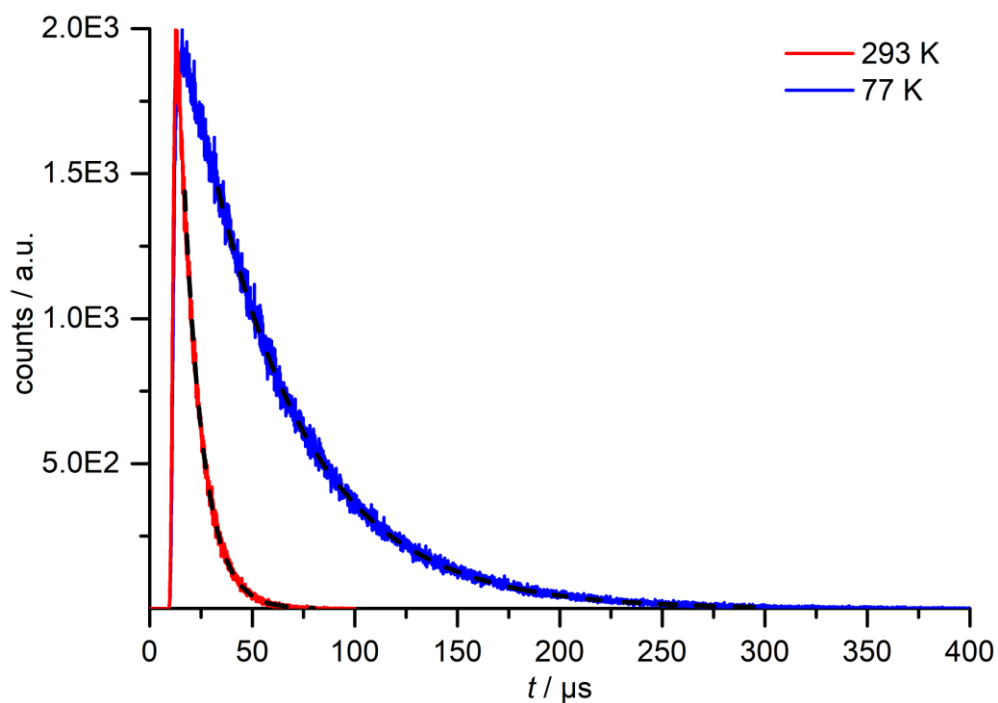


Figure S8. Lifetime scans of *fac*-Cr(ppy)₃ in 2-MeTHF at 77 K (blue, $\lambda_{\text{em}} = 890$ nm, $\lambda_{\text{exc}} = 420$ nm) and 293 K (red, $\lambda_{\text{em}} = 870$ nm, $\lambda_{\text{exc}} = 420$ nm). Applied monoexponential tailfits indicated as black dotted lines.

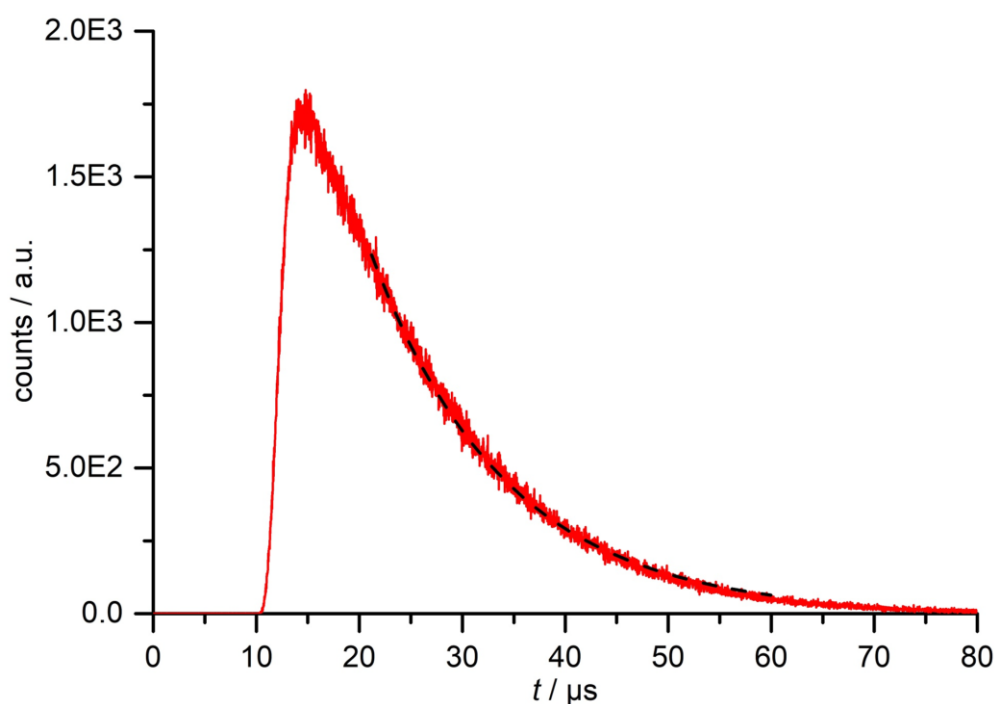


Figure S9. Lifetime scan of *fac*-Cr(ppy)₃ in CH₂Cl₂ at 293 K (red, $\lambda_{\text{em}} = 870$ nm, $\lambda_{\text{exc}} = 473$ nm). Applied monoexponential tailfit indicated as black dotted line.

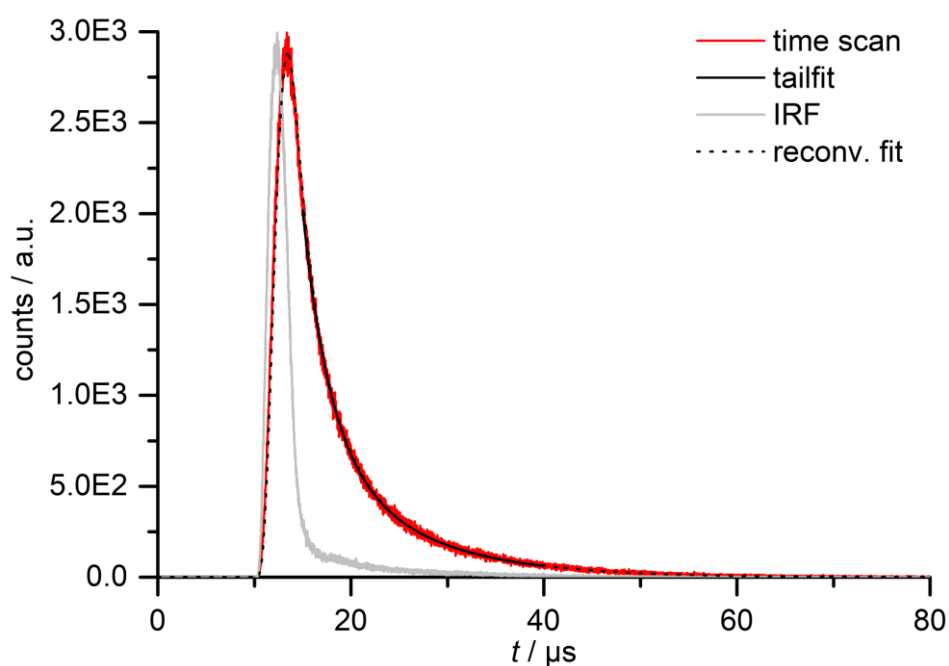


Figure S10. Lifetime scan (red) of solid *fac*-Cr(ppy)₃ at 293 K ($\lambda_{\text{em}} = 880$ nm). Tailfit and reconvolution fit (IRF in grey) indicated in black, solid and dotted, respectively. The lifetime in the solid state was determined with a biexponential tailfit as well as with a reconvolution fit including the IRF, resulting in the same output.

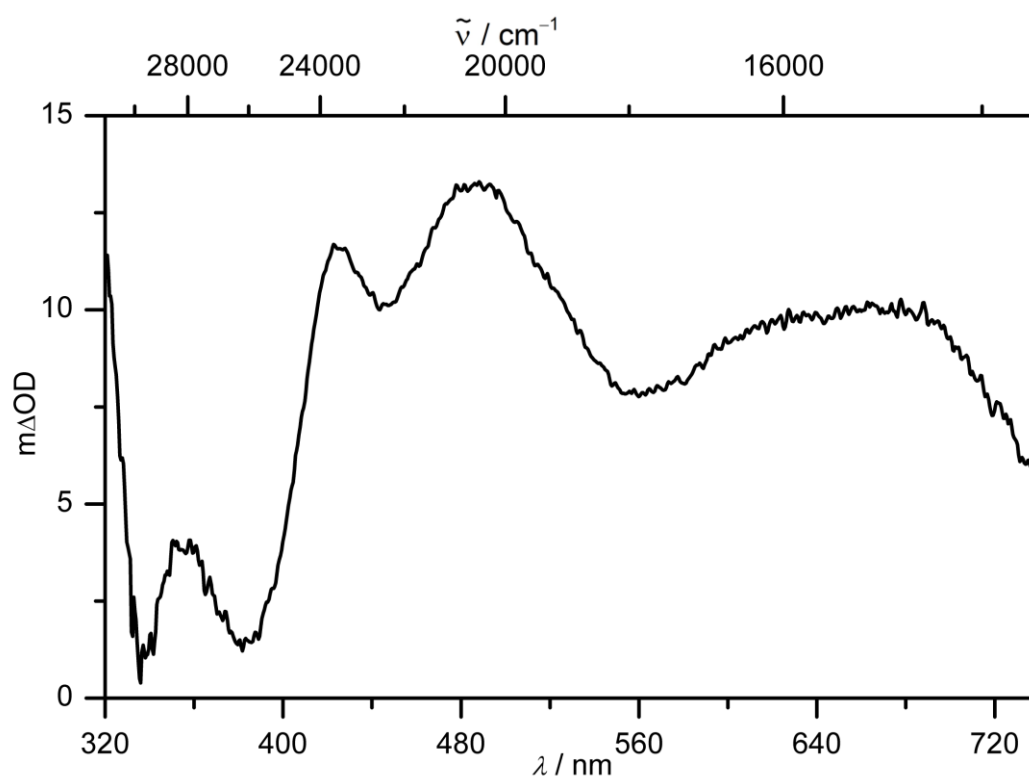


Figure S11. Transient absorption spectrum of *fac*-Cr(ppy)₃ in Ar-saturated CH₂Cl₂ at 293 K ($\lambda_{\text{exc}} = 355$ nm; ≈ 30 mJ pulse energy).

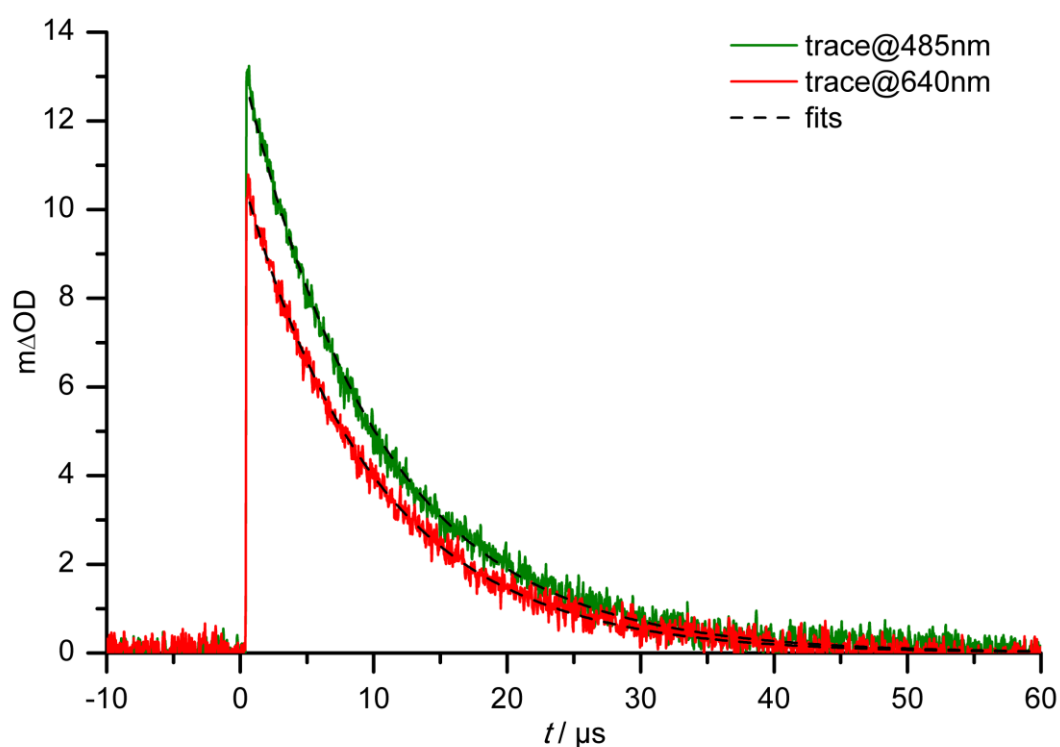


Figure S12. Transient absorption traces upon laser excitation ($\lambda_{\text{exc}} = 355$ nm; ≈ 30 mJ pulse energy) of *fac*-Cr(ppy)₃ in Ar-saturated CH₂Cl₂ at 293 K monitored at 485 nm (green) and at 640 nm (red). Applied monoexponential fits indicated as black dotted lines (485 nm: $y = 13.4082 \exp(-0.0977355 t)$; 640 nm: $y = 10.9038 \exp(-0.10069 t)$).

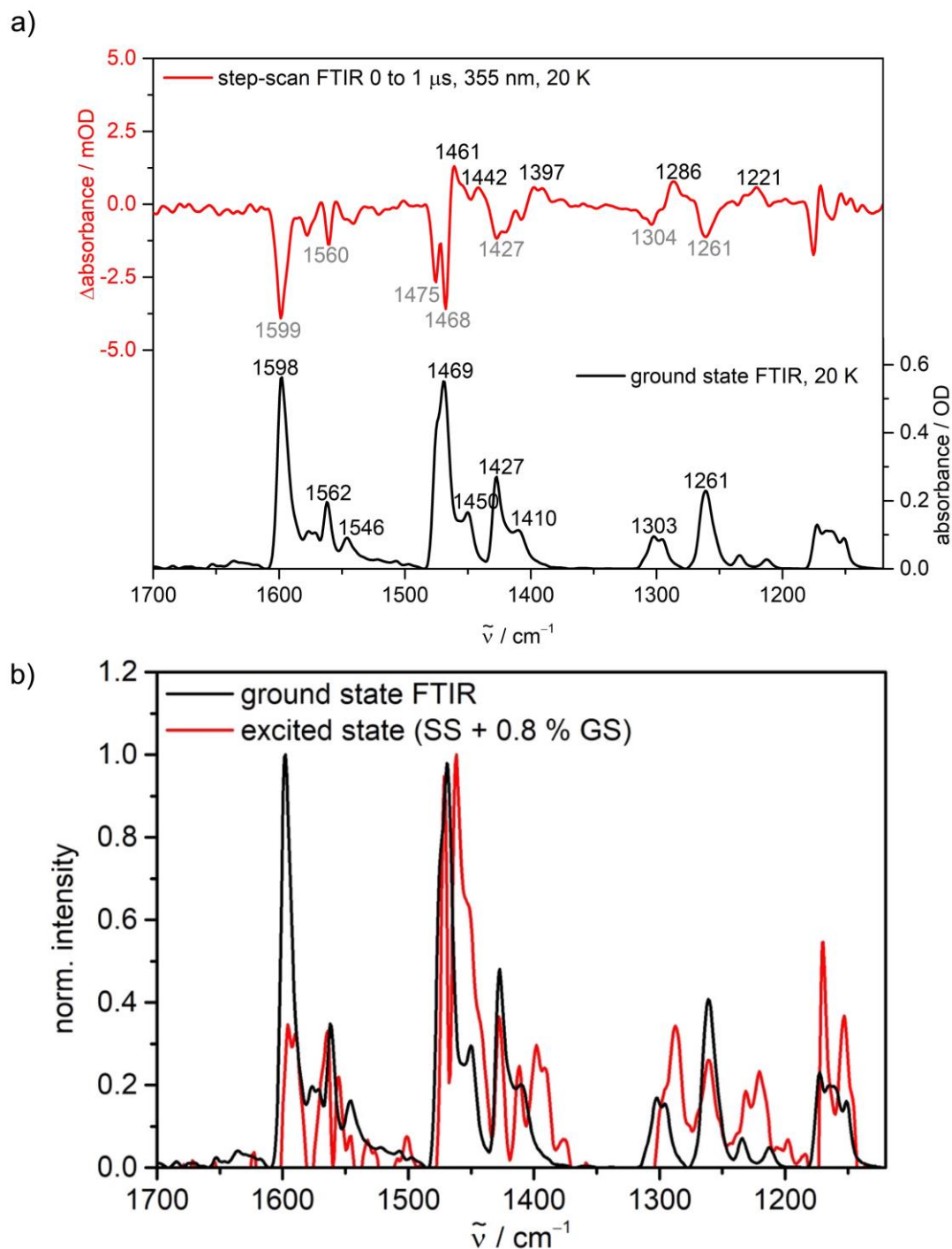


Figure S13. a) Step-scan difference spectrum (red, $\lambda_{\text{exc}} = 355 \text{ nm}$) and ground state FTIR spectrum (black) of *fac*-Cr(ppy)₃ in the solid state (KBr matrix) at 20 K and b) ground state (black) and excited state (red, $\lambda_{\text{exc}} = 355 \text{ nm}$) FTIR spectra of *fac*-Cr(ppy)₃ in a KBr pellet at 20 K. 0.8 % of the ground state spectrum was added to the step-scan difference spectrum to obtain the excited state spectrum.

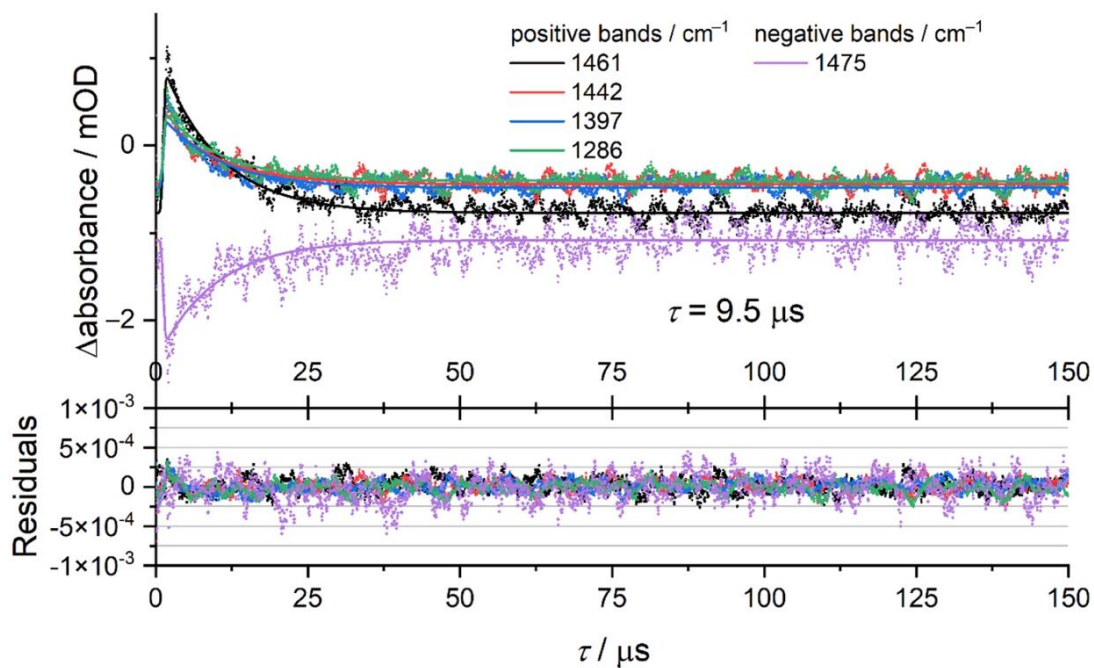


Figure S14. Global monoexponential fit applied to the decay curves of the most intense transient IR signals in the step-scan difference spectrum of *fac*-Cr(ppy)₃ at 20 K.

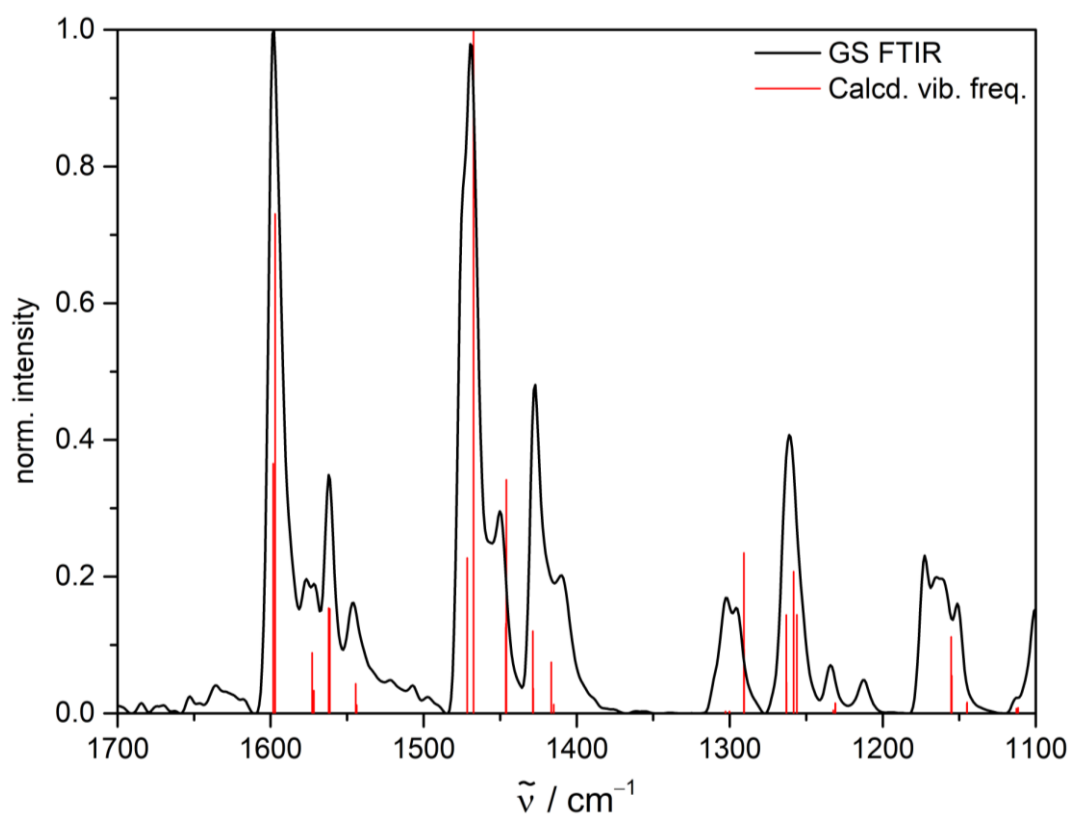


Figure S15. Ground state FTIR spectrum (black) of *fac*-Cr(ppy)₃ in the solid state (KBr matrix) at 20 K with calculated vibrational frequencies (scaled by 0.975) for the optimized ground state geometry of *fac*-Cr(ppy)₃.

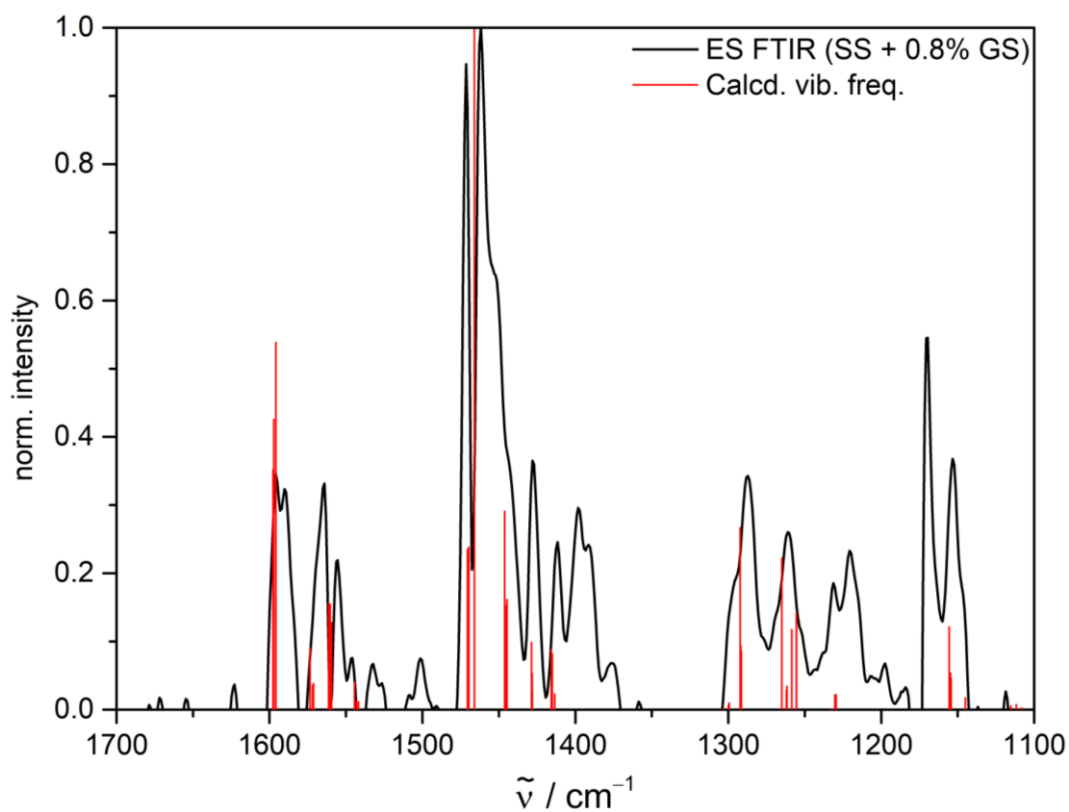


Figure S16. Step-scan difference spectrum (black, $\lambda_{\text{exc}} = 355$ nm) in the solid state (KBr matrix) at 20 K and calculated vibrational frequencies (scaled by 0.975) for the optimized doublet excited state geometry of *fac*-Cr(ppy)₃.

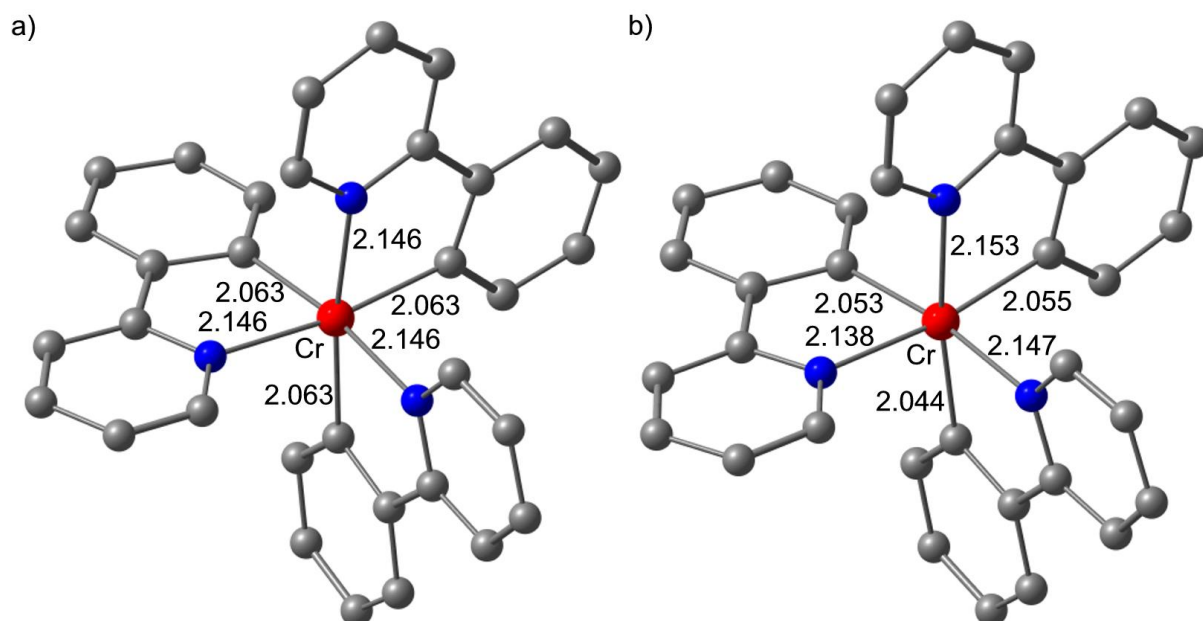


Figure S17. DFT optimized geometries of a) the quartet ground state and b) the lowest doublet state of *fac*-Cr(ppy)₃. The Mulliken spin densities at the chromium ion amount to 3.36 and 1.15, respectively.

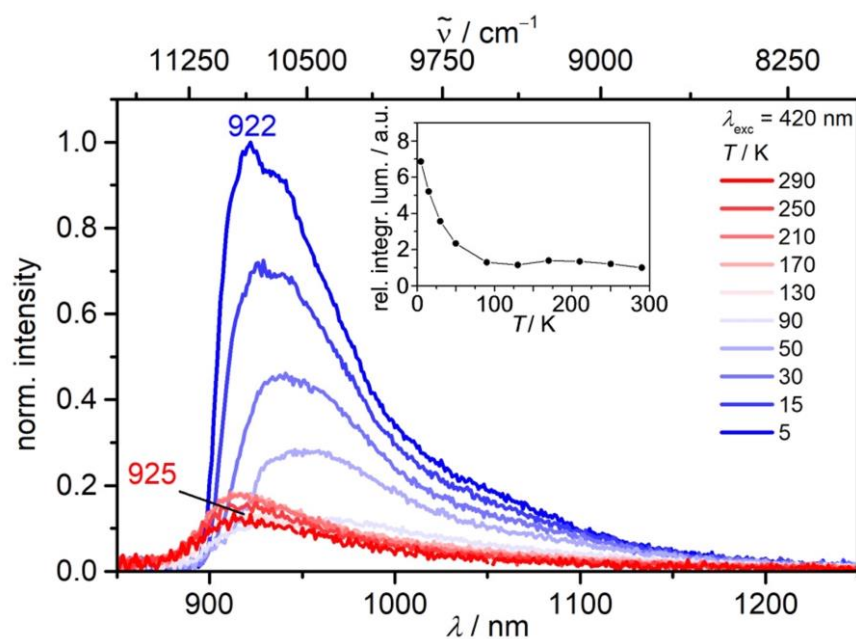


Figure S18. Emission spectra of *fac*-Cr(ppy)₃ in a KBr pellet at 290–5 K after excitation at 420 nm. The inset shows the corresponding relative integrated luminescence intensity vs. temperature plot.

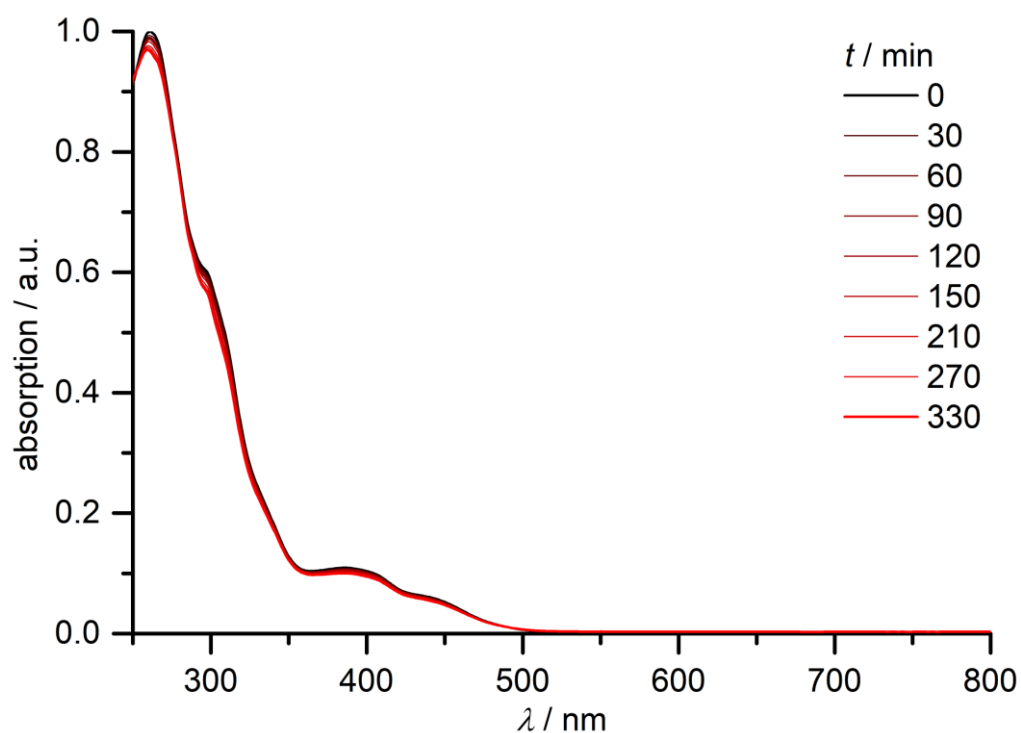


Figure S19. UV/Vis absorption spectra of *fac*-Cr(ppy)₃ in 2-MeTHF (saturated solution, ca. $c = 3.5 \times 10^{-5}$ M) during irradiation at 420 nm over time.

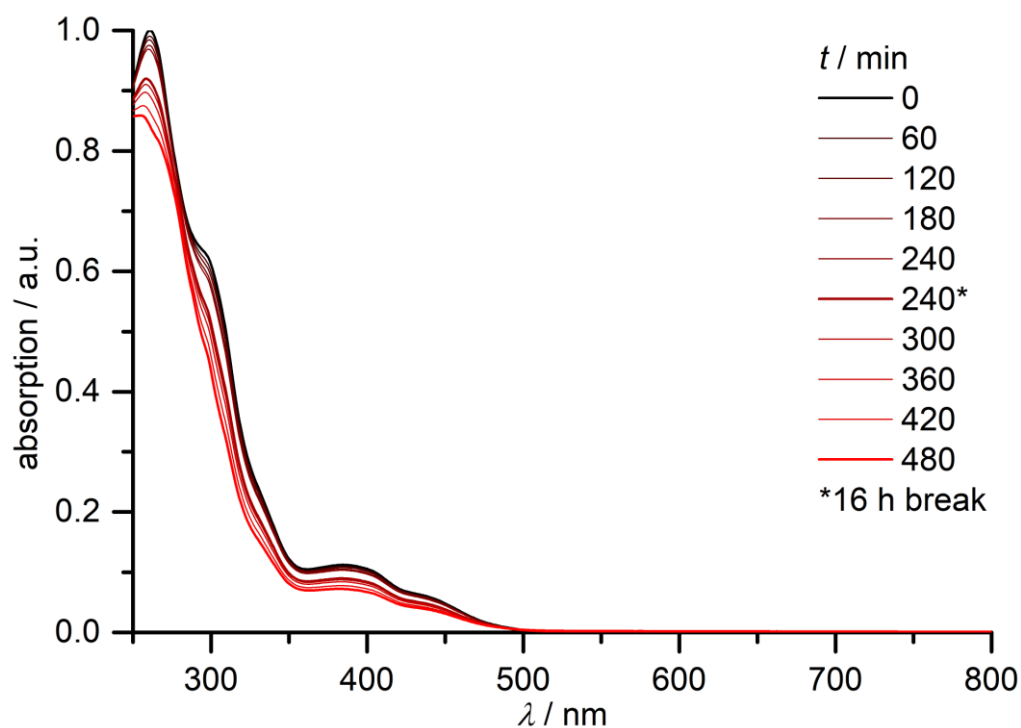


Figure S20. UV/Vis absorption spectra of *fac*-Cr(ppy)₃ in CH₂Cl₂ ($c = 5.3 \times 10^{-5}$ M) during irradiation at 420 nm over time.

Table S5. Cartesian Coordinates of calculated geometries of *fac*-Cr(ppy)₃ (quartet ground state and lowest doublet excited state) (CPCM(acetonitrile)-RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP).

Atom	quartet ground state			doublet excited state		
	X	Y	Z	X	Y	Z
24	-0.036293	-0.035312	-0.036011	-0.043552	-0.048731	-0.038663
7	-0.225446	0.017467	2.100852	-0.221295	0.017408	2.091302
6	-0.002051	0.160851	-2.089426	-0.003819	0.163327	-2.082253
6	-2.088967	0.009198	0.165139	-2.085305	-0.008136	0.167368
7	2.099565	-0.237552	0.011155	2.093836	-0.242996	0.010227
6	0.152484	-2.089344	0.001835	0.14849	-2.083656	-0.008841
7	0.02287	2.100887	-0.230501	0.014385	2.095754	-0.226253
6	1.490023	-2.548348	0.026738	1.48568	-2.550137	0.019689
6	0.788227	-0.001168	2.973209	0.796009	0.00977	2.961543
6	2.977999	0.770878	-0.006785	2.971821	0.766477	-0.004125
6	0.029725	2.54729	-1.509807	0.02987	2.547728	-1.503839
6	-3.074381	0.013221	-0.82821	-3.071853	-0.014363	-0.826083
6	0.029615	1.499881	-2.543593	0.031695	1.502401	-2.538348
6	-1.503664	0.028574	2.550283	-1.49825	0.035394	2.548916
6	-2.539877	0.038025	1.505318	-2.536693	0.031652	1.508012
6	0.01268	2.975704	0.781185	-0.000024	2.96819	0.787848
6	2.541244	-1.518478	0.017669	2.537701	-1.523706	0.017548
6	-0.006996	-0.834717	-3.0726	-0.006856	-0.832898	-3.066237
6	-0.846623	-3.068926	0.005544	-0.854651	-3.061992	-0.012922
6	-1.758683	0.024232	3.925164	-1.747006	0.05054	3.924428
6	0.59915	-0.004898	4.342888	0.612042	0.025262	4.331498
6	4.346501	0.573531	-0.014239	4.340255	0.569864	-0.006284
6	3.914549	-1.78178	0.009397	3.9112	-1.786037	0.015266
6	0.013925	4.344944	0.588893	0.006068	4.338002	0.599541
6	0.03023	3.921575	-1.768036	0.035948	3.922462	-1.758275
6	0.050699	1.810182	-3.910304	0.058559	1.811812	-3.904745
6	0.013124	-0.534962	-4.432763	0.018279	-0.533265	-4.426035
6	-3.905749	0.065113	1.818817	-3.902317	0.057792	1.821536
6	-4.433731	0.039308	-0.525274	-4.430606	0.011155	-0.522322
6	-0.551661	-4.430117	0.027783	-0.563833	-4.423225	0.004507
6	1.7955	-3.916111	0.050084	1.785153	-3.918842	0.039325
6	-4.852206	0.065278	0.804429	-4.848855	0.046802	0.807434
6	-0.706533	0.008563	4.823621	-0.691288	0.046736	4.818832
6	0.02345	4.822558	-0.717959	0.025269	4.820219	-0.705474
6	4.819327	-0.735057	-0.005478	4.814759	-0.738433	0.004501
6	0.775562	-4.856574	0.050129	0.761967	-4.855456	0.030917
6	0.041918	0.793671	-4.854433	0.051143	0.794998	-4.848474
1	-2.775284	0.030776	4.286399	-2.762451	0.063578	4.288907
1	1.781772	-0.012825	2.548945	1.788105	-0.008582	2.534633
1	1.449921	-0.018995	5.008177	1.466063	0.019375	4.9928
1	-0.90101	0.005458	5.887722	-0.88086	0.058865	5.883704
1	2.822003	-4.257985	0.06904	2.810643	-4.263576	0.061223

1	1.012159	-5.912484	0.067928	0.994239	-5.91233	0.045372
1	-1.351781	-5.161228	0.028189	-1.36673	-5.151237	-0.001682
1	-1.886517	-2.763401	-0.011378	-1.893127	-2.75296	-0.032947
1	-2.774947	-0.0066	-1.869818	-2.77267	-0.042438	-1.867446
1	-5.169584	0.03983	-1.321034	-5.166784	0.003287	-1.317711
1	-5.906647	0.085952	1.047269	-5.903307	0.066327	1.050262
1	-4.241677	0.086755	2.847261	-4.237462	0.08646	2.85009
1	-0.029256	-1.875573	-2.770715	-0.032015	-1.873364	-2.764127
1	0.006742	-1.332393	-5.166777	0.012821	-1.331182	-5.159497
1	0.057913	1.034029	-5.909524	0.071248	1.034755	-5.903609
1	0.074354	2.837781	-4.24863	0.085216	2.839476	-4.242658
1	4.269739	-2.800548	0.012265	4.266759	-2.80475	0.01967
1	5.882218	-0.93598	-0.011609	5.877905	-0.93803	0.003012
1	5.016889	1.420302	-0.027577	5.009932	1.417252	-0.016933
1	2.559746	1.767006	-0.014769	2.553004	1.762336	-0.013145
1	0.003883	2.553818	1.775768	-0.016032	2.544335	1.781347
1	0.006641	5.012267	1.438155	-0.004867	5.002456	1.451038
1	0.024154	5.886204	-0.914934	0.030284	5.884493	-0.898926
1	0.033745	4.280438	-2.785499	0.046841	4.283769	-2.774871

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6.4 Supporting Information: Luminescent Cyclometalated Chromium(III) Complexes

Supporting Information

Luminescent Cyclometalated Chromium(III) Complexes

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1. Materials and Methods

General procedures. All reagents were used as received from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer, Sigma-Aldrich and TCI). Acetonitrile and dichloromethane were dried and distilled from calcium hydride; diethyl ether, *n*-hexane, *n*-pentane and toluene were dried over sodium; THF was dried over potassium. All solvents were distilled under argon prior to use. Butyronitrile was dried according to a literature known procedure.¹ 2-MeTHF and DMF were received dry, degassed with argon and stored over molecular sieves. All reactions and measurements were performed under an argon and water-free atmosphere unless otherwise noted. A glovebox (UniLab/MBraun – Ar 4.8, O₂ < 0.1 ppm, H₂O < 0.1 ppm) was used to store and weigh sensitive compounds for synthesis as well as to prepare any measurement samples that required the absence of oxygen and/or water.

LIFDI mass spectra were recorded on a Thermo Fischer DFS mass spectrometer by liquid injection field desorption ionization.

ATR-IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer with an ATR unit containing a diamond crystal (**fac-2**) or a Bruker Alpha II FT-IR spectrometer with a Platinum Di-ATR unit (**fac-1**, covered in nujol).

Electrochemical experiments (cyclic voltammetry) were carried out on a BioLogic SP-200 voltammetric analyzer using platinum wires as counter and working electrodes and 0.01 M Ag/AgNO₃ as the reference electrode. The measurements were carried out at a scan rate of 100 mV s⁻¹ using 0.1 M [ⁿBu₄][PF₆] as supporting electrolyte and 0.001 M of the sample in dry and degassed dimethylformamide. Potentials are referenced relative to the ferrocene/ferrocenium couple.

NMR spectra were recorded on Bruker Avance DSX 400 spectrometers at 400.3 MHz (¹H), 162.1 MHz (solution) and 161.8 MHz (solid) (³¹P{¹H}). All resonances are reported in ppm versus the solvent signal as internal standard [CDCl₃ (¹H: δ = 7.26 ppm)], or H₃PO₄ (³¹P: δ = 0.9 ppm)] as external standard.

Absorption spectra were recorded on a Jasco V770 spectrometer using 1.0 cm quartz cells with a Schott valve to maintain an inert atmosphere. Spin-forbidden absorptions were recorded on a Cary 5000 UV/Vis/NIR spectrophotometer from Agilent using a 10.0 cm quartz cell.

Emission and excitation spectra in solution and powder samples were recorded with an FLS1000 spectrometer from Edinburgh Instruments which is equipped with the cooled photomultiplier detectors PMT-980 and N-G09 PMT-1700, together covering the spectral range between 200 nm and 1700 nm. For excitation in steady-state measurements a xenon arc lamp Xe2 (450 W) was used. Time-resolved luminescence experiments were performed in the multi-channel scaling mode (MCS, FLS1000) employing the VPL450 laser (λ_{exc} = 451.3 nm) from Edinburgh Instruments for μs-timescales. Measurements at low temperature were conducted using a liquid nitrogen cooled cryostat Optistat-DN from Edinburgh Instruments. Samples were prepared in a glovebox using dry degassed solvents and measured in airtight cuvettes.

Crystal Structure Determinations

Intensity data for crystal structure determinations of **fac-1** and **fac-2** 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-Area² software package and were corrected for absorption with MULABS³ of the PLATON software package.⁴ The structures were solved with SHELXT⁵ and refined by the full-matrix method based on F^2 using SHELXL⁶ of the SHELX⁷ software package and the ShelXle⁸ 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- 2306094 (**fac-1**), 2306093 (**fac-2**).

Crystallographic Data of fac-Cr(C^N)₃ (fac-1). C₃₉H₆₀CrN₃ (622.93); orthorhombic; $Pna2_1$; $a = 16.825(3)$ Å, $b = 12.777(3)$ Å, $c = 17.040(3)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$; $V = 3663.0(13)$ Å³; $Z = 4$; density (calculated) 1.129 g/cm³, $T = 120(2)$ K, $\mu = 0.341$ mm⁻¹, $F(000) = 1356$; crystal size 0.570 x 0.210 x 0.020 mm³; $\theta = 2.331$ to 27.993 deg.; $-18 \leq h \leq 22$, $-16 \leq k \leq 14$, $-19 \leq l \leq 22$; rfln collected = 18621; rfln unique = 7774 [$R(\text{int}) = 0.1897$]; completeness to $\theta = 25.242$ deg. = 99.8%; semi empirical absorption correction from equivalents; max. and min. transmission 1.11354 and 0.86056; data 7774; restraints 1, parameters 403; goodness-of-fit on $F^2 = 1.083$, final indices [$I > 2\sigma(I)$] $R_1 = 0.0947$, $wR_2 = 0.1749$; R indices (all data) $R_1 = 0.1901$, $wR_2 = 0.2205$; largest diff. peak and hole 0.527 and -0.544 e Å⁻³.

Crystallographic Data of fac-Cr(C^P)₃ (fac-2). C₅₇H₄₈CrP₃ (877.86); triclinic; $P\bar{1}$; $a = 13.342(3)$ Å, $b = 13.376(3)$ Å, $c = 13.392(3)$ Å, $\alpha = 80^\circ$, $\beta = 79^\circ$, $\gamma = 78^\circ$; $V = 2267.8(9)$ Å³; $Z = 2$; density (calculated) 1.286 g/cm³, $T = 120(2)$ K, $\mu = 0.396$ mm⁻¹, $F(000) = 918$; crystal size 0.500 x 0.400 x 0.240 mm³; $\theta = 2.827$ to 28.035 deg.; $-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-17 \leq l \leq 17$; rfln collected = 70375; rfln unique = 10824 [$R(\text{int}) = 0.0462$]; completeness to $\theta = 25.242$ deg. = 99.8%; semi empirical absorption correction from equivalents; max. and min. transmission 0.88493 and 1.26559; data 10824; restraints 0, parameters 550; goodness-of-fit on $F^2 = 1.177$, final indices [$I > 2\sigma(I)$] $R_1 = 0.0492$, $wR_2 = 0.1232$; R indices (all data) $R_1 = 0.0539$, $wR_2 = 0.126$; largest diff. peak and hole 1.090 and -0.538 e Å⁻³.

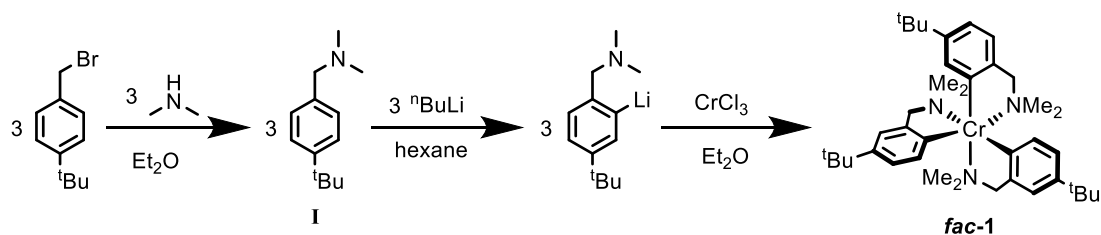
Density functional theory and CASSCF-NEVPT2 calculations were carried out using the ORCA program package 5.0.3.⁹

The **DFT** calculations were performed using the B3LYP functional^{10,11} employing the RIJCOSX approximation.^{12,13} 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.¹⁴ To account for solvent effects, a conductor-like screening model (CPCM) modeling acetonitrile was used in all calculations.^{15,16} Geometry optimizations were performed using Ahlrichs' polarized valence triple- ζ basis set (def2-TZVPP).^{17,18} Atompairwise dispersion correction was performed with the Becke-Johnson damping scheme (D3BJ).^{19,20} 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 assignment of the state characters has been done dividing the molecule into three fragments (metal center, phenyl ligands (Ph) and amine (NMe₂CH₂-) or phosphane ligand (PPh₂CH₂-), respectively) and calculating charge transfer (CT) numbers, as implemented in the TheoDore software package.^{21,22}

The **CASSCF(7,12)-FIC-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 including spin-orbit coupling (SOC-CASSCF)^{23,24} in conjunction with the fully internally contracted N-electron valence perturbation theory to second order (FIC-NEVPT2)^{25,26} in order to recover missing dynamic electron correlation. All electronic states are classified by irreducible representations of the *O* point group, in spite of the lower actual symmetry of the considered complex. In order 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 shell²⁷ were included in these calculations giving an active space of (7,12). 10 quartet and 10 doublet roots were calculated with this active space.

2. Synthetic Procedures

Synthesis of *fac*-Cr(C^N)₃ (*fac*-1) was performed according to literature known procedures.^{28,29}



Crystals of *fac*-1 suitable for single crystal X-ray crystallography were obtained from recrystallization of a hexane solution as orange crystals.

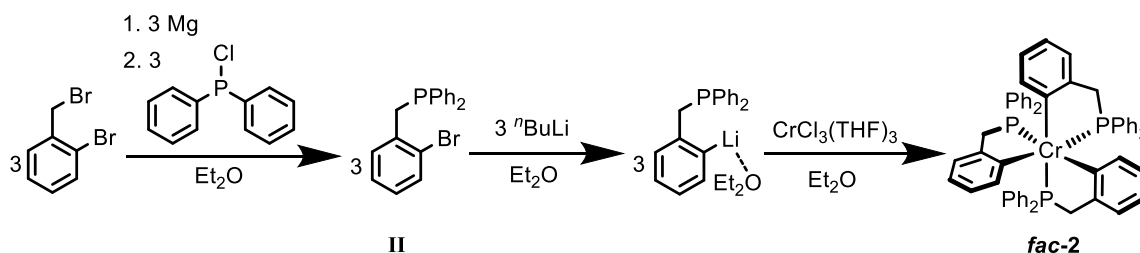
MS (FD): Calcd. for [C₃₉H₆₀CrN₃]⁺: *m/z* (%) = 622.42; found: *m/z* (%) = 622.52 (100).

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 1576 (w), 1359 (m), 1251 (m), 1200 (w), 1169 (w), 1134 (w), 1106 (w), 1016 (m), 990 (s), 974 (m), 902 (w), 844 (vs), 806 (s), 735 (w), 708 (vw), 663 (w), 591 (m), 469 (s), 443 (m), 412 (w).

UV/Vis/NIR (MeCN): λ_{max} / nm (ϵ / M⁻¹ cm⁻¹): 326 (1000), 359 (800), 402 (sh, 330) 470 (350), 720 (1.3), 760 (0.6).

UV/Vis/NIR (THF): λ_{max} / nm (ϵ / M⁻¹ cm⁻¹): 329 (992), 360 (867), 404 (sh, 369), 469 (342).

Synthesis of *fac*-Cr(C^P)₃ (*fac*-2) was performed according to literature known procedures.^{30–32}



Crystals of *fac*-2 suitable for single crystal X-ray crystallography were obtained from ether diffusion into a THF solution of the complex as dark red crystals.

Elemental analysis. calcd. (%) for C₆₁H₅CrOP₃ (949.03): C, 77.20; H, 5.84; found: C, 77.25; H, 5.70.

MS (FD): Calcd. for [C₅₇H₄₈CrP₃]⁺: *m/z* (%) = 877.24; found: *m/z* (%) = 877.94 (100).

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 3030 (w), 2863 (vw), 2371 (vw), 2010 (vw), 1653 (w), 1560 (w), 1482 (m), 1431 (s), 1244 (w), 1096 (m), 1025 (w), 913 (w), 872 (w), 831 (m), 770 (s), 738 (vs), 691 (vs), 617 (w), 583 (w), 505 (vs), 490 (m), 477 (s) 453 (m), 438 (s), 404 (m).

UV/Vis/NIR (THF): λ_{max} / nm (ϵ / M⁻¹ cm⁻¹): 265 (52200), 392 (2750), 488 (420).

UV/Vis/NIR (toluene): λ_{max} / nm (ϵ / M⁻¹ cm⁻¹): 392 (1810), 492 (310), 810 (0.4).

3. FD mass spectra

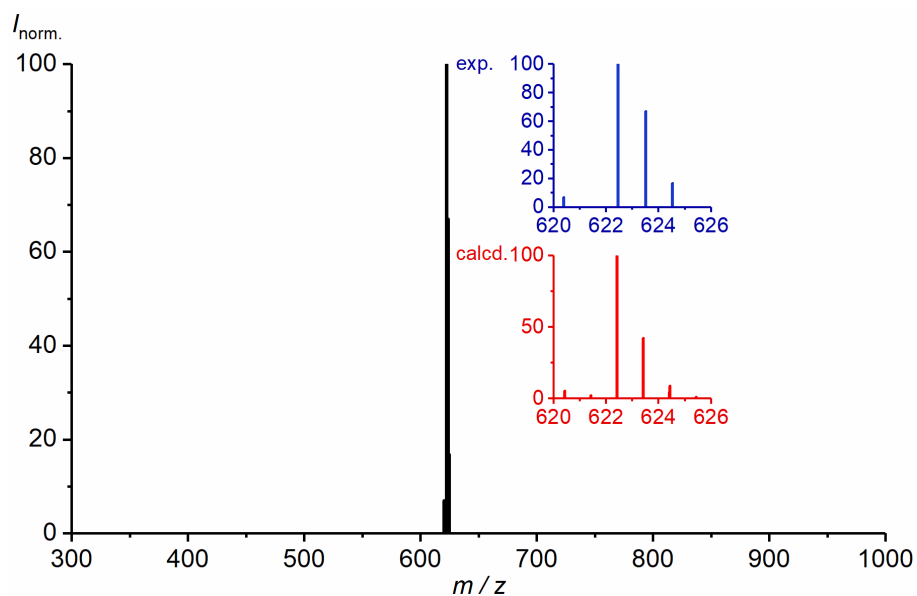


Figure S1 FD-MS spectrum of **fac-1** in THF with comparison of experimental and calculated isotope patterns of the $[M]^+$ peak.

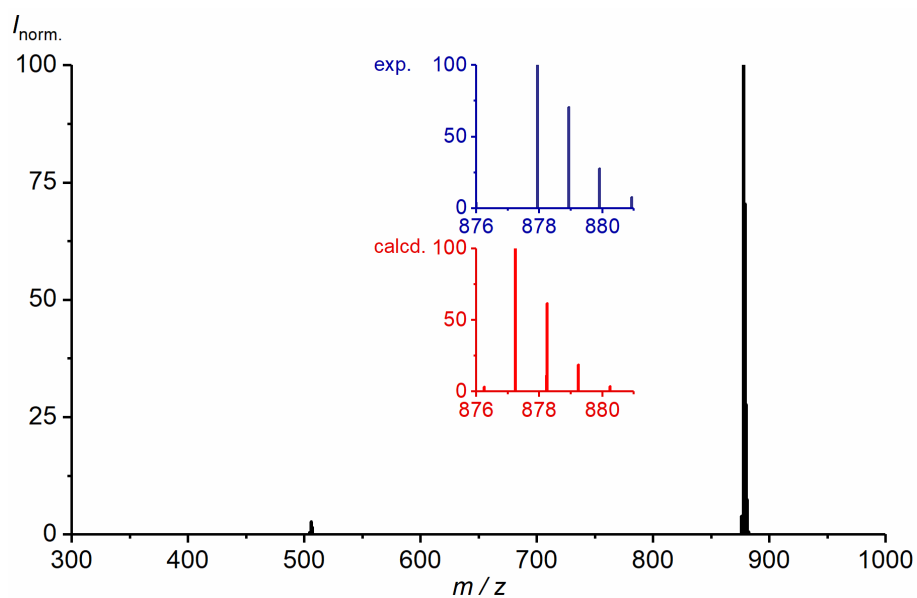


Figure S2 FD-MS spectrum of **fac-2** in THF with comparison of experimental and calculated isotope patterns of the $[M]^+$ peak.

4. IR spectra

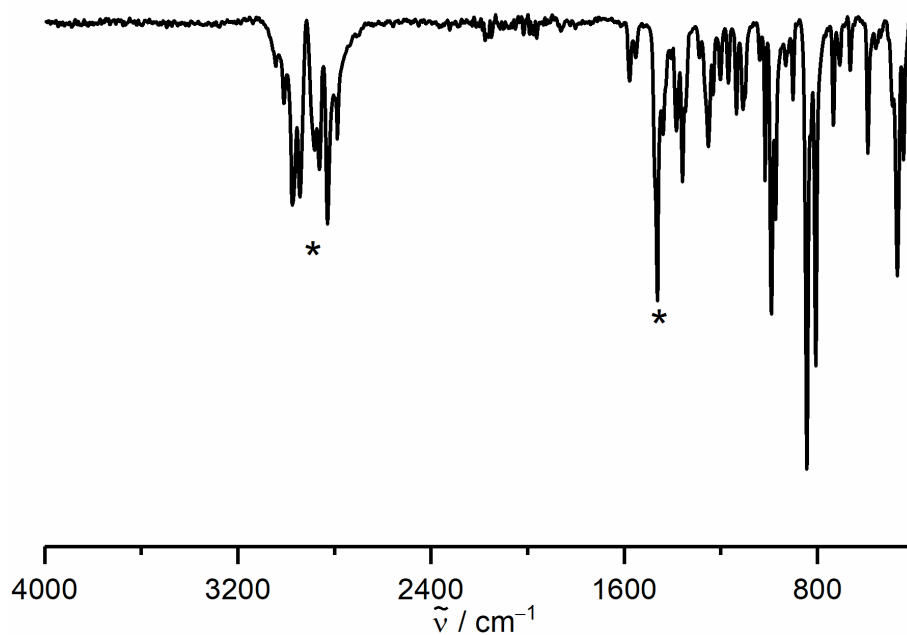


Figure S3 ATR-IR spectrum of *fac-1* in nujol. *From nujol.

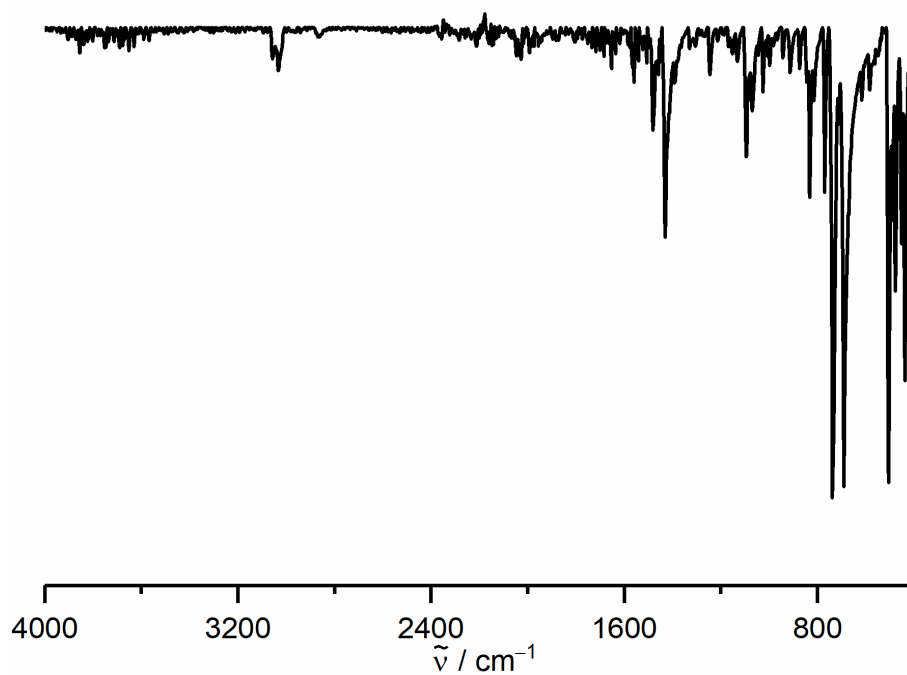


Figure S4 ATR-IR spectrum of *fac-2*.

5. Cyclic voltammetry

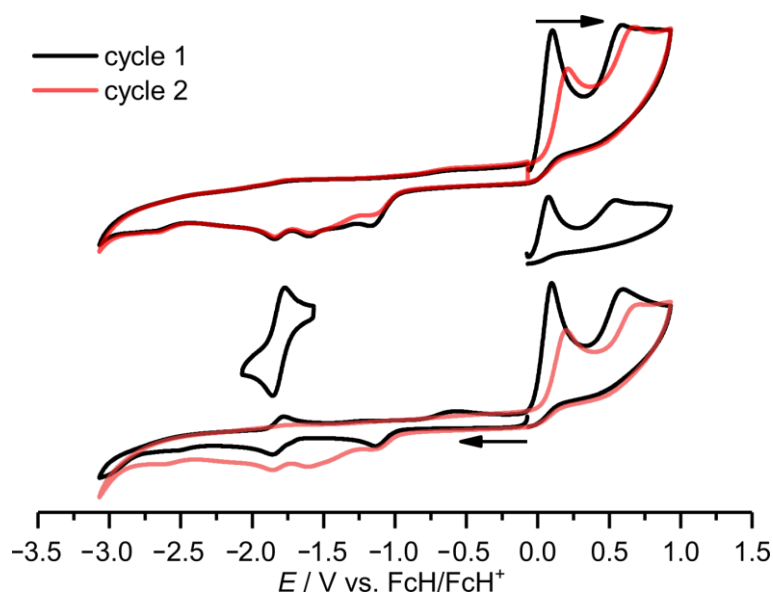


Figure S5 Cyclic voltammograms of **fac-1** in DMF/[$n\text{Bu}_4\text{N}$][PF_6]; E vs. ferrocene.

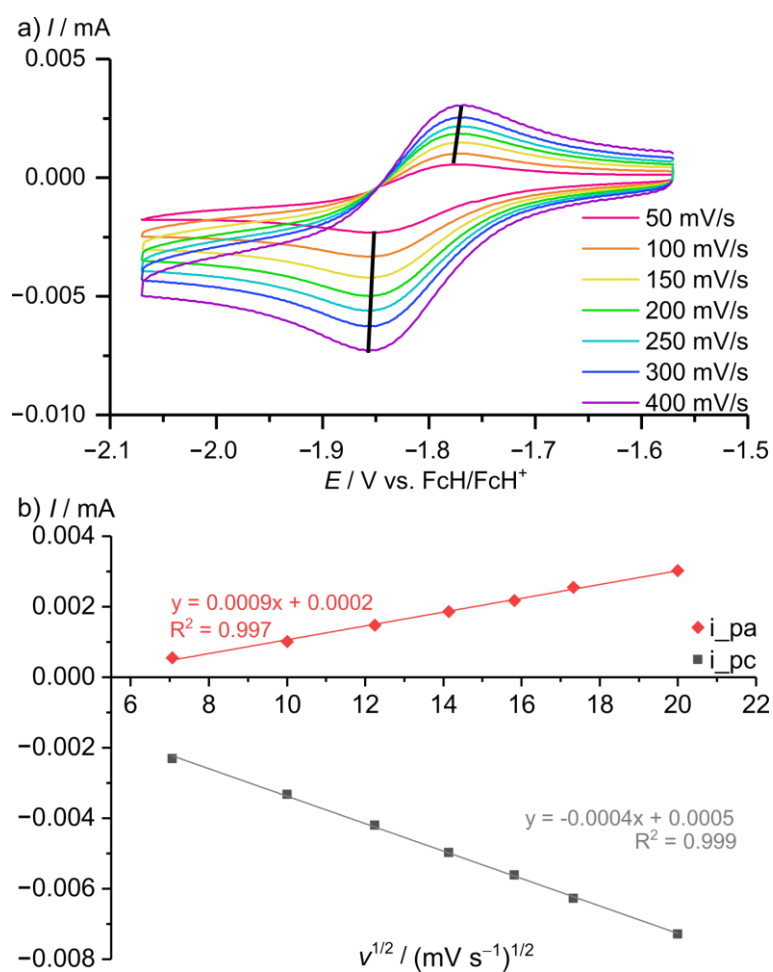


Figure S6 a) Cyclic voltammograms of the $\text{Cr}^{\text{III/II}}$ wave of **fac-1** in DMF/[$n\text{Bu}_4\text{N}$][PF_6]; E vs. ferrocene, at different scan rates. b) Cathodic and anodic peak currents at different scan rates, plotted vs. square root of the corresponding scan rate. Linear fit of the data points indicated.

→ $E_{1/2}$ (vs. FcH/FcH^+) = -1.81 V ; $\Delta E_{1/2} = 81 \text{ mV}$ ($\Delta E_{1/2}(\text{Fc}) = 78 \text{ mV}$)

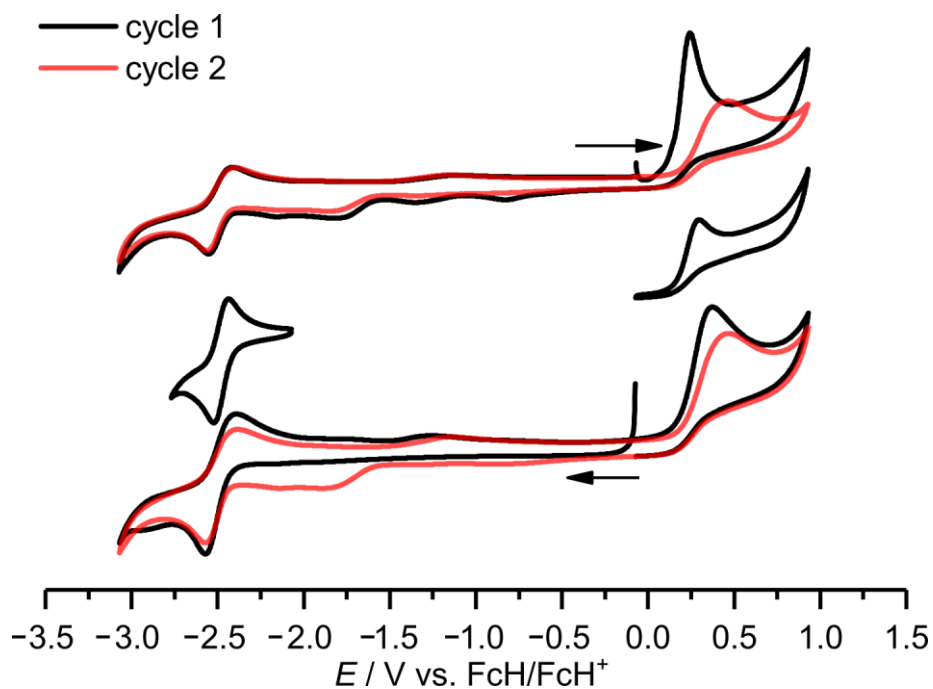


Figure S7 Cyclic voltammograms of **fac-2** in DMF/[ⁿBu₄N][PF₆]; *E* vs. ferrocene.

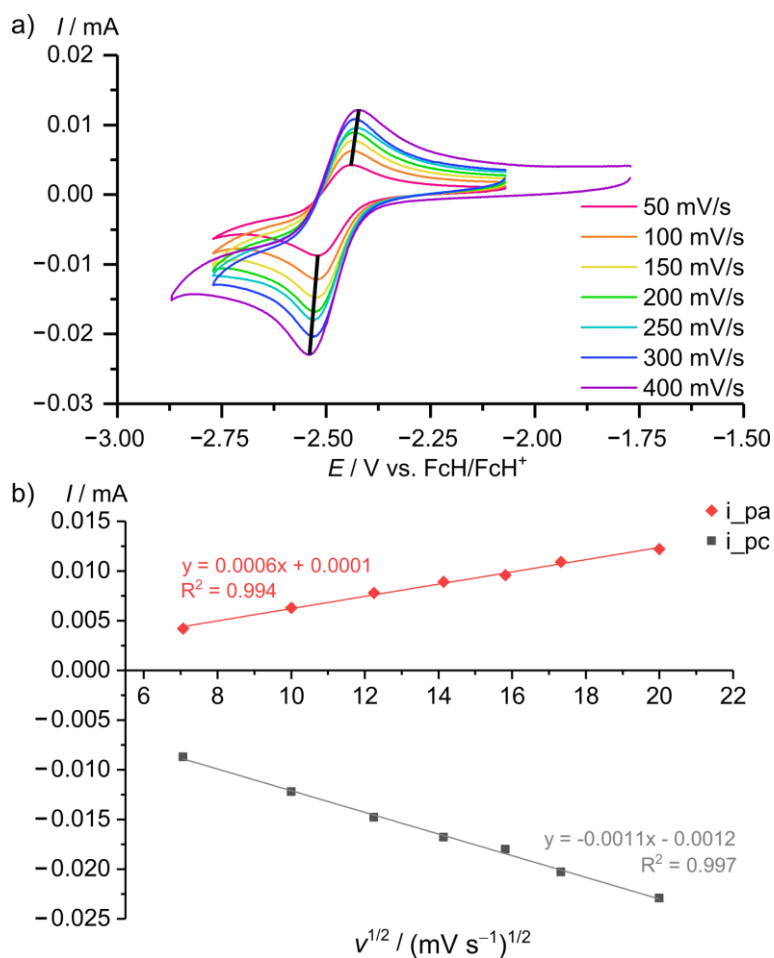
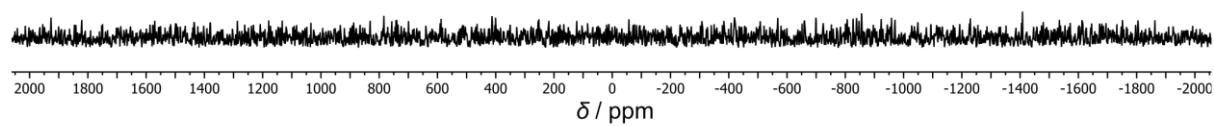


Figure S8 a) Cyclic voltammograms of the Cr^{III/II} wave of **fac-2** in DMF/[ⁿBu₄N][PF₆]; *E* vs. ferrocene, at different scan rates. b) Cathodic and anodic peak currents at different scan rates, plotted vs. square root of the corresponding scan rate. Linear fit of the data points indicated.

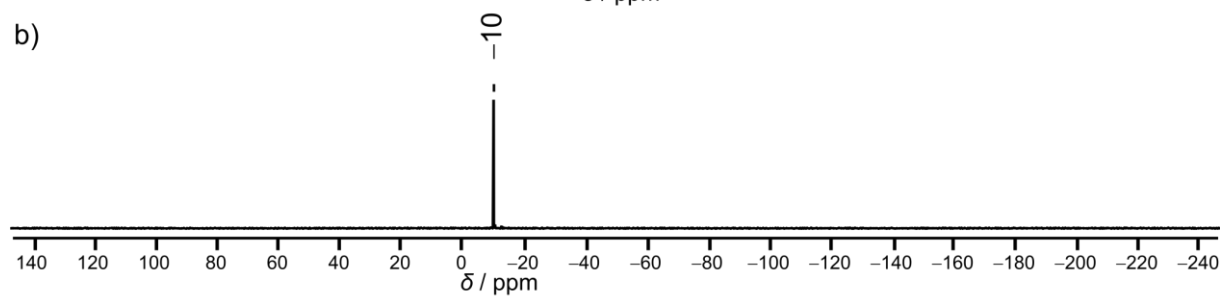
➔ $E_{1/2}$ (vs. FcH/FcH⁺) = -2.42 V; $\Delta E_{1/2}$ = 83 mV

6. NMR spectra

a)



b)



c)

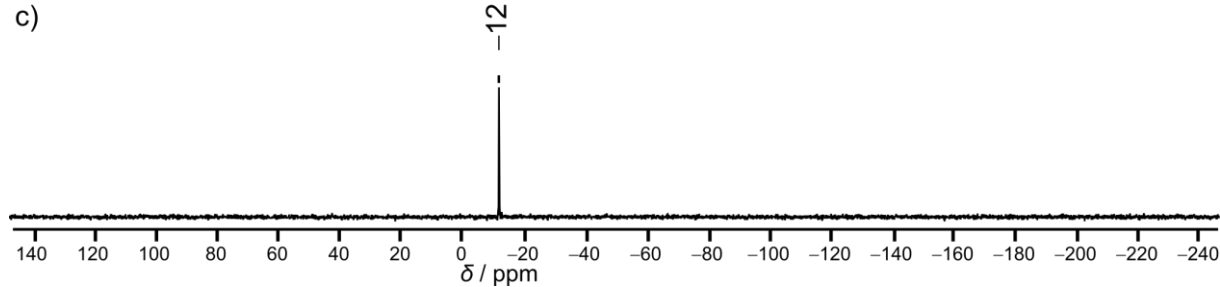


Figure S9 a) $^{31}\text{P}\{^1\text{H}\}$ MAS-NMR spectrum *fac-2* in the solid state. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra *fac-2/trans-2'* in b) toluene-d_8 and c) THF-d_8 .

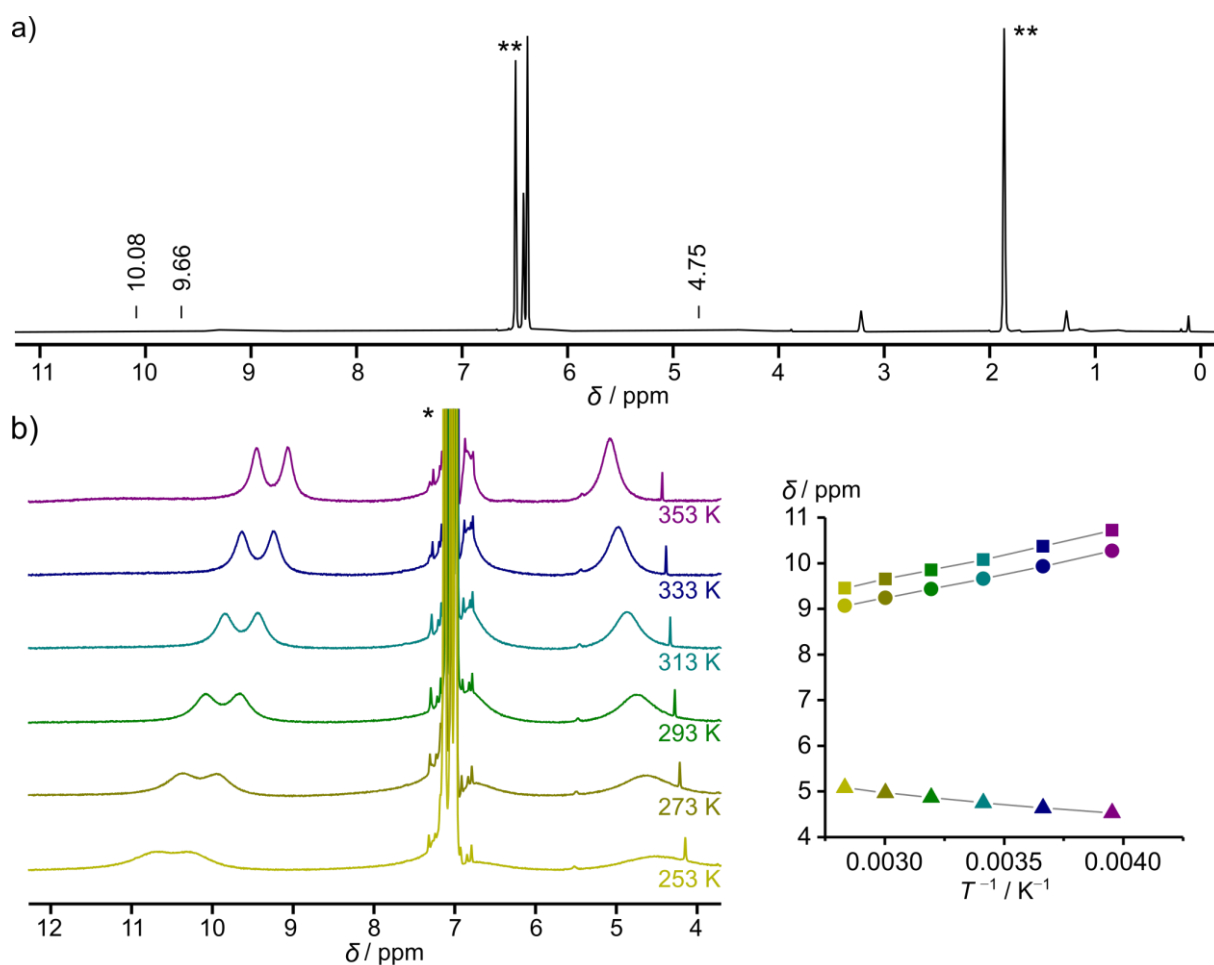


Figure S10-1 ^1H NMR spectra of *fac-2/trans-2'* in toluene- d_8 at a) 293 K (**residual toluene- d_7), b) at variable temperatures and a chemical shift vs. reciprocal temperature plot. The relative integral between 9 and 12 ppm increases with T as follows: 5.61 (253 K), 6.62 (273 K), 6.79 (293 K), 7.68 (313 K), 7.86 (333 K), 8.00 (353 K) relative to the integral of the resonance at 0.2 ppm.

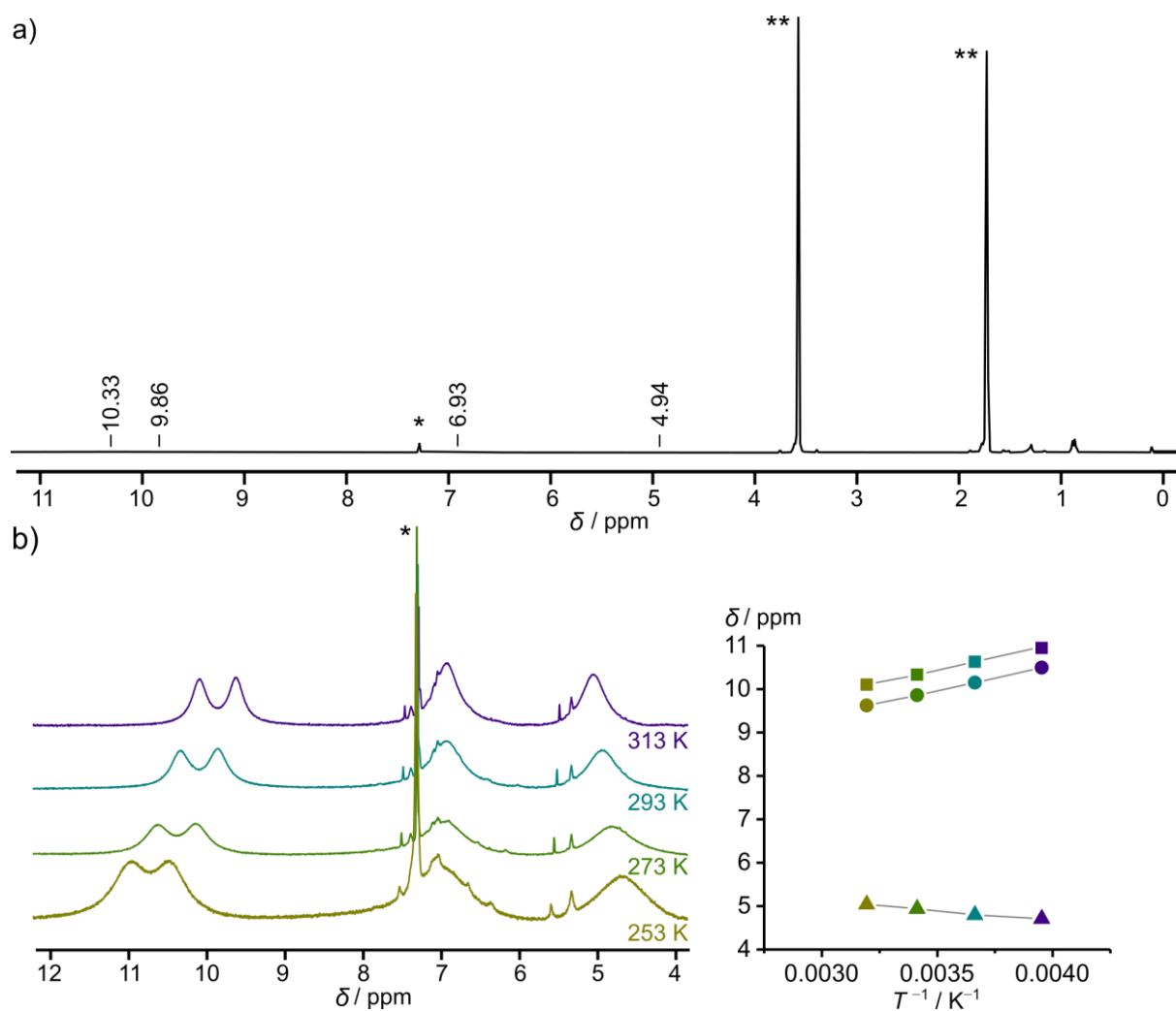


Figure S10-2 ^1H NMR spectra of *fac-2/trans-2'* in THF-d_8 at a) 293 K (**residual THF-d_7 , *benzene.) and b) at variable temperatures and a chemical shift vs. reciprocal temperature plot.

7. Structural and computational data

Table S1 Bond lengths [Å] and angles [deg] of **fac-1**, **fac-2**, *fac*-Cr(ppy)₃ and [Cr(bpy)₃][PF₆]₃ from XRD measurements. Intraligand and interligand angles highlighted in orange and green, respectively.

	<i>fac</i> -Cr(C [^] N) ₃ (X = N)	<i>fac</i> -Cr(C [^] P) ₃ (X = P)	<i>fac</i> -Cr(ppy) ₃ (X = N) ³³		[Cr(bpy) ₃] ^{3+ 34}
Cr–X1	2.336(1)	2.573(1)	2.145(2)	Cr–N1	2.042(5)
Cr–X2	2.389(9)	2.574(1)	2.149(2)	Cr–N2	2.042(5)
Cr–X3	2.349(9)	2.588(1)	2.140(2)	Cr–N3	2.042(5)
Cr–C1	2.043(1)	2.108(2)	2.059(2)	Cr–N4	2.042(5)
Cr–C2	2.083(1)	2.107(2)	2.061(2)	Cr–N5	2.042(5)
Cr–C3	2.054(1)	2.110(2)	2.058(2)	Cr–N6	2.042(5)
X1–Cr–X2	96.1(3)	97.95(2)	92.86(6)	N1–Cr–N2	94.6(2)
X1–Cr–X3	95.6(3)	97.37(2)	94.50(6)	N1–Cr–N3	94.6(2)
X1–Cr–C1	170.1(4)	172.46(7)	171.25(7)	N1–Cr–N4	171.0(2)
X1–Cr–C2	78.2(4)	78.26(7)	79.26(7)	N1–Cr–N5	79.1(2)
X1–Cr–C3	92.4(4)	90.85(7)	93.60(7)	N1–Cr–N6	92.3(2)
X2–Cr–X3	95.2(3)	95.46(2)	90.39(6)	N2–Cr–N3	94.6(2)
X2–Cr–C1	91.8(3)	88.44(7)	93.05(7)	N2–Cr–N4	92.3(2)
X2–Cr–C2	169.9(4)	173.09(7)	167.52(7)	N2–Cr–N5	171.0(2)
X2–Cr–C3	77.3(3)	78.31(7)	79.28(7)	N2–Cr–N6	79.1(2)
X3–Cr–C1	77.6(3)	77.95(7)	79.03(7)	N3–Cr–N4	79.1(2)
X3–Cr–C2	93.6(3)	90.79(7)	99.81(7)	N3–Cr–N5	92.3(2)
X3–Cr–C3	169.6(3)	170.34(7)	167.17(7)	N3–Cr–N6	171.0(2)
C1–Cr–C2	94.8(4)	95.77(9)	95.93(8)	N4–Cr–N5	94.6(2)
C1–Cr–C3	95.2(4)	94.38(9)	93.83(7)	N4–Cr–N6	94.6(2)
C2–Cr–C3	94.5(4)	95.86(9)	91.47(8)	N5–Cr–N6	94.6(2)

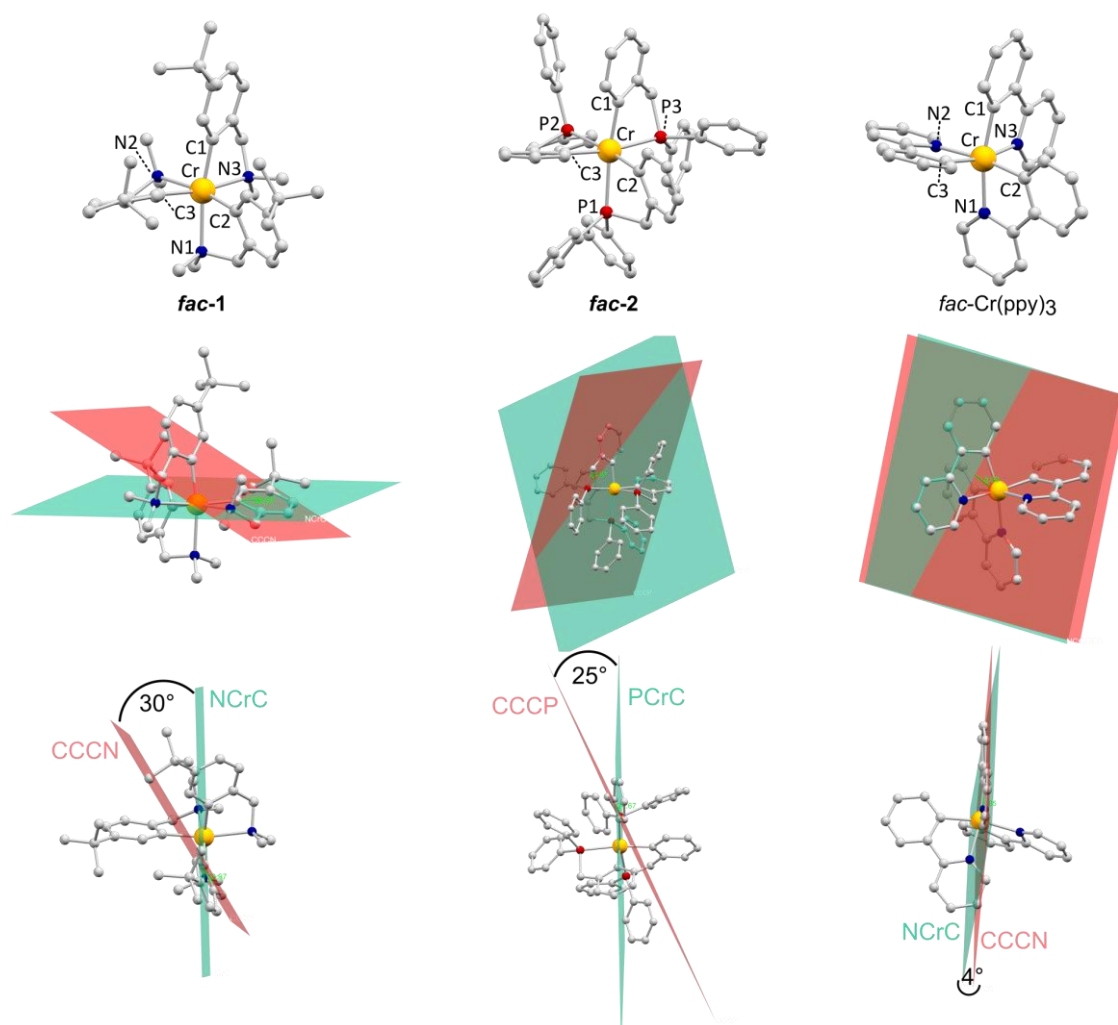


Figure S11 Molecular structures of *fac-1*, *fac-2* and *fac-Cr(ppy)₃* with atom numbering used in Tables S1 and S2. Planes between C-Cr-X and C-C-C-X bonds indicated in green and red. Hydrogen atoms omitted for clarity.

Table S2 Bond lengths [Å] and angles [deg] of *fac-1*, *fac-2*, *fac*-Cr(ppy)₃ and [Cr(bpy)₃]³⁺ from DFT calculations. Intraligand and interligand angles highlighted in orange and green, respectively.*

	<i>fac-1</i> (X = N _{NMe2})		<i>fac-2</i> (X = P _{PPh2})		<i>fac</i> -Cr(ppy) ₃ (X = N)			[Cr(bpy) ₃] ³⁺
	quartet ground state	lowest doublet state	quartet ground state	lowest doublet state	quartet ground state	lowest doublet state		quartet ground state
Cr1–X1	2.387	2.388	2.527	2.514	2.147	2.139	Cr1–N1	2.057
Cr1–X2	2.415	2.409	2.546	2.530	2.147	2.148	Cr1–N2	2.054
Cr1–X3	2.426	2.423	2.573	2.566	2.147	2.155	Cr1–N3	2.055
Cr1–C1	2.061	2.047	2.102	2.087	2.062	2.053	Cr1–N4	2.053
Cr1–C2	2.071	2.059	2.113	2.099	2.062	2.051	Cr1–N5	2.056
Cr1–C3	2.063	2.045	2.116	2.103	2.062	2.043	Cr1–N6	2.051
X1–Cr–X2	99.6	99.5	98.5	98.6	94.0	93.7	N1–Cr–N2	94.45
X1–Cr–X3	100.3	99.9	99.0	98.4	94.0	93.4	N1–Cr–N3	96.50
X1–Cr–C1	169.5	169.3	172.3	172.6	172.1	171.5	N1–Cr–N4	173.8
X1–Cr–C2	77.6	77.8	78.7	78.9	79.3	79.4	N1–Cr–N5	79.6
X1–Cr–C3	88.8	88.9	84.7	84.3	90.7	91.3	N1–Cr–N6	90.0
X2–Cr–X3	95.5	95.1	99.0	98.9	94.0	93.8	N2–Cr–N3	95.4
X2–Cr–C1	90.9	91.1	89.1	88.7	90.7	90.6	N2–Cr–N4	90.7
X2–Cr–C2	168.8	168.9	171.5	172.0	172.1	172.0	N2–Cr–N5	172.7
X2–Cr–C3	77.3	77.7	77.8	77.9	79.3	79.4	N2–Cr–N6	79.7
X3–Cr–C1	77.6	77.5	79.1	79.0	79.3	79.0	N3–Cr–N4	79.5
X3–Cr–C2	95.8	95.9	89.4	89.0	90.7	90.8	N3–Cr–N5	89.6
X3–Cr–C3	169.3	169.4	175.5	176.1	172.1	172.0	N3–Cr–N6	172.2
C1–Cr–C2	92.3	92.1	93.8	94.1	96.4	96.8	N4–Cr–N5	95.5
C1–Cr–C3	94.4	94.7	97.6	98.7	96.4	96.7	N4–Cr–N6	94.4
C2–Cr–C3	91.7	91.5	93.9	94.3	96.4	96.5	N5–Cr–N6	95.9

*Level of theory: (CPCM(solvent) RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP) with THF for *fac-1*, *fac-2* and *fac*-Cr(ppy)₃; MeCN for [Cr(bpy)₃]³⁺.

Table S3 Shape parameters for octahedron S(OC-6) and trigonal prism S(TPR-6) of *fac-1*, *fac-2*, *fac*-Cr(ppy)₃ and [Cr(bpy)₃]³⁺ from DFT calculated geometries and from XRD data.

	<i>fac-1</i>		<i>fac-2</i>		<i>fac</i> -Cr(ppy) ₃		[Cr(bpy) ₃] ³⁺	
	DFT	XRD	DFT	XRD	DFT	XRD ³³	DFT	XRD ³⁴
S(OC-6)	2.01	1.56	2.02	1.93	0.88	1.17	0.83	0.93
S(TPR-6)	14.38	13.74	15.35	15.66	14.58	11.92	14.78	13.68

Table S4 Mulliken spin densities at the chromium ion from DFT calculations (CPCM(THF) RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP).

$^4[\text{fac-1}]$	$^2[\text{fac-1}]$	$^3[\text{fac-1}]^-$	$^5[\text{fac-1}]^-$	$^3[\text{fac-1}]^+$
3.48	1.23	2.79	4.25	2.67
$^4[\text{fac-2}]$	$^2[\text{fac-2}]$	$^3[\text{fac-2}]^-$	$^5[\text{fac-2}]^-$	$^3[\text{fac-2}]^+$
3.50	1.17	2.67	3.90	2.76
$^4[\text{trans-2}']$	$^2[\text{trans-2}']$			
3.50	1.13			

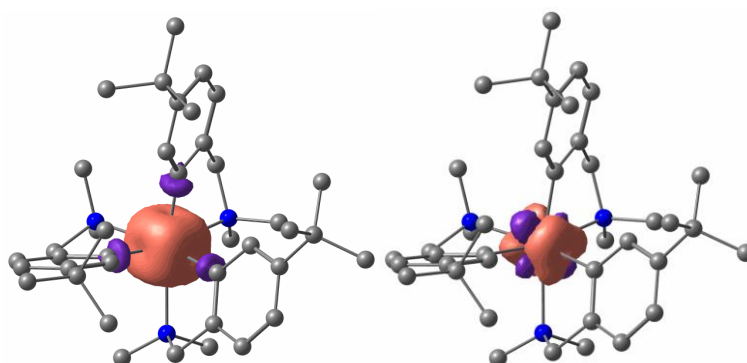


Figure S12 DFT optimized geometries and spin densities (isosurface value = 0.01 a.u.) of **fac-1** in the quartet ground (left) and doublet excited state (right). The Mulliken spin density at the chromium ion amounts to 3.48 and 1.23, respectively in **fac-1**. Hydrogens omitted for clarity.

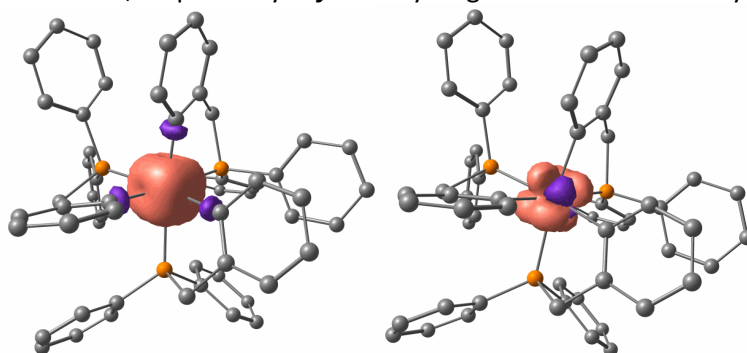


Figure S13 DFT optimized geometries and spin densities (isosurface value = 0.01 a.u.) of **fac-2** in the quartet ground (left) and doublet excited state (right). The Mulliken spin density at the chromium ion amounts to 3.50 and 1.17, respectively in **fac-2**. Hydrogens omitted for clarity.

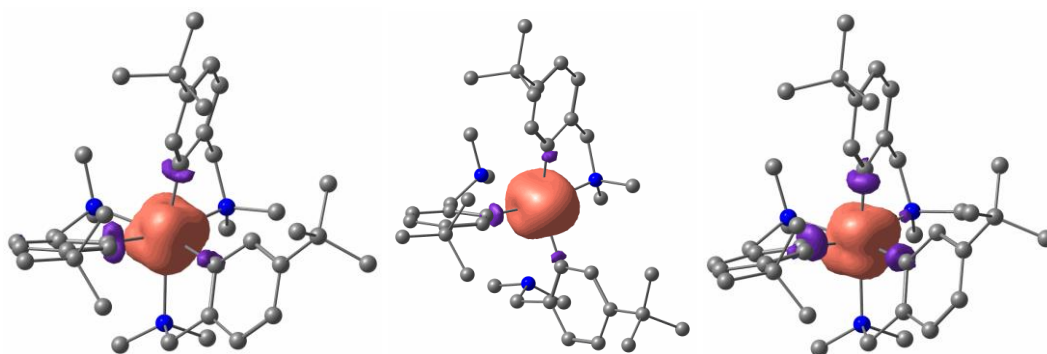


Figure S14 DFT optimized geometries and spin densities (isosurface value = 0.01 a.u.) of **[fac-1]^{•−}** (left: triplet, center: quintet) and **[fac-1]^{•+}** (right). The Mulliken spin density at the chromium ion amounts to 2.79 (triplet) / 4.25 (quintet) and 2.67 (triplet), respectively. Hydrogens omitted for clarity.

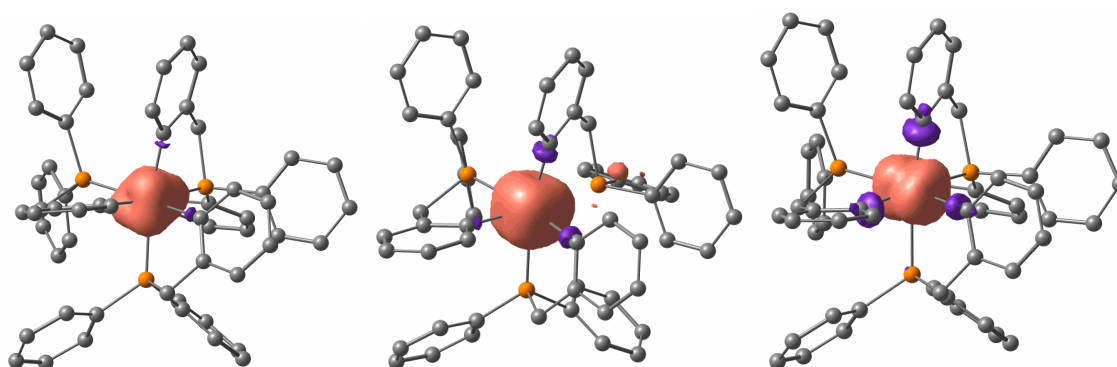


Figure S15 DFT optimized geometries and spin densities (isosurface value = 0.01 a.u.) of **[fac-2]^{•−}** (left: triplet, center: quintet) and **[fac-2]^{•+}** (right). The Mulliken spin density at the chromium ion amounts to 2.67 (triplet) / 3.90 (quintet) and 2.76 (triplet), respectively. Hydrogens omitted for clarity.

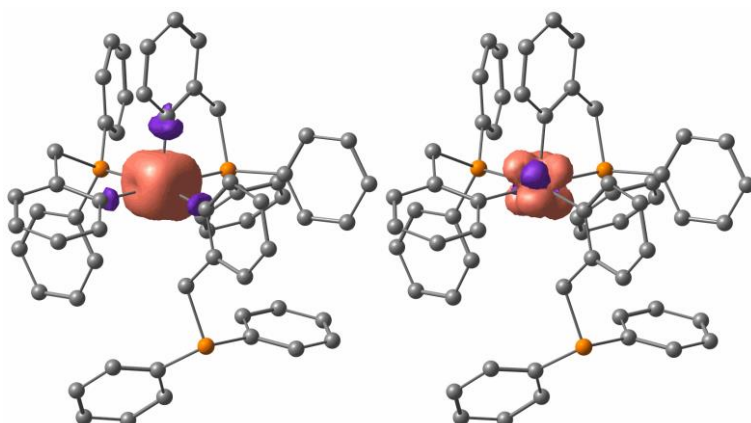


Figure S16 DFT optimized geometries and spin densities (isosurface value = 0.01 a.u.) of **trans-2'** in the quartet ground (left) and doublet excited state (right). The Mulliken spin density at the chromium ion amounts to 3.50 and 1.13, respectively. Hydrogens omitted for clarity.

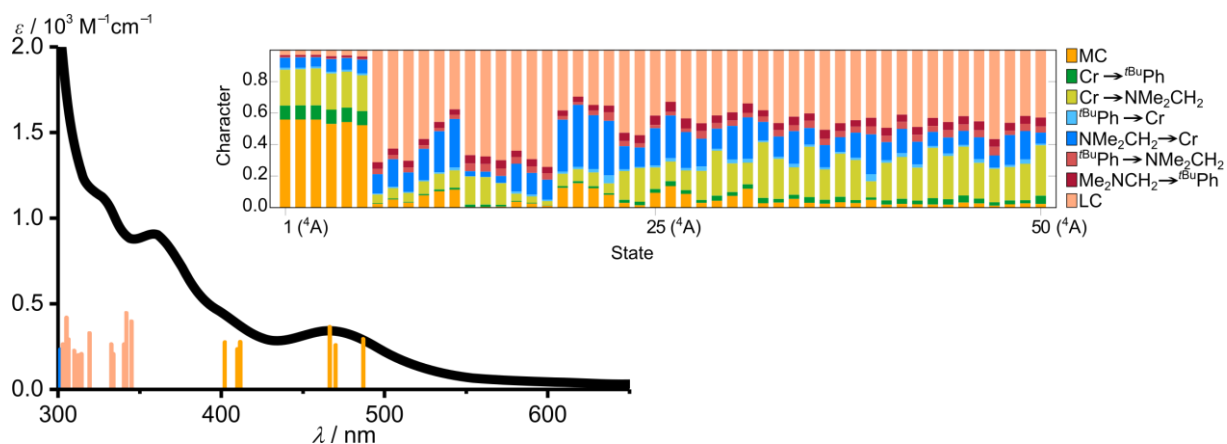


Figure S17 TD-DFT-UKS charge transfer numbers of *fac-1* defined from 0 to 1 of the lowest-lying 50 quartet states using the TheoDore software package.^{21,22} Calculated transitions were shifted by 2400 cm⁻¹ to lower energy to fit the experimental spectrum.

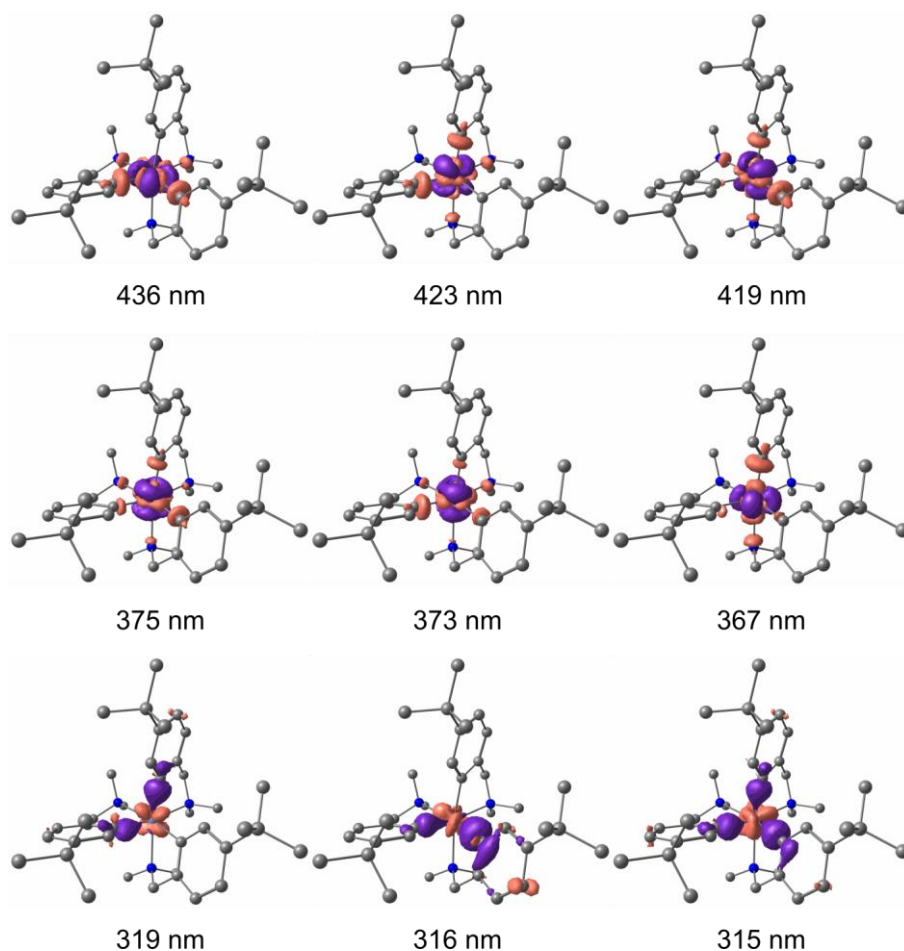


Figure S18 Selected difference electron densities of TD-DFT calculated electronic transitions of *fac-1* (CPCM(THF) RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP), orange: gain, purple: loss; isosurface value = 0.005 a.u.).

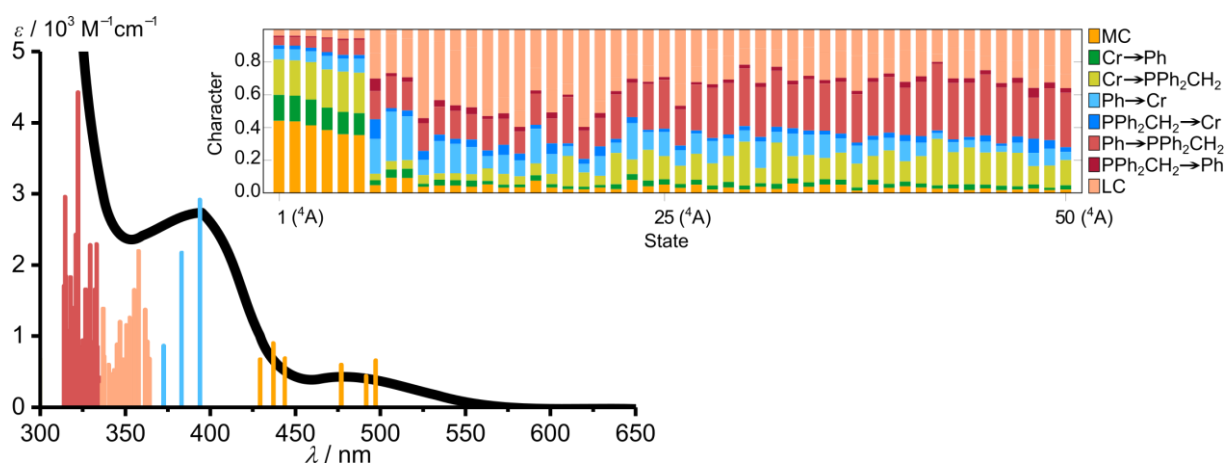


Figure S19 TD-DFT-UKS charge transfer numbers of **fac-2** defined from 0 to 1 of the lowest-lying 50 quartet states using the TheoDore software package.^{21,22} Calculated transitions were shifted by 2600 cm⁻¹ to lower energy to fit the experimental spectrum.

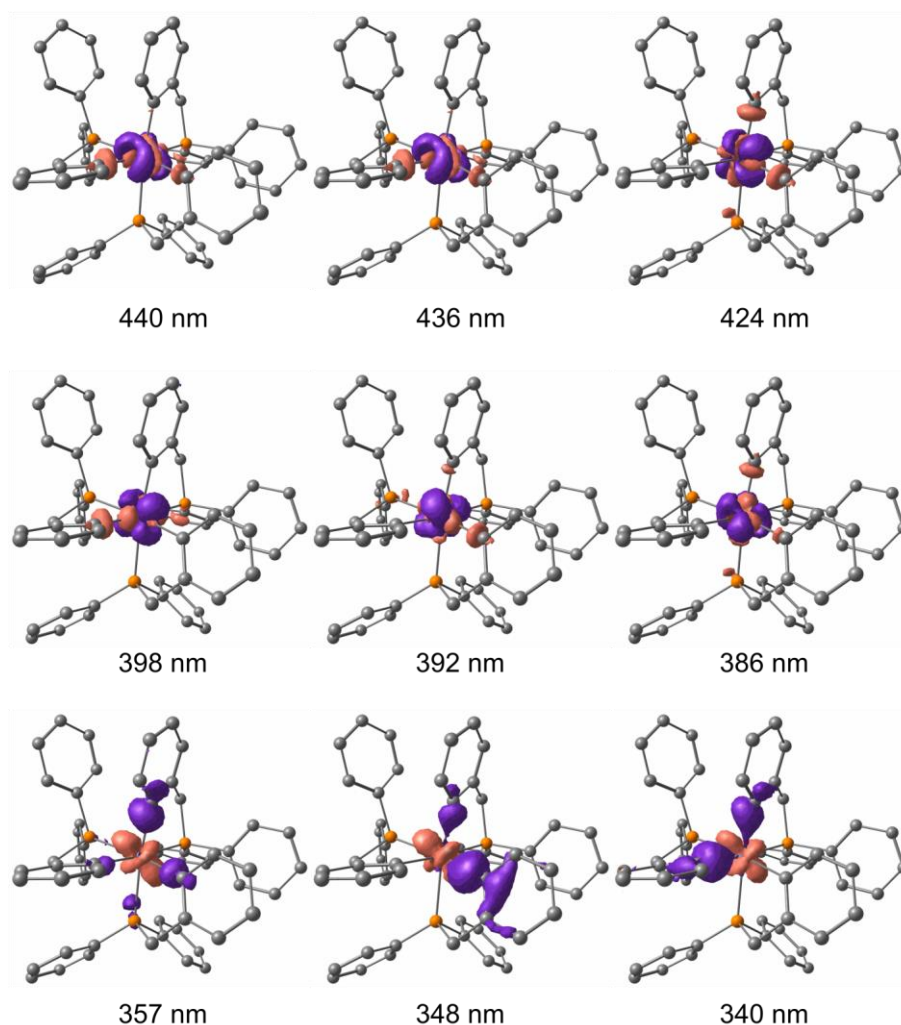


Figure S20 Selected difference electron densities of TD-DFT calculated electronic transitions of **fac-2** (CPCM(THF) RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP), orange: gain, purple: loss; isosurface value = 0.005 a.u.).

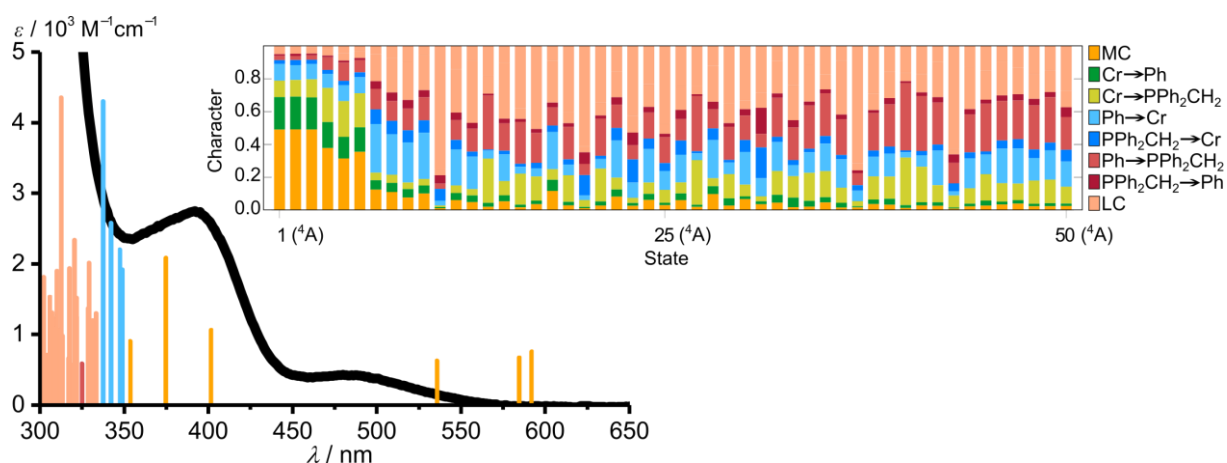


Figure S21 Absorption spectrum of *fac-2* in THF and TD-DFT-UKS charge transfer numbers of *trans-2'* defined from 0 to 1 of the lowest-lying 50 quartet states using the TheoDore software package.^{21,22}

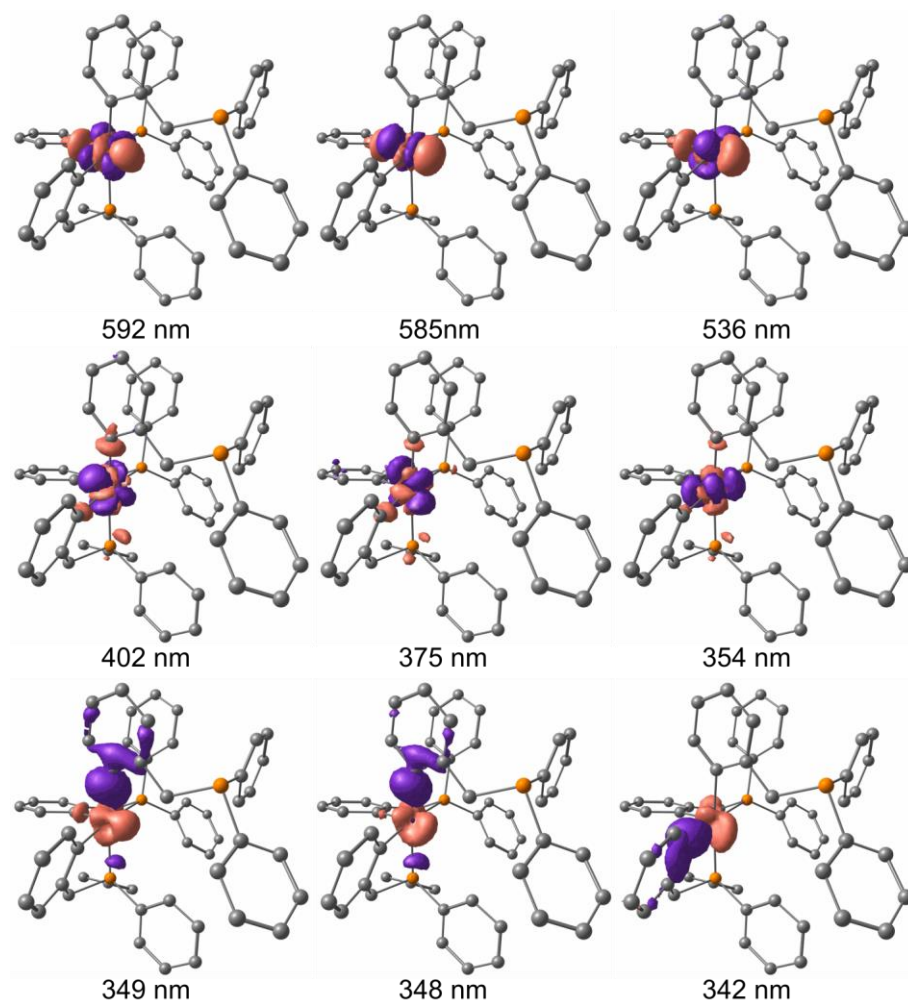


Figure S22 Selected difference electron densities of TD-DFT calculated electronic transitions of *trans-2'* (CPCM(THF) RIJCOSX B3LYP D3BJ ZORA-Def2-TZVPP), orange: gain, purple: loss; isosurface value = 0.005 a.u.).

Table S5 Energies of the orbitals used in the active space of the CASSCF(7,12)-FIC-NEVPT2 calculation of *fac-1*, depicted at a contour value of 0.03 a.u. (hydrogen atoms omitted for clarity).

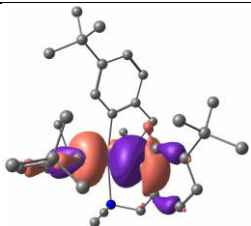
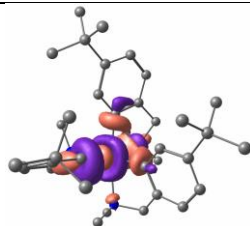
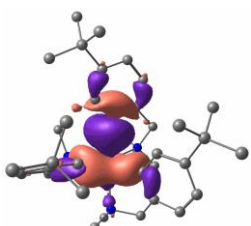
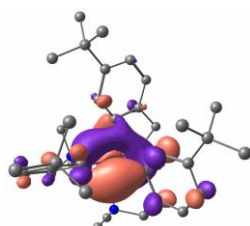
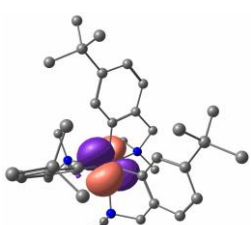
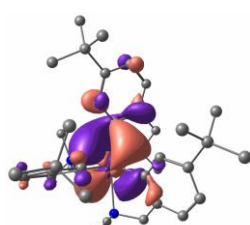
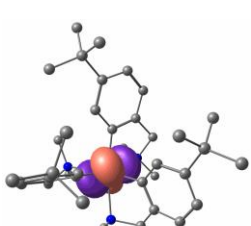
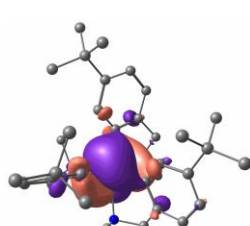
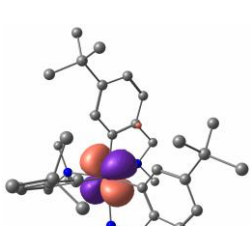
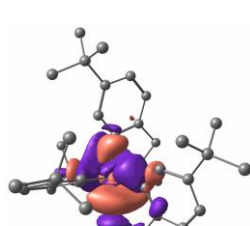
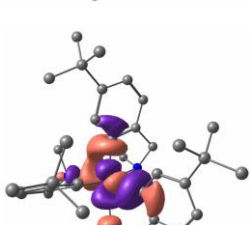
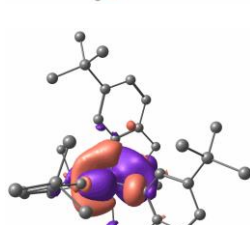
#	E / H	orbital	#	E / H	orbital
166	-0.354397		172	+0.23714	
167	-0.349236		173	+0.675952	
168	-0.038437		174	+0.752117	
169	-0.032671		175	+0.850552	
170	-0.015902		176	+0.884591	
171	+0.213092		177	+0.903333	

Table S6 Energies of the orbitals used in the active space of the CASSCF(7,12)-FIC-NEVPT2 calculation of *fac-2*, depicted at a contour value of 0.03 a.u. (hydrogen atoms omitted for clarity).

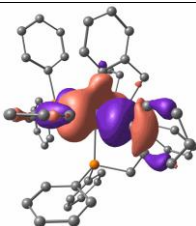
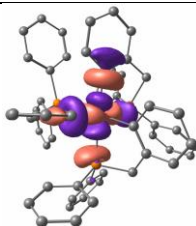
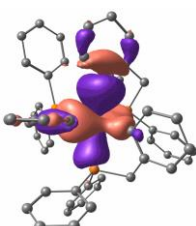
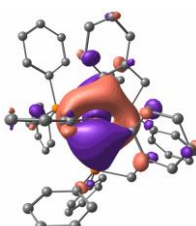
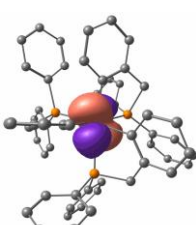
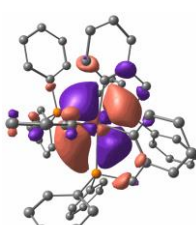
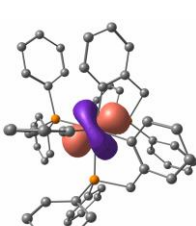
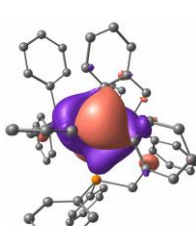
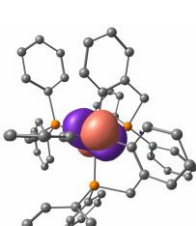
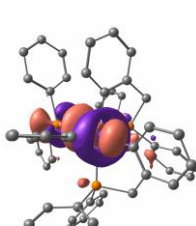
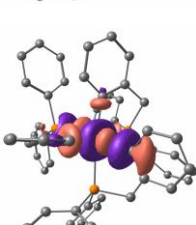
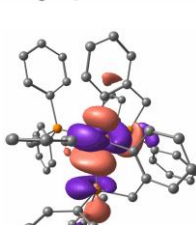
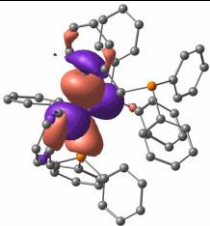
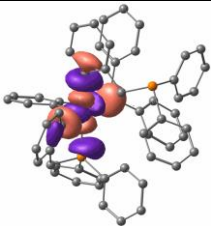
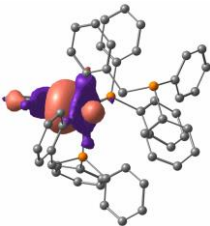
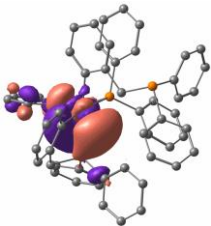
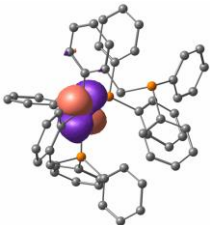
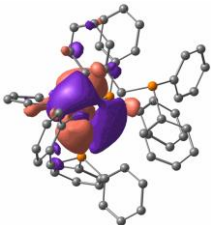
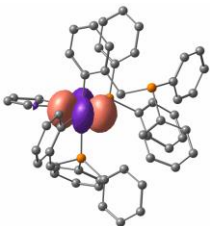
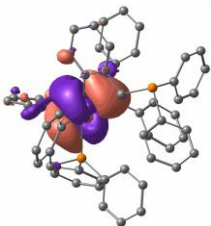
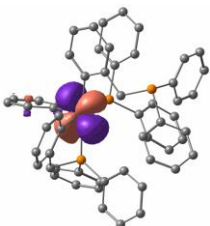
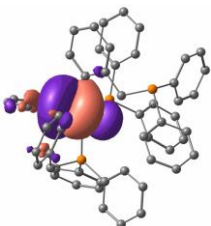
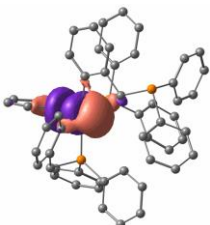
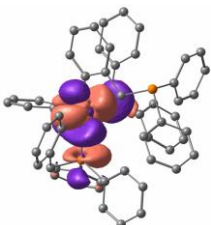
#	E / H	orbital	#	E / H	orbital
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227	-0.355683		233	+0.572138	
228	-0.056621		234	+0.676066	
229	-0.049839		235	+0.715531	
230	-0.025098		236	+1.09958	
231	+0.193922		237	+1.184093	

Table S7 Energies of the orbitals used in the active space of the CASSCF(7,12)-FIC-NEVPT2 calculation of *trans*-2', depicted at a contour value of 0.03 a.u. (hydrogen atoms omitted for clarity).

#	<i>E</i> / H	orbital	#	<i>E</i> / H	orbital
226	−0.38319		232	+0.21773	
227	−0.36883		233	+0.53199	
228	−0.05993		234	+0.59317	
229	−0.05129		235	+0.65404	
230	−0.04959		236	+0.76767	
231	+0.14915		237	+1.10449	

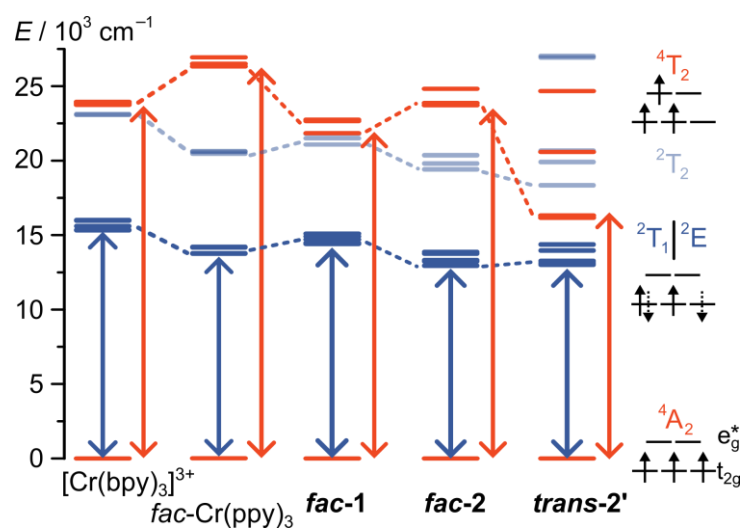


Figure S23 Energy levels of quartet (orange) and doublet (blue) states from CASSCF(7,12)-NEVPT2 calculations of $[\text{Cr}(\text{bpy})_3]^{3+}$, $\text{fac-Cr}(\text{ppy})_3$, fac-1 , fac-2 and trans-2' .

8. Absorption and emission spectroscopy, luminescence lifetimes

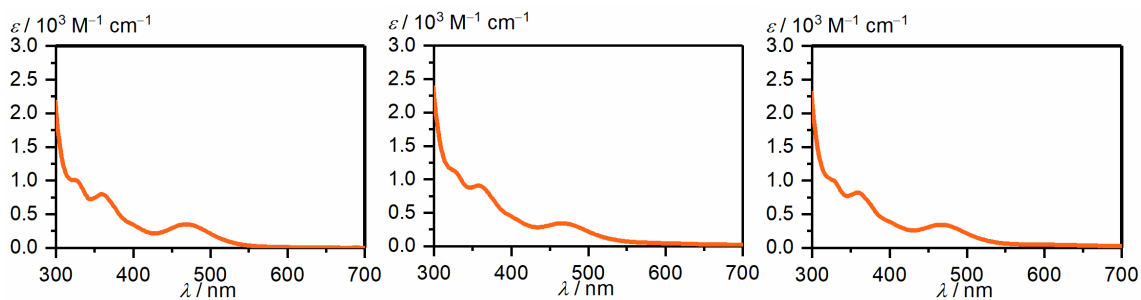


Figure S24 Absorption spectra of **fac-1** in MeCN, 2-MeTHF and THF at 293 K ($c = 1 \cdot 10^{-4}$ M).

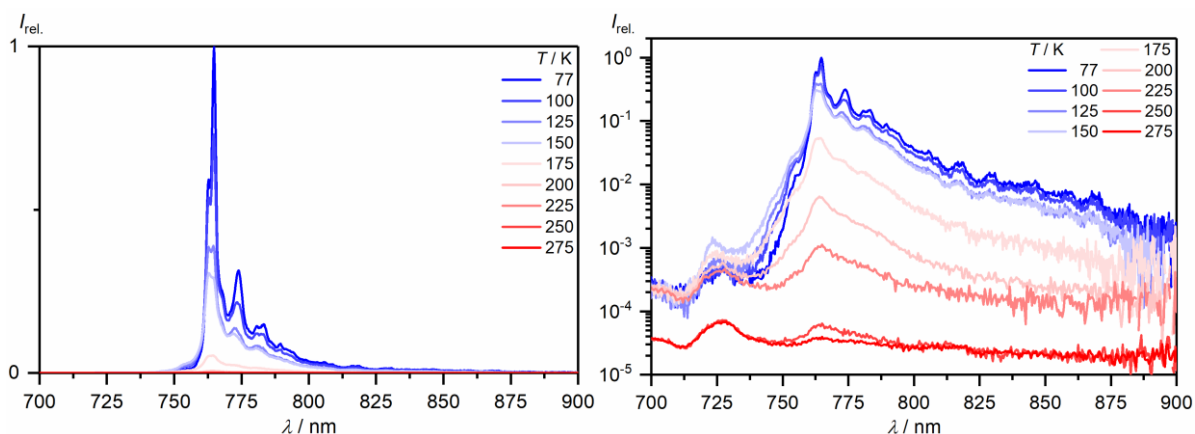


Figure S25 Emission spectra of **fac-1** in the solid state at different temperatures ($\lambda_{\text{exc}} = 465$ nm) on a) a linear and b) a logarithmic scale, intensity relative to spectrum at 77 K.

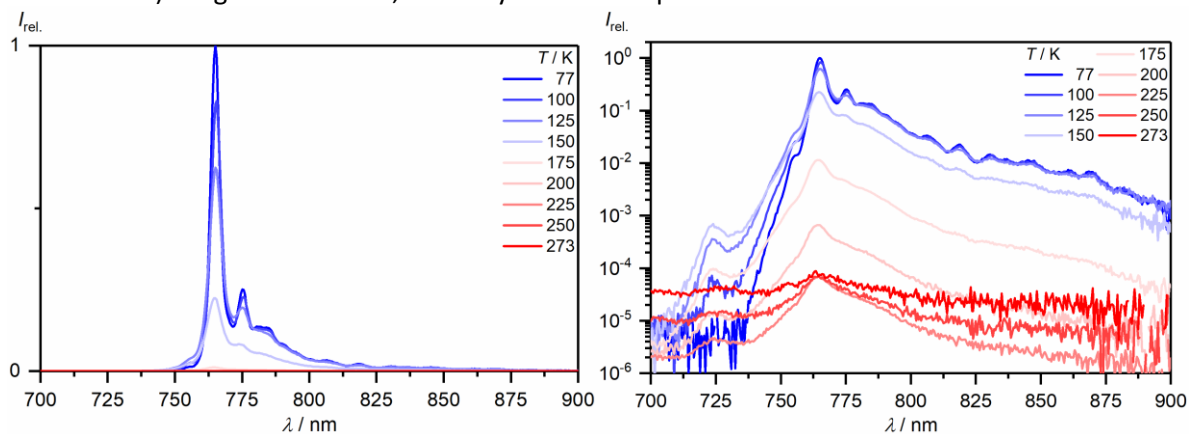


Figure S26 Emission spectra of **fac-1** in 2-MeTHF ($c = 1.4 \cdot 10^{-3}$ M) at different temperatures ($\lambda_{\text{exc}} = 465$ nm) on a) a linear and b) a logarithmic scale, intensity relative to spectrum at 77 K.

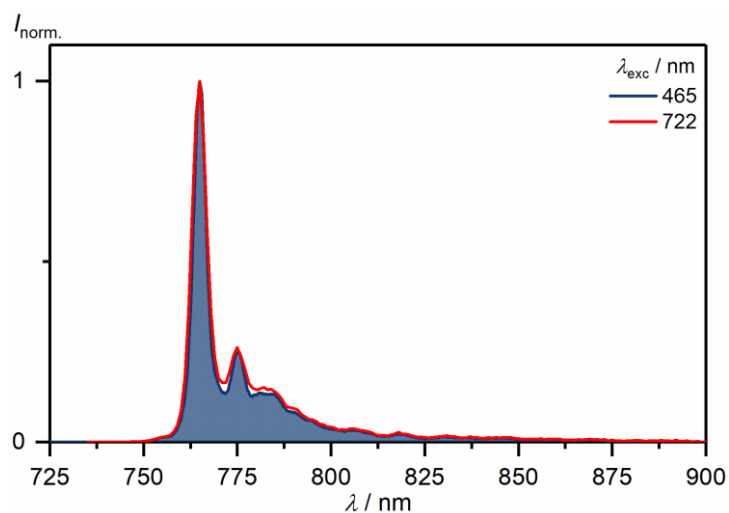


Figure S27 Normalized emission spectra of **fac-1** in 2-MeTHF with different excitation wavelengths at 77 K: blue $\lambda_{\text{exc}} = 465$ nm ($c = 1.4 \cdot 10^{-3}$ M) and red $\lambda_{\text{exc}} = 722$ nm ($c = 2.0 \cdot 10^{-3}$ M).

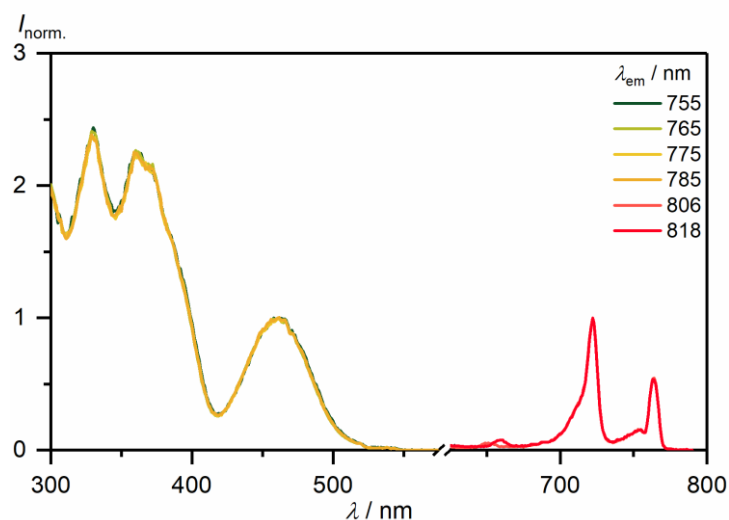


Figure S28 Normalized excitation spectra with different emission wavelengths of **fac-1** in 2-MeTHF at 77 K. Concentration of solution for excitation in VIS region $c = 1.7 \cdot 10^{-4}$ M, in IR region $c = 2.0 \cdot 10^{-3}$ M.

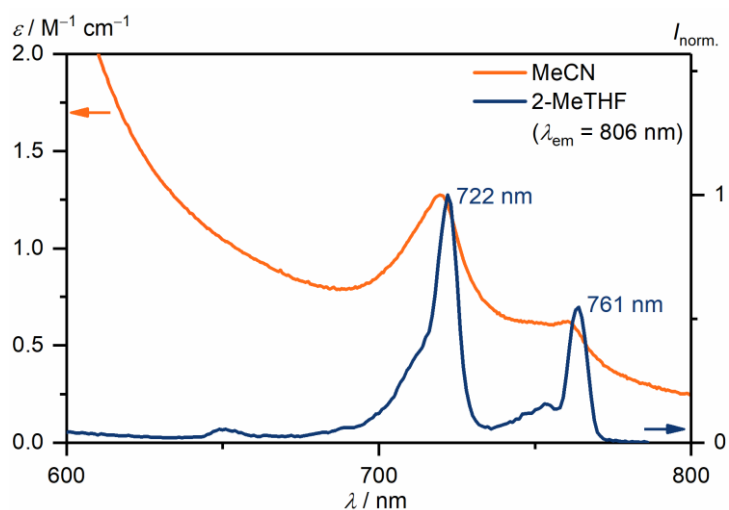


Figure S29 Absorption spectrum of **fac-1** in MeCN at 293 K (orange, $c = 5.0 \cdot 10^{-3}$ M) and normalized excitation spectrum of **fac-1** in 2-MeTHF at 77 K (blue, $c = 2.0 \cdot 10^{-3}$ M, $\lambda_{\text{em}} = 806$ nm).

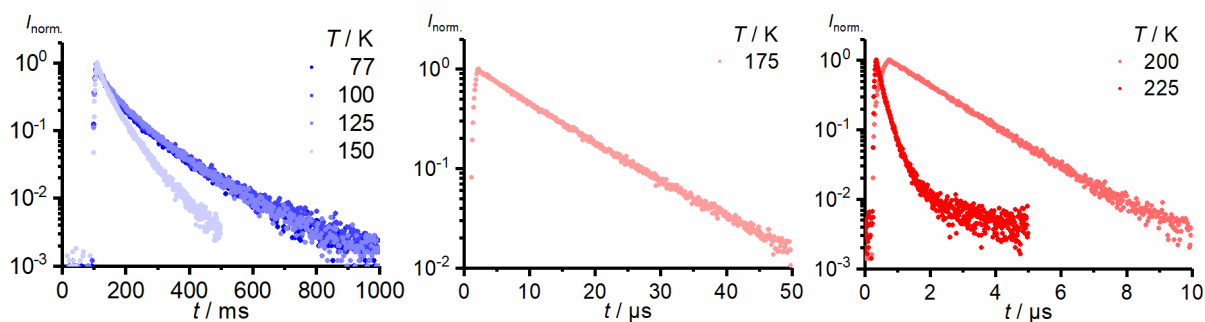


Figure S30 Lifetime scans of *fac-1* in the solid state at variable temperatures ($\lambda_{\text{em}} = 765 \text{ nm}$, $\lambda_{\text{exc}} = 451 \text{ nm}$).

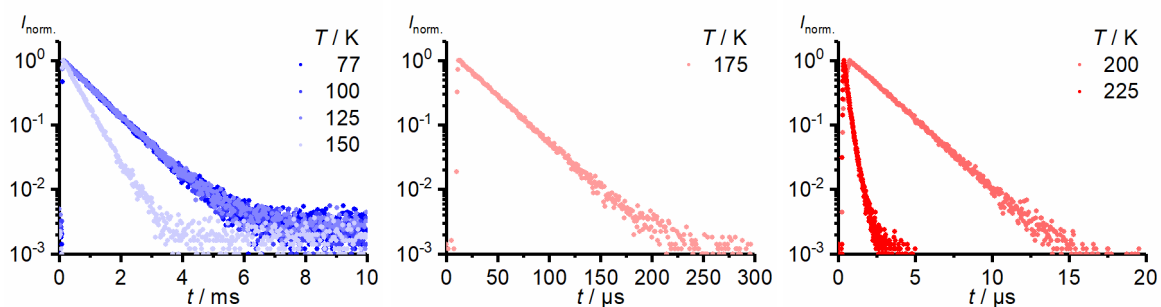


Figure S31 Lifetime scans of *fac-1* in 2-MeTHF at variable temperatures ($\lambda_{\text{em}} = 765 \text{ nm}$, $\lambda_{\text{exc}} = 451 \text{ nm}$, $c = 1.4 \cdot 10^{-3} \text{ M}$).

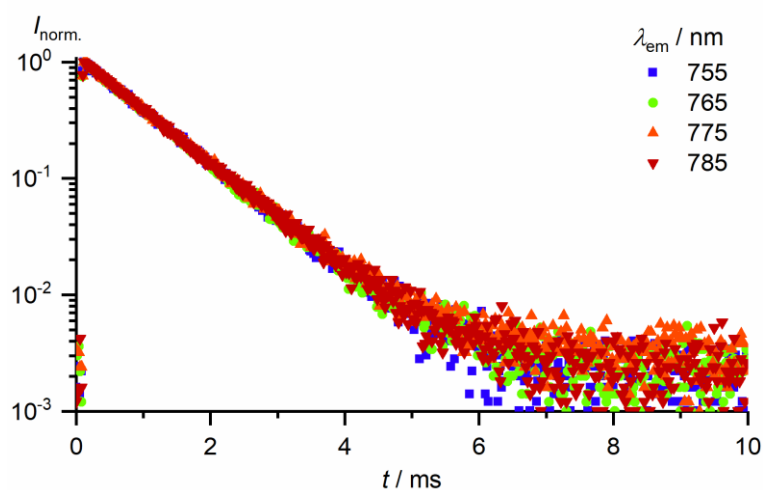


Figure S32 Lifetime scans of *fac-1* in 2-MeTHF at 77 K ($\lambda_{\text{exc}} = 451 \text{ nm}$, $c = 1.7 \cdot 10^{-4} \text{ M}$).

Table S8 Summary of emission data of **fac-1**: Emission maxima and excited state lifetimes in brackets, at different temperatures, in the solid state and 2-MeTHF.

<i>T</i> / K	$\lambda_{\text{em}} / \text{nm}$ [$\tau / \mu\text{s}$] ($\lambda_{\text{exc}} = 465 \text{ nm}$ [($\lambda_{\text{exc}} = 451 \text{ nm}$)])	
	Solid	2-MeTHF
77	727.25	
	755.00	755.0 [943]
	762.75	765.0 [931]
	764.75 [163 + 62]	775.0 [928]
	768.00	785.0 [930]
	773.75	790.5
	783.25	795.0
	789.50	806.0
	805.50	818.5
	818.25	830.5
	829.50	
100	727.25	723.5
	755.00	755.0
	762.75	765 [928]
	764.75 [142 + 44]	775.0
	768.00	785.0
	773.75	790.5
	783.25	795.0
	789.50	806.0
	805.50	818.5
	818.25	830.5
	829.50	
125		723.5
	725.50	755.0
	753.50	765 [937]
	762.75	775.0
	764.50 [134+ 45]	785.0
	772.25	790.5
	780.50	795.0
	817.00	806.0
	828.25	818.5
		830.5
150	723.25	
	753.50	
	762.75	724.0 [541]
	764.50 [73 + 28]	765.0 [512]
	772.25	774.5
	780.50	817.5
	817.00	
	828.25	
175	724.25	
	753.50	
	762.75	724.0 [29]
	764.50 [12 + 6.7]	764.5 [29]
	773.50	
200	781.50	
	727.0	724 [2.0]
225	764.0 [1.5]	764.5 [2.0]
	727.0	724.5
250	764.5 [0.43 + 0.17]	764.5 [0.25]
	727.0	724.0
275	764.5	764.5
	727.0	724.0
	764.5	764.5

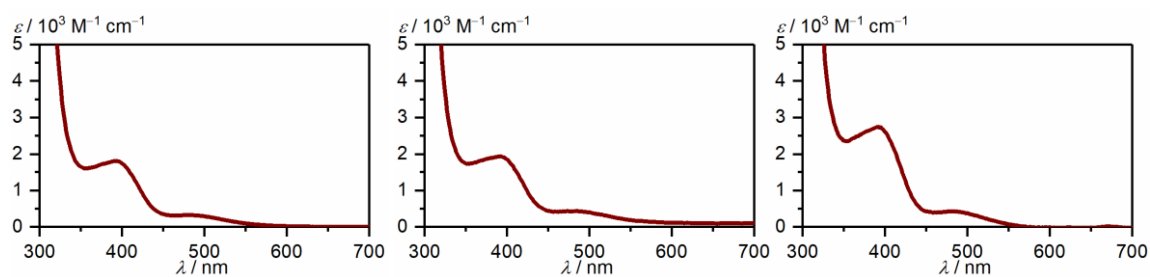


Figure S33 Absorption spectrum of *fac-2* in toluene, 2-MeTHF and THF at 293 K ($c = 1.0 \cdot 10^{-4}$ M).

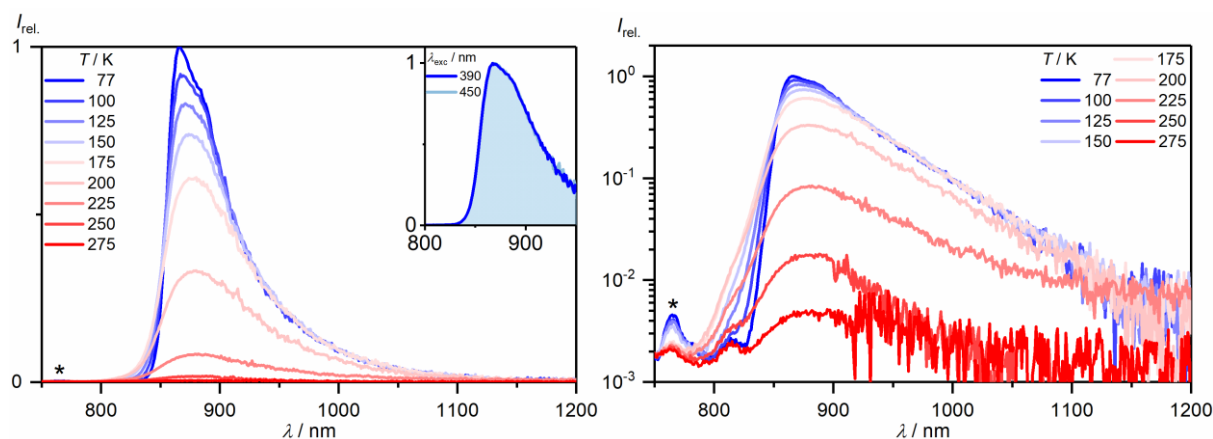


Figure S34 Emission spectra of *fac-2* in the solid state at different temperatures ($\lambda_{\text{exc}} = 390$ nm) on a) a linear and b) a logarithmic scale, intensity relative to spectrum at 77 K. * Artifact from cuvette.

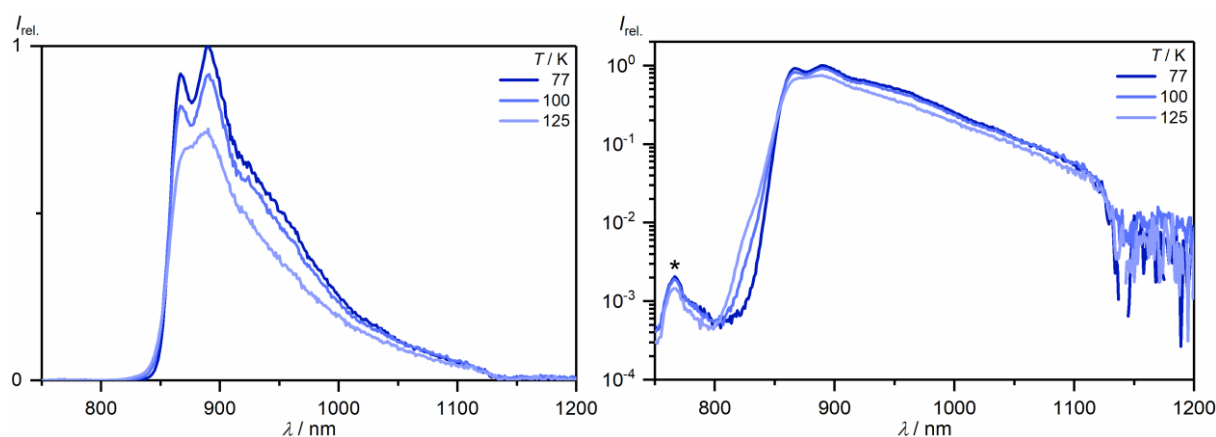


Figure S35 Emission spectra of *fac-2* / *trans-2'* in toluene at different temperatures ($\lambda_{\text{exc}} = 390$ nm, $c = 1.0 \cdot 10^{-3}$ M) on a) a linear and b) a logarithmic scale, intensity relative to spectrum at 77 K. * Artifact from cuvette.

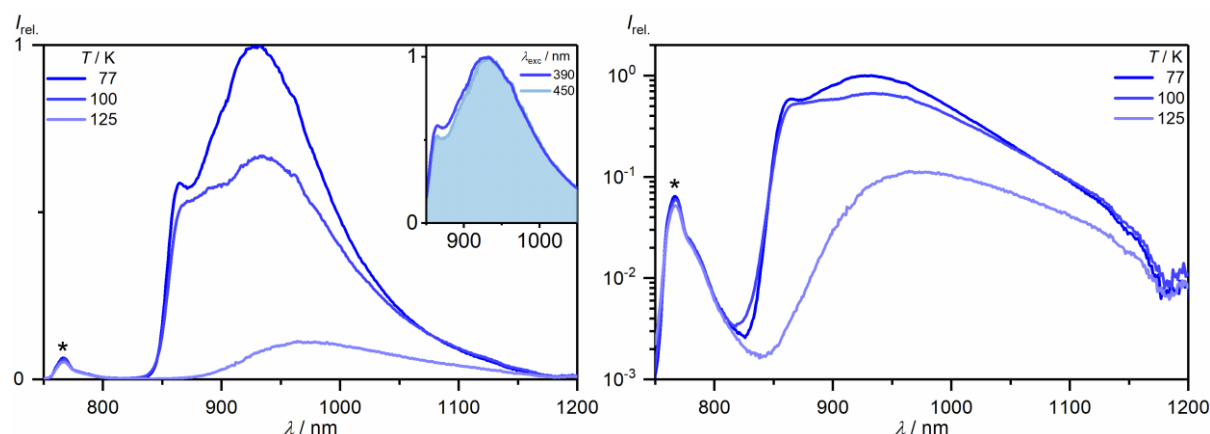


Figure S36 Emission spectra of *fac-2* / *trans-2'* in 2-MeTHF at different temperatures ($\lambda_{\text{exc}} = 390$ nm, $c = 2.0 \cdot 10^{-4}$ M) on a) a linear and b) a logarithmic scale, intensity relative to spectrum at 77 K. * Artifact from cuvette.

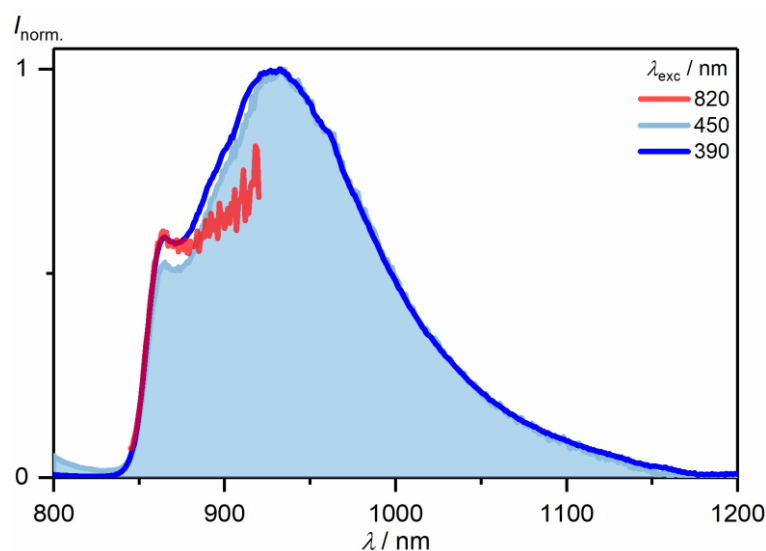


Figure S37 Normalized emission spectra of *fac-2* / *trans-2'* in 2-MeTHF at 77 K with different excitation wavelengths: blue excitation in VIS ($c = 0.2 \cdot 10^{-3}$ M), red excitation in ($c = 1.0 \cdot 10^{-3}$ M). Measurement of red spectrum only up to 940 nm possible due to weak luminescence signal and sensitivity limit of the detector.

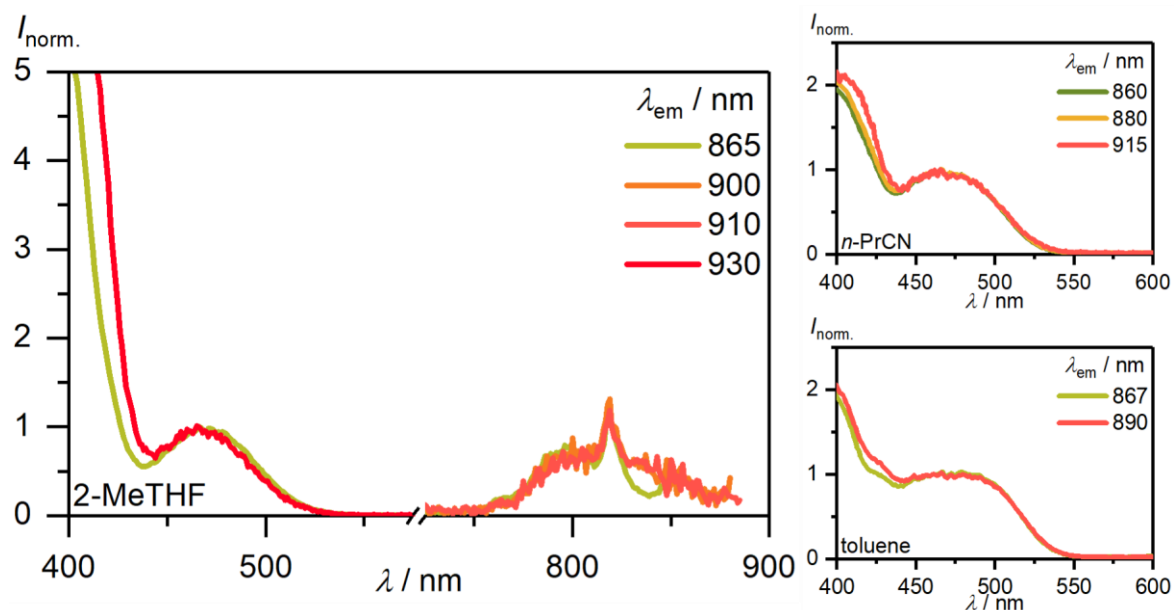


Figure S38 Normalized excitation spectra of different emission wavelengths of **fac-2 / trans-2'** at 77 K in 2-MeTHF (VIS region $c = 2.0 \cdot 10^{-4}$ M, NIR region $c = 1.0 \cdot 10^{-3}$ M), *n*-PrCN ($c = 1.0 \cdot 10^{-3}$ M) and toluene ($c = 1.0 \cdot 10^{-3}$ M).

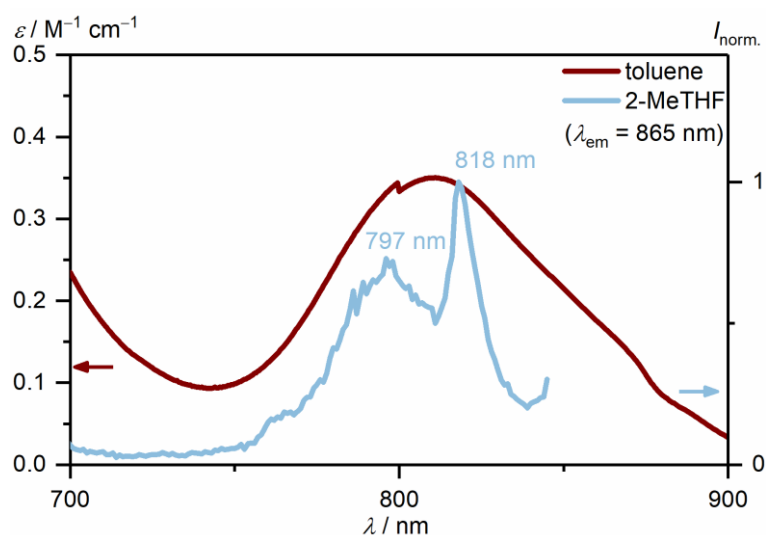


Figure S39 Absorption spectrum of **fac-2 / trans-2'** in toluene at 293 K (red, $c = 10 \cdot 10^{-3}$ M) and normalized excitation spectrum of **fac-2 / trans-2'** in 2-MeTHF at 77 K (blue, $c = 1.0 \cdot 10^{-3}$ M, $\lambda_{em} = 865$ nm).

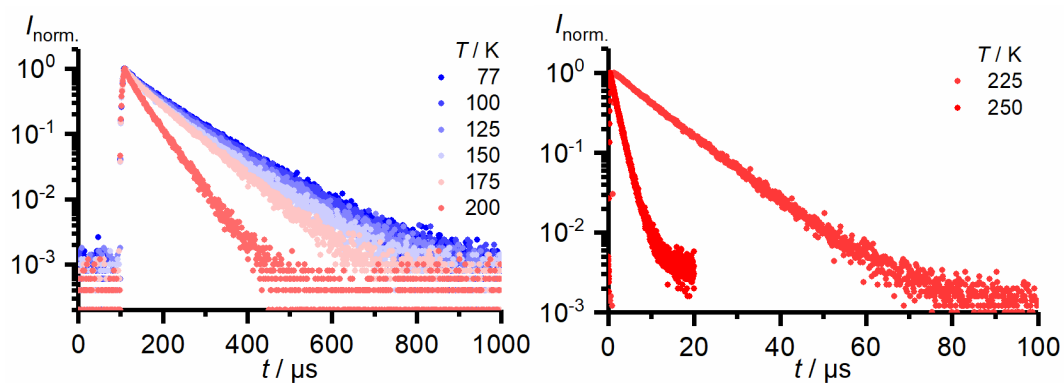


Figure S40 Lifetime scans of *fac-2* in the solid state at different temperatures ($\lambda_{\text{exc}} = 451 \text{ nm}$; $\lambda_{\text{em}} = 866 \text{ nm}$).

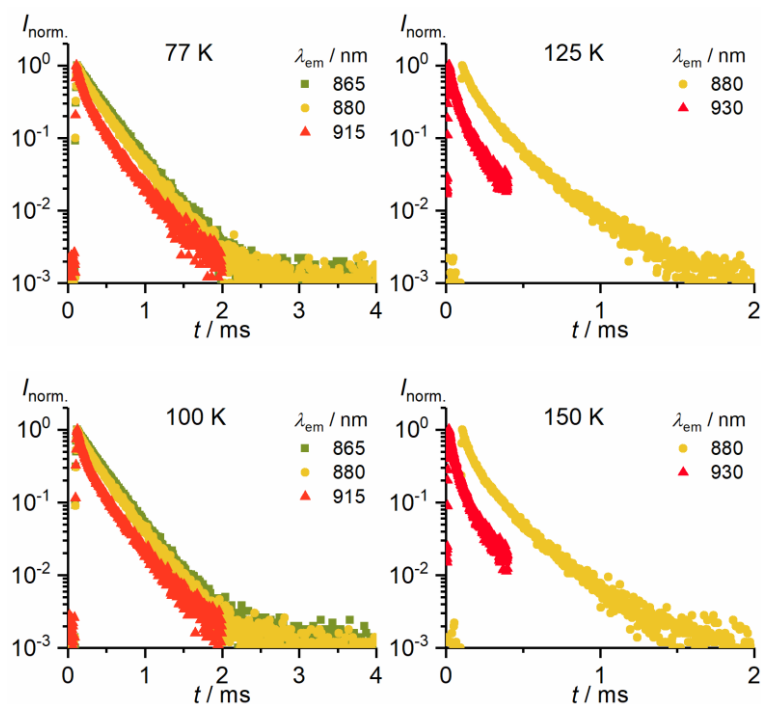


Figure S41 Lifetime scans of *fac-2* / *trans-2'* in *n*-PrCN ($c = 1.0 \cdot 10^{-3} \text{ M}$) at different temperatures ($\lambda_{\text{exc}} = 451 \text{ nm}$).

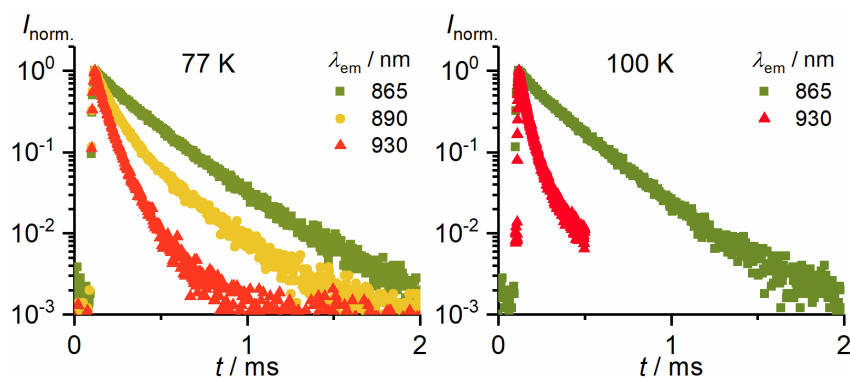


Figure S42 Lifetime scans of *fac-2* / *trans-2'* in 2-MeTHF at different temperatures ($\lambda_{\text{exc}} = 451 \text{ nm}$, $c = 0.2 \cdot 10^{-3} \text{ M}$).

Table S9 Summary of emission data of **fac-2** / **trans-2'**: Emission maxima (maxima in bold) and corresponding excited state lifetimes in brackets, at different temperatures in the solid state, 2-MeTHF and *n*-PrCN. Excitation wavelengths given in parenthesis.

<i>T</i> / K	$\lambda_{\text{em}} / \text{nm} [\tau / \mu\text{s}] (\lambda_{\text{exc}} / \text{nm} [(\lambda_{\text{exc}} = 451 \text{ nm})])$			
	Solid (390)	2-MeTHF (390)	PrCN (450)	toluene (390)
77	813 866 [32 + 109] 884	865 [272 + 117] 930 [50 + 113]	858 [296] 880 [316 + 140] 915 [285 + 77]	867 890
100	867 [35 + 107] 885	865 [244 + 72] 890 935 [30 + 72]	-	
125	871 [36 + 102] 885	965	-	
150	874 [93 + 25]	-	-	
175	877 [81 + 23]	-	-	
200	878 [45]	-	-	
225	878 [10]	-	-	
250	813 878 [6.3 + 1.7]	-	-	
275	813 878 [0.24 + 0.69]	-	-	

Table S10 Summary of absorption, excitation and emission data for **fac-1**, **fac-2** and **fac-Cr(ppy)₃** with calculated transitions from TD-DFT and CASSCF(7,12) NEVPT2 calculations with corresponding assignments.

	$\lambda_{\text{abs}} / \text{nm}^a$	$\lambda_{\text{exc}} / \text{nm}$ ($\lambda_{\text{em}} / \text{nm}$) ^b	$\lambda_{\text{em}} / \text{nm}^c$	TD-DFT λ / nm	CASSCF λ / nm	Assignment
fac-1^d	326			367, 373, 375	366, 374, 375	$^4\text{A}_2 \rightarrow ^4\text{T}_1$
	359	360 (765)				
	402 (sh)			419, 423, 460	440, 443, 460	$^4\text{A}_2 \rightarrow ^4\text{T}_2$
	470	462 (765)				
	720	722 (806)	727		665, 674, 683, 693, 697	$^4\text{A}_2 \rightarrow ^2\text{E} / ^2\text{T}_1$
	760	761 (806)	765			
fac-2^e	392			386, 392, 398	349, 353, 363	$^4\text{A}_2 \rightarrow ^4\text{T}_1$
	492	470 (865)		434, 436, 440	404, 420, 424	$^4\text{A}_2 \rightarrow ^4\text{T}_2$
		797 (865)				
	810	818 (865)	813		722, 733, 753, 760, 776	$^4\text{A}_2 \rightarrow ^2\text{E} / ^2\text{T}_1$
			866			
fac-Cr(ppy)₃^f					311, 314, 320	$^4\text{A}_2 \rightarrow ^4\text{T}_1$
	390	370		345 (A), 349 (E)	370, 376, 379	$^4\text{A}_2 \rightarrow ^4\text{T}_2$
			890		707, 708 (E) 732, 734	$^4\text{A}_2 \rightarrow ^2\text{E} / ^2\text{T}_1$

^a Absorption spectra at r.t.. ^b Excitation spectra at 77 K in 2-MeTHF. ^c Emission spectra in solid state at 77 K. ^d Absorption spectra of **fac-1** in MeCN; sh = shoulder. ^e Absorption spectra of **fac-2** in toluene.

^f Absorption spectra of **fac-Cr(ppy)₃** in THF, excitation and emission spectra at 77 K in 2-MeTHF.³³

Table S11 Ligand field parameters of **fac-1**, **fac-2**, and selected NIR luminescent chromium(III) complexes.

Complex	Conditions abs./em.	$\lambda_{\text{abs}} / \text{nm}$	$\Delta_{\text{o}} / \text{cm}^{-1}$	$\lambda_{\text{em}} / \text{nm}$	$\tilde{\nu}_{\text{em}} / \text{cm}^{-1}$	B / cm^{-1}	β	β'
Cr^{3+}	free ion	-	-	-	14590 ³⁵	918 ³⁶	-	-
fac-1	THF, r.t./ solid 77 K	465 ^a	21510	765	13070	670	0.73	0.90
fac-2	THF, r.t./ solid 77 k	480 ^a	20330	865	11560	590	0.64	0.79
<i>fac</i> -Cr(ppy) ₃ ³³	THF, r.t./ 2-MeTHF 77 K	380 ^a	26320	890	11240	550	0.60	0.77
[Cr(dpc) ₂] ⁺ ³⁷	MeCN r.t./ MeCN 77 K	521	19190	1067	9370	520	0.52	0.64
[Cr(dpi ^{H,H}) ₂] ⁺ ³⁸	<i>n.a.</i> / 2-MeTHF 77 K	<i>n.a.</i>	<i>n.a.</i>	925	10810	<i>n.a.</i>	<i>n.a.</i>	0.74

Values rounded to 10 cm⁻¹. ^aAverage value from excitation spectra at 77 K and absorption spectra at r.t.

β' according to calculations for [Cr(dpi^{H,H})₂]⁺³⁸: $\beta' = \frac{\tilde{\nu}_{\text{em}}(\text{complex})}{\tilde{\nu}_{\text{em}}(\text{free Cr}^{3+})}$

9. References

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Acknowledgements

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