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Luminescent Dinuclear Chromium(III) Complexes with Ferromagnetic Exchange Interactions

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Recent advances with luminescent mononuclear chromium(III) complexes have provided important molecular design guidelines for enhancing their photoluminescence properties. Applying these modern aspects of coordination chemistry to dinuclear Cr^{III} complexes, which are mostly not luminescent but show interesting magnetic properties, seems attractive for exploring functional coordination compounds with magnetic exchange interactions and light-induced activity. In this concept, the key structural requirements for dinuclear Cr^{III} complexes with ferromagnetic exchange interactions and with photoluminescence properties, respectively, are analyzed. Rational merger of these key magneto-optical–structural correlations leads to new types of dinuclear Cr^{III} complexes with ferromagnetic coupling and room temperature luminescence, and their photophysical properties make them promising photosensitizers for energy transfer. These design concepts open the door of exploring novel dinuclear Cr^{III} complexes, which can allow the crosstalk of photophysics, photochemistry, and magnetic exchange interactions.

1. Introduction

Polynuclear coordination compounds based on $3d^3$ Cr^{III} have been an active research topic since several decades due to their unique magnetic and optical properties.[1–4] For dinuclear Cr^{III} complexes, the exchange interactions between the paramagnetic Cr^{III} ions determine the magnetic properties, leading to either antiferromagnetic (AFM) or ferromagnetic (FM) coupling between the metal ions in their ground states (**Figure 1**a).[5] The latter is potentially attractive for molecular-based magnets, which currently rely mostly on lanthanide ions.[6] However, AFM exchange interactions between the Cr^{III} ions remain the majority for such dinuclear complexes,[2,7,8] whereas only a few examples of FM-coupled dinuclear Cr^{III} complexes have been reported.[9–13] In contrast to the substantial magnetostructural studies for dinuclear Cr^{III} complexes,[2,4,7] only limited attention has been paid to explore their luminescence properties.[14–16] FM-coupled dinuclear Cr^{III} complexes that show room temperature luminescence remain severely scarce.

Since recent years, the desire for sustainable chemistry has led to remarkable achievements with photoactive mononuclear complexes based on first-row transition metals, such as chromium,[17–22] manganese,[23,24] iron,[25–27] and copper.[28–30] Rational molecular design for these coordination compounds leads to favorable photophysical and photochemical properties,[31–33] which make them promising alternatives to those based on platinum group metals in the fields of bioimaging and sensing,[34–38] lighting,[30,39,40] photon upconversion,[41–49] and photocatalysis.[21,23,50–62] In particular, important molecular design guidelines for mononuclear luminescent Cr^{III} complexes (molecular rubies) with spin-flip doublet excited states ($^2T_1/^2E$) were gained over the past decade.[17–20,22,63–65] These Cr^{III} complexes show highly emissive doublet excited states with lifetimes of up to milliseconds in solution at room temperature,[17–20,22,63–65] and some of them are photoredox active.[54,55,66] These favorable excited state properties make photoactive Cr^{III} complexes promising photosensitizers for photoinduced processes.[41,54,55,62,66–69]

Applying the abovementioned molecular design principles to dinuclear Cr^{III} complexes has recently led to new types of dimers that exhibit room-temperature luminescence and FM coupling.[13] In this concept, we will provide comprehensive and thorough analysis of the magneto-structural correlations for FM-coupled Cr^{III} dimers (Section 2.1), the key structural requirements for luminescent Cr^{III} complexes (Section 2.2), the combined design principles for luminescent dinuclear Cr^{III} complexes with FM coupling (Section 2.3), and the investigation of a luminescent Cr^{III} dimer for sensitizing energy transfer and photon upconversion (Section 2.4).

2. Molecular Design Principles for Dinuclear Cr^{III} Complexes

2.1. Ferromagnetically Coupled Dinuclear Cr^{III} Complexes

The type of magnetic coupling in dinuclear complexes depends on the alignment of the electron spins between two metal ions. Parallel alignment of the electron spins of two Cr^{III} ions ($S = 3/2$)

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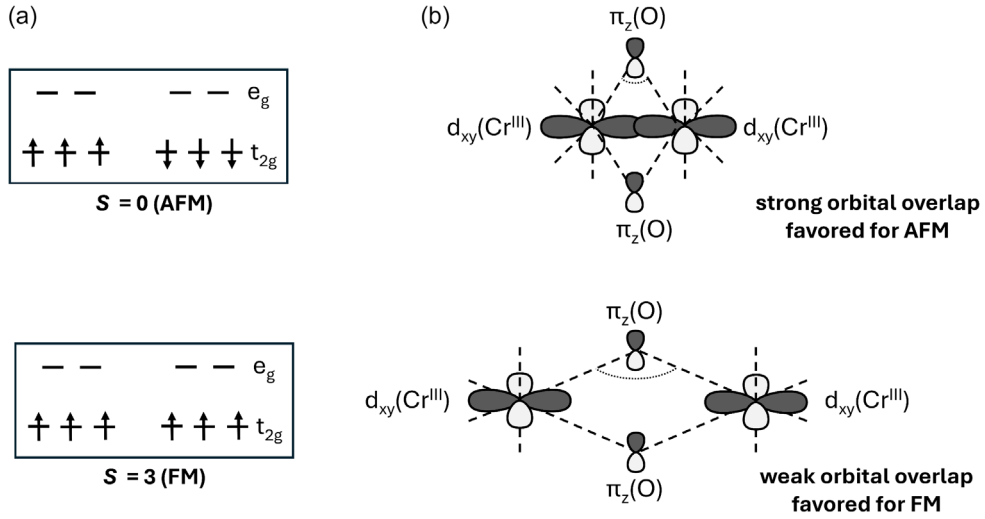

Figure 1. a) Electronic configurations of two bridged Cr^{III} ions in octahedral ligand fields. Antiparallel alignment of the electron spins leads to AFM coupling (top), while their parallel alignment gives FM coupling (bottom). b) Simplified schematic illustration of the d_{xy} orbital overlap between two Cr^{III} ions in an edge-sharing dimer with bi-hydroxo-bridges. A small Cr—O—Cr bridging angle often leads to strong orbital overlap between the Cr^{III} ions and consequently AFM exchange interactions, whereas a large bridging angle results in a weak orbital overlap and therefore FM coupling.

gives the dinuclear complex with FM coupling ($S = 3$), while their antiparallel arrangement leads to AFM exchange interactions ($S = 0$) (Figure 1a). The magnitude of such coupling can be described by the coupling constant J, which arises from the spin Hamiltonian $\hat{H}$ (Equation (1)), with the positive J values corresponding to FM coupling:

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + 2g\mu_B\vec{B}(\vec{S}_1 + \vec{S}_2) \quad (1)$$

$\hat{S}_1$ and $\hat{S}_2$ are the electron spins of the two Cr^{III} ions, μ_B is the Bohr magneton, and B stands for the magnetic flux density. The g-factors are assumed to be identical for the two Cr^{III} ions.

The alignment of the electron spins depends on the molecular orbital overlap of the singly occupied d-orbitals of the metal centers, which can be mediated by the π- or π^*-orbitals of the bridging units.[8,70] The extent of this orbital overlap determines the energy levels of the resulting molecular orbitals, which are either occupied by paired electrons (AFM coupling) for strong overlap or unpaired electrons (FM coupling) for a weak overlap.[8,70] Figure 1b exemplarily shows bi-hydroxo-bridged Cr^{III} dimers with different Cr—O—Cr bridging angles representing strong orbital overlap favored for AFM and weak orbital overlap for FM coupling.

Dinuclear Cr^{III} complexes involve mostly oxo- or hydroxo-bridging units, and they exhibit predominantly AFM interactions.[2,7,8] The magnetic interactions depend strongly on the structural factors, including the Cr—O bond length, the Cr—Cr distances, the Cr—O—Cr bridging angle, and the OR vector of the bridging group.[2,8,71] These structural factors have different influences on the magnetic exchange interactions, depending on the general geometry of the dimer, e.g., corner-sharing, edge-sharing, or face-sharing bridging geometry.[1,2,72] Despite the well understood magneto-structural correlations, examples of FM-coupled dinuclear Cr^{III} complexes have long remained the exceptions until recently (**Figure 2**).[9–13,71,73]

Early reports of FM-coupled Cr^{III} dimers contain mostly di-hydroxo or di-fluoro-bridging groups, all of which exhibit very weak coupling with J values of up to $\approx +5\ cm^{-1}$ (Figure 2).[9–11,73] A recent report found that addition of a carboxylato-bridge to the di-alkoxido-bridged dinuclear Cr^{III} complexes yields FM-coupled dimers $[Cr_2(\mu\text{-}OR^1)_2(\mu\text{-}O_2CR^2)Cl_2]^+$ with J ranging from +0.37 to $+8.02\ cm^{-1}$ (Figure 2).[71] This is attributed to the so-called counter-complementarity effect[74] caused by the interaction of the π^*-orbital of the carboxylate with the metal orbitals.[71] The absence of either one alkoxido- or the carboxylato-bridge leads to dominating AFM exchange interactions.[71] Replacing the

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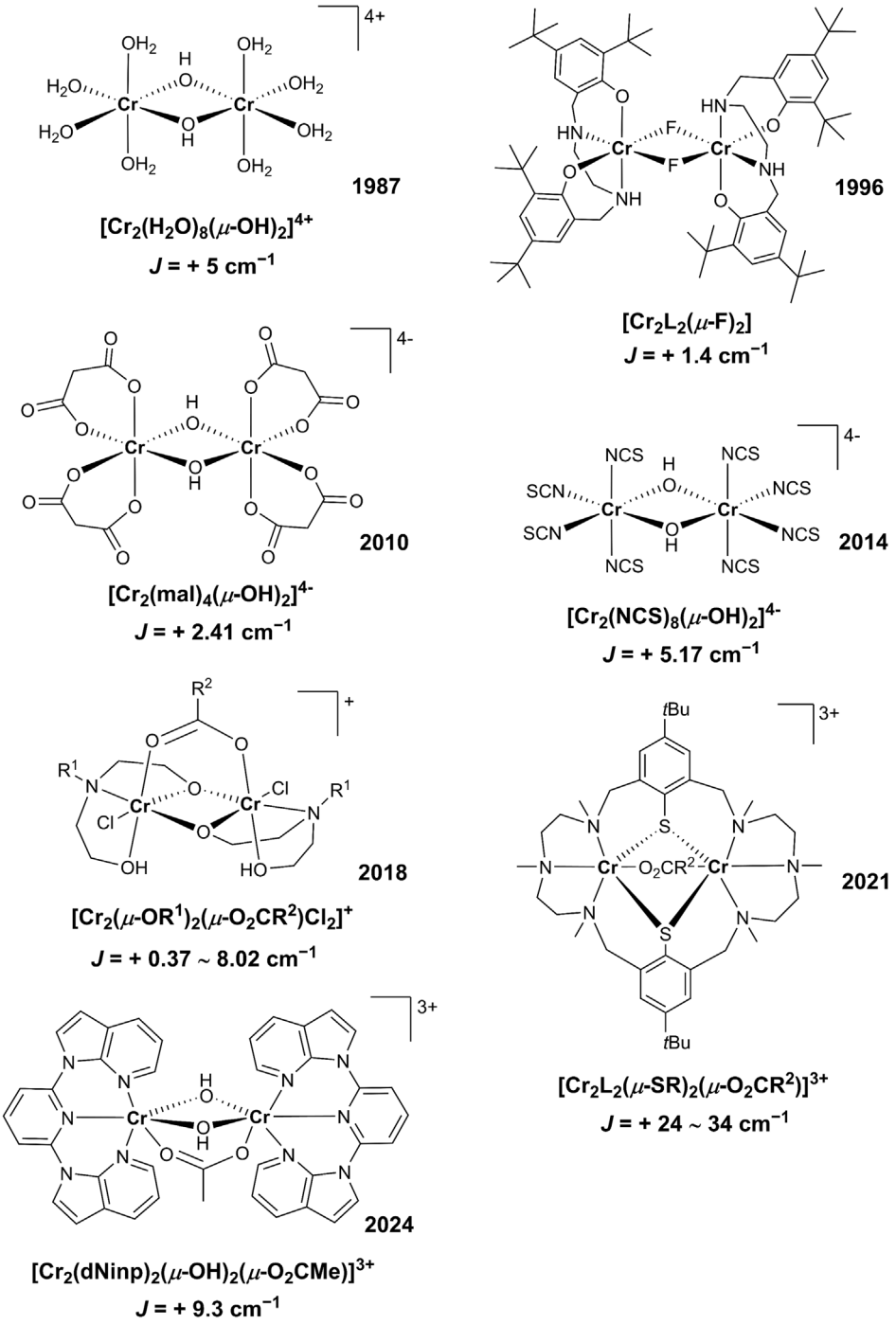

Figure 2. Molecular structures of reported dinuclear Cr^{III} complexes with FM exchange interactions and their corresponding coupling constant *J*.

di-alkoxido-bridges with di-thiolato-groups while preserving the carboxylate bridge leads to FM-coupled dinuclear Cr^{III} complexes $[Cr_2L_2(\mu\text{-}SR)_2(\mu\text{-}O_2CR^2)]^{3+}$ with high *J* values of up to 34.8 cm^{-1}.[12] The thiolato-bridged Cr^{III} dimer shows a Cr—Cr distance of ≈3.5 Å,[12] which is clearly longer than 2.9–3.0 Å found in the alkoxido-bridged dimers.[71] The efficient decoupling of the two Cr^{III} ions by the thiolato-groups seems to suppress the contribution from the direct AFM exchange,[16,75] which gives higher FM-coupled *J* values in the thiolato-bridged Cr^{III} dimers than the alkoxido-bridged ones.

2.2. Luminescent Dinuclear Cr^{III} Complexes

Photoexcitation of Cr^{III} complexes in the metal-centered (MC) transition ($^4A_2 \rightarrow {}^4T_2$) populates the Cr^{III} ion in the doublet spin-flip $^2T_1/^2E$ excited states that are found in thermal equilibrium.[37] Luminescence occurs slowly from these excited states, due to the spin-forbidden nature of the $^2T_1/^2E \rightarrow {}^4A_2$ transition, as typically seen with mononuclear Cr^{III} complexes (**Figure 3**a). For dinuclear Cr^{III} complexes, photoexcitation in the MC transition occurs formally only to one of the two Cr^{III} ions,[1,76] giving singly

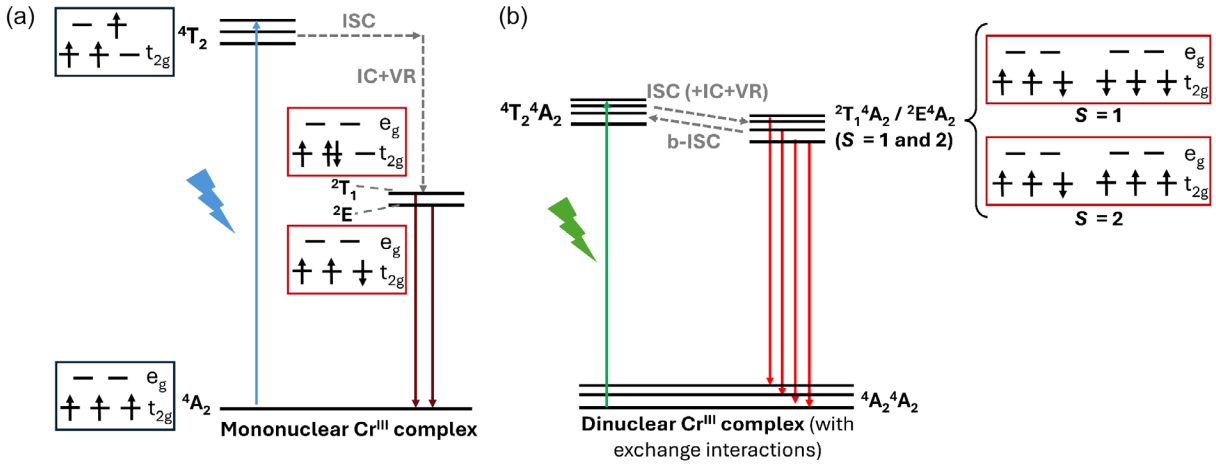

Figure 3. Simplified energy level diagram of a) mononuclear and b) dinuclear Cr^{III} complex with their corresponding microstates. ISC, intersystem crossing; b-ISC, back-intersystem crossing; IC, internal conversion; VR, vibrational relaxation.

excited states $^2T_1{}^4A_2/{}^2E{}^4A_2$ as seen in Figure 3b. The ground and excited states of one Cr^{III} ion undergo convoluted exchange interactions with another Cr^{III} ion, leading to manifolds of the ground and excited states (Figure 3b).[14,16,77,78] Luminescence bands from these exchange-coupled $^2T_1{}^4A_2/{}^2E{}^4A_2$ excited states are therefore often broader in dinuclear Cr^{III} complexes than those observed in mononuclear ones.[12,79] The magnetic exchange interactions in these excited states yield dinuclear spin states of $S = 1$ or 2 (Figure 3b), according to early reports.[9,79]

Photoluminescence from dinuclear Cr^{III} complexes was observed only in a few cases at very low temperatures (<80 K) or in single crystals, yet with very weak luminescence in the red spectral regime below 700 nm.[14–16,77,78] The Cr^{III} ions in these complexes are often hydroxo-bridged and octahedrally coordinated with small amine-based ligands, such as NH_3 or ethylenediamine (en) (**Figure 4**a).[14–16,77,78] These ligands yield relatively weak ligand field splitting, as evidenced with the small energy gap between the lowest energetic absorption band and luminescence bands in dinuclear Cr^{III} complexes.[77,78] Such weak ligand field splitting can lead to back-intersystem crossing from the doublet excited states to the $^4T_2{}^4A_2$ state (Figure 3b), therefore severely diminishing the luminescence behavior.[80–83] For these

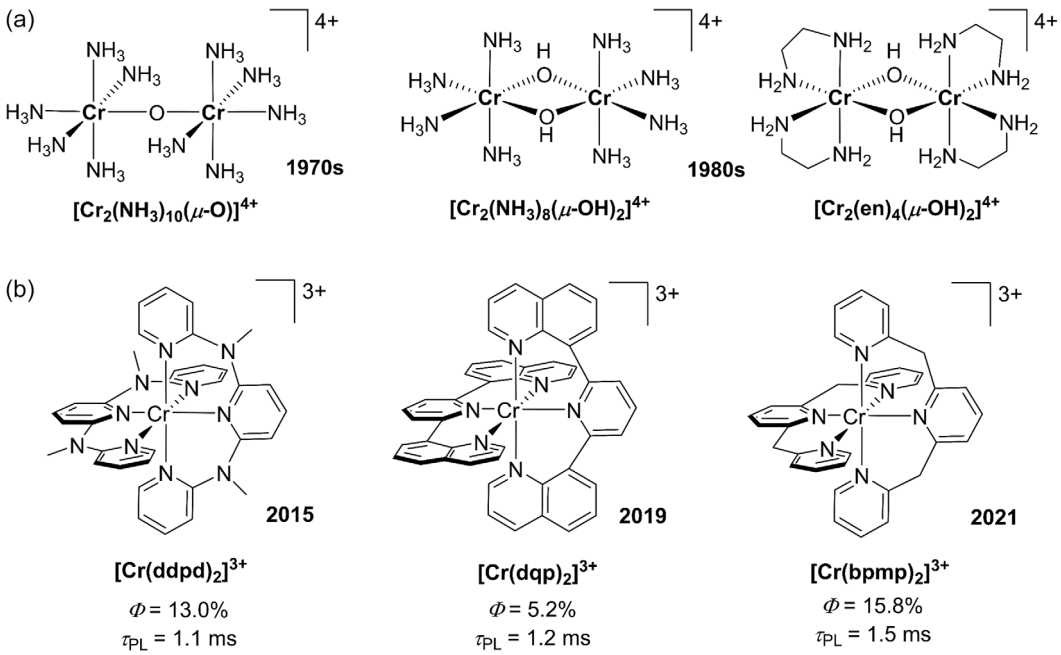

Figure 4. Molecular structures of a) earlier reported dinuclear Cr^{III} complexes exhibiting luminescence at very low temperatures[14–16,77,78] and b) selected examples of recently developed highly luminescent molecular rubies $[Cr(ddpd)_2]^{3+}$ (ddpd = *N*,*N*′-dimethyl-*N*,*N*′-dipyridin-2-ylpyridine-2,6-diamine),[17] $[Cr(dqp)_2]^{3+}$ (dqp = 2,6-di(quinolin-8-yl)pyridine),[22] and $[Cr(bpmp)_2]^{3+}$ (bpmp = 2,6-bis(2-pyridylmethyl)pyridine)[20] with their corresponding luminescence quantum yield and lifetime.

dinuclear Cr^{III} complexes shown in Figure 4a, substantial nonradiative relaxations occur additionally to the excited states via multiphonon relaxations with high energetic N—H oscillators from the amine-based ligands and O—H bridges.[18,63] Collectively, the photoluminescence properties of dinuclear Cr^{III} complexes have remained very poor until recently.

Replacing the small amine-based ligands with a macrocyclic binucleating hexaamine-dithiophenolate ligand yields the abovementioned $[Cr_2L_2(\mu\text{-}SR)_2(\mu\text{-}O_2CR^2)]^{3+}$ complex (Figure 2) with improved molecular rigidity, which can suppress the nonradiative relaxations of the excited states.[18,84] This thiolato- and carboxylato-bridged dinuclear Cr^{III} complex shows broad deep red spin-flip luminescence maximized at 750 nm (**Figure 5**b),[12] which corresponds to a lower excited state energy than that of the abovementioned Cr^{III} dimer with hydroxo-bridges,[14–16,77,78] due to a stronger nephelauxetic effect caused by the thiolato ligands.[65,85–87] This enlarges the energy gap between the $^4T_2{}^4A_2$ and the $^2T_1{}^4A_2/{}^2E^4A_2$ excited states and prevents the back-intersystem crossing (Figure 5a), which leads, together with the higher molecular rigidity, to a high luminescence quantum yield of ≈45% and a long lifetime of ≈114 μs for this dinuclear Cr^{III} complex at 77 K (Figure 5c).[12] However, the photoluminescence becomes very weak at room temperature.[12]

Recent advances with mononuclear Cr^{III} complexes have offered important molecular design guidelines for improving their photoluminescence quantum yields and lifetimes.[17–20,22,63–65] As exemplarily shown in Figure 4b with $[Cr(ddpd)_2]^{3+}$ (ddpd = *N*,*N*′-dimethyl-*N*,*N*′-dipyridin-2-ylpyridine-2,6-diamine),[17] $[Cr(dqp)_2]^{3+}$ (dqp = 2,6-di(quinolin-8-yl)pyridine),[22] and $[Cr(bpmp)_2]^{3+}$ (bpmp = 2,6-bis(2-pyridylmethyl)pyridine),[20] these complexes bear mostly two tridentate chelating ligands with strong σ-donating and π-accepting character, leading to large ligand field splitting that prevents back intersystem crossing.[31,81] Importantly, these tridentate ligands form six-membered chelating rings with the Cr^{III} center to reach an almost perfect octahedral geometry (with N—Cr—N bite angles approaching 90°), together with a high molecular rigidity.[17–20,22,63–65] These fundamentally novel design principles could be attractive for exploring luminescent poly- or dinuclear Cr^{III} complexes, but extremely few attempts have been made so far.[88]

2.3. Luminescent Dinuclear Cr^{III} Complexes with Ferromagnetic Coupling

Luminescent dinuclear Cr^{III} complexes with FM exchange interactions could be fundamentally interesting compounds to explore the interface of molecular magnetism, photophysics, and photochemistry.[89] Such complexes can now be made by applying design principles that involve the magneto-structural correlations (Section 2.1) and the ligand field theory as well as the coordination geometry for the Cr^{III} ions (Section 2.2), as recently shown by us.[13]

Based on the recent progress with molecular rubies,[17–20,22,63–65] the choice of tridentate chelating ligands with strong σ-donating/π-accepting character and the ability to form six-membered rings is crucial to make Cr^{III} complexes luminescent. The flexibility of these six-membered rings allows in principle both the meridional and facial coordination mode,[90] as observed with $[Co(ddpd)_2]^{2+}$ complexes with both coordination configuration.[91,92] For dinuclear or polynuclear metal complexes, facial coordination mode allows a better spatial orientation for packing[93] and is therefore often observed.[94–96] As a structural analogue to the ddpd and dqp ligands in the well-known molecular rubies, dNinp (2,6-di(*N*-7-azaindol-1-yl)pyridine) is chosen as the ligand to form six-membered chelating rings with the metal center and a nearly octahedral geometry.[97] Depending on the reaction conditions, coordination of dNinp with the Cr^{III} center yields either a meridionally coordinated mononuclear complex $[Cr(dNinp)_2]^{3+}$ or a dimer $[Cr_2(dNinp)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)]^{3+}$ (Figure 2) featuring a facial coordination character.[13]

The two Cr^{III} centers in $[Cr_2(dNinp)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)]^{3+}$ are triply bridged by two hydroxo- and one carboxylato-groups (**Figure 6**b), which contribute synergistically to a FM coupling between the metal ions, in line with previous studies (Section 2.1).[71] The coupling constant *J* was determined with magnetic susceptibility measurements at variable temperatures to be $+9.3\ cm^{-1}$ for $[Cr_2(dNinp)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)]^{3+}$

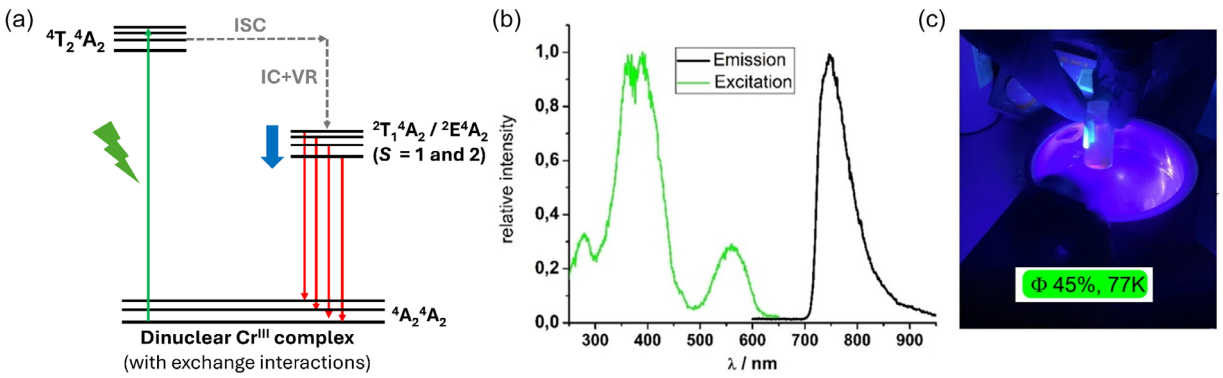

Figure 5. a) Simplified energy-level diagram of dinuclear $[Cr_2L_2(\mu\text{-}SR)_2(\mu\text{-}O_2CR^2)]^{3+}$. b) Excitation spectrum monitored at 750 nm and luminescence spectrum for $[Cr_2L_2(\mu\text{-}SR)_2(\mu\text{-}O_2CR^2)]^{3+}$ with excitation at 405 nm. Spectra were obtained with the dinuclear Cr^{III} complex at 77 K in a frozen CH_2Cl_2/MeOH 1 : 1 glassy matrix. c) Image of the dinuclear Cr^{III} complex at 77 K under UV light irradiation.[12] Reproduced with permission.[12] Copyright 2021, Wiley-VCH.

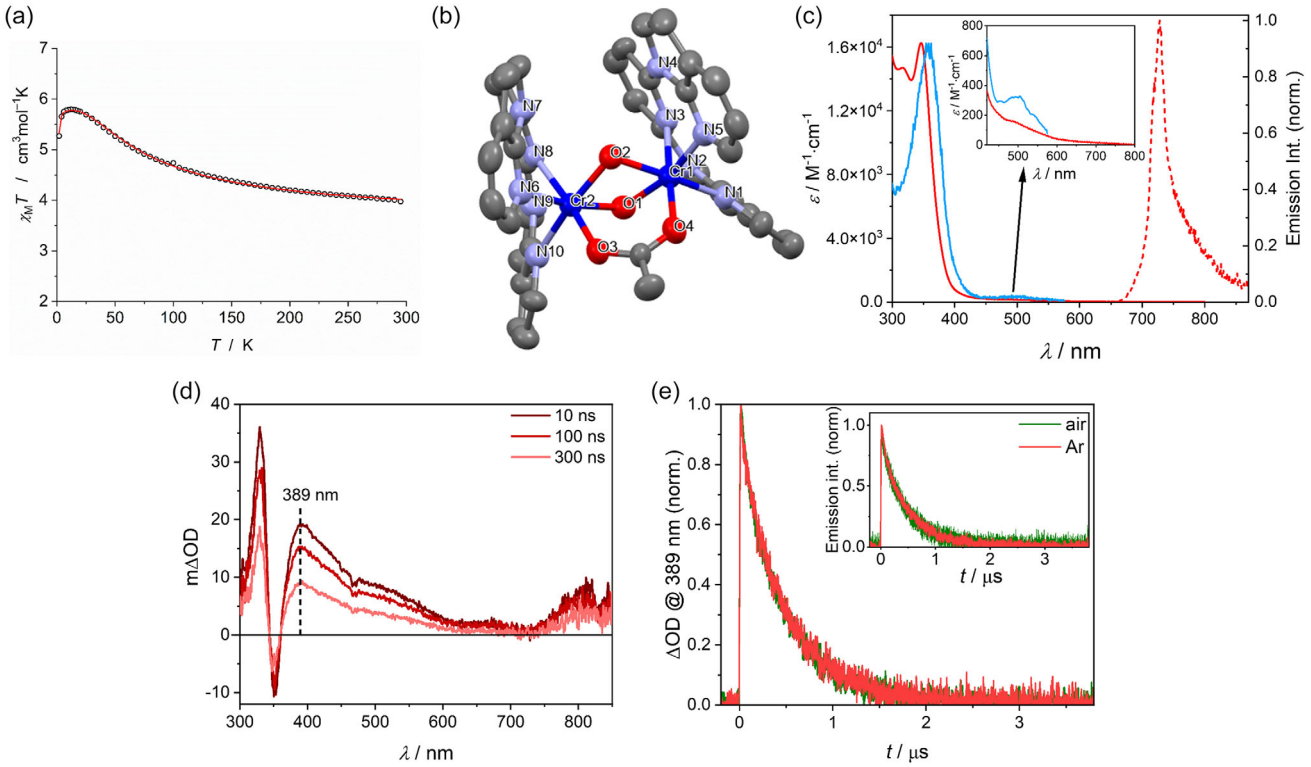

Figure 6. a) Variable-temperature magnetic susceptibility data for dinuclear $[Cr_2(dNinp)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)]^{3+}$. The red curve represents the best fit with the parameters: $J = +9.3\ cm^{-1}$ and $g_1 = g_2 = 1.97$. b) Single-crystal structure of the dinuclear Cr^{III} complex. Hydrogen atoms, counter ions, and solvents are omitted. Thermal ellipsoids drawn at 50% probability. c) UV/vis absorption spectrum of $[Cr_2(dNinp)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)]^{3+}$, together with the excitation spectrum (emission at 728 nm) (bright blue solid trace) and the normalized luminescence spectrum in deaerated acetonitrile at 20 °C (excitation at 350 nm) (red dotted trace). Inset: Enlarged UV/vis absorption and excitation spectra. d) Transient absorption spectra of the dinuclear Cr^{III} complex (80 µM) in aerated acetonitrile at 20 °C recorded with different time delays after excitation with a ns-pulsed laser at 355 nm. e) Normalized decays of the transient absorption signal of the Cr^{III} dimer at 389 nm from (d) together with the normalized luminescence decay at 728 nm (inset) in aerated and deaerated acetonitrile at 20 °C. Reproduced under the terms of the CC-BY license.[13] Copyright 2024, The Authors. Published by Wiley-VCH.

(Figure 6a), which is comparable to those for Cr^{III} dimers featuring the same bridging moieties,[71] but clearly lower than that found in di-thiolato- and carboxylato-bridged $[Cr_2L_2(\mu\text{-}SR)_2(\mu\text{-}O_2CR^2)]^{3+}$.[12] This is predominantly attributed to the shorter Cr—Cr distances for the alkoxido-bridged dimers than those with the thiolato-bridges, as previously discussed in Section 2.1.

For the dinuclear Cr^{III} complex, each metal center is tridentately coordinated with a dNinp ligand with strong σ-donating character, which gives an octahedral CrN_3O_3 coordination sphere with a ligand-field strength approximated to 10 Dq ≈ 20,000 cm^{-1}, according to the lowest-lying MC absorption band maximized at ≈ 500 nm (Figure 6c, inset).[13] This ligand-field strength is larger than that observed for the CrN_3S_2O coordination environment in $[Cr_2L_2(\mu\text{-}SR)_2(\mu\text{-}O_2CR^2)]^{3+}$ (10 Dq ≈ 17,500 cm^{-1}), due to the stronger σ-donating character of dNinp than the amine-based ligand.[12] Photoexcitation of $[Cr_2(dNinp)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)]^{3+}$ with green light leads to deep red luminescence maximized at ≈ 728 nm (Figure 6c, red dotted trace), with a luminescence quantum yield of Φ_{PL} ≈ 0.01 % and a lifetime of ≈ 450 ns in acetonitrile at room temperature.[13] UV/vis transient absorption studies with nanosecond-pulsed lasers revealed the same decay kinetics of the excited state absorption signal at 389 nm (Figure 6d,e). These photophysical properties are remarkable for dinuclear Cr^{III} complexes, and this study provides a novel design concept for luminescent Cr^{III} dimers with FM coupling.

2.4. Luminescent Dinuclear Cr^{III} Complexes for Energy Transfer and Photon Upconversion

Oxygen quenching of the spin-flip excited states occurs to many mononuclear Cr^{III} complexes via energy transfer with relatively low quenching rate constants in the order of $10^7\ M^{-1}\ s^{-1}$ in solution at room temperature.[17,20,98–101] For $[Cr_2(dNinp)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)]^{3+}$, this quenching event is kinetically hindered due to the relatively short lifetime of the $^2T_1{}^4A_2/^2E^4A_2$ excited states, which corresponds to a faster intrinsic decay from the excited states than the energy transfer to molecular oxygen.[13] However, this lifetime is sufficiently long for bimolecular energy transfer from the exchange-coupled quintet ($S = 2$) $^2T_1{}^4A_2/^2E^4A_2$ excited states to the lowest triplet state (T_1) of an organic chromophore (**Figure 7**a). This process is in principle a doublet–triplet energy transfer (DTET) because only one Cr^{III} ion is formally excited and involved in the energy transfer.[1,76] DTET is a spin-allowed process according to the Wigner spin conservation rule, in which the total spin of the donor/acceptor pair remains constant (Figure 7a).[102–104] This fundamentally novel type of bimolecular reaction allows the utilization of photosensitizers

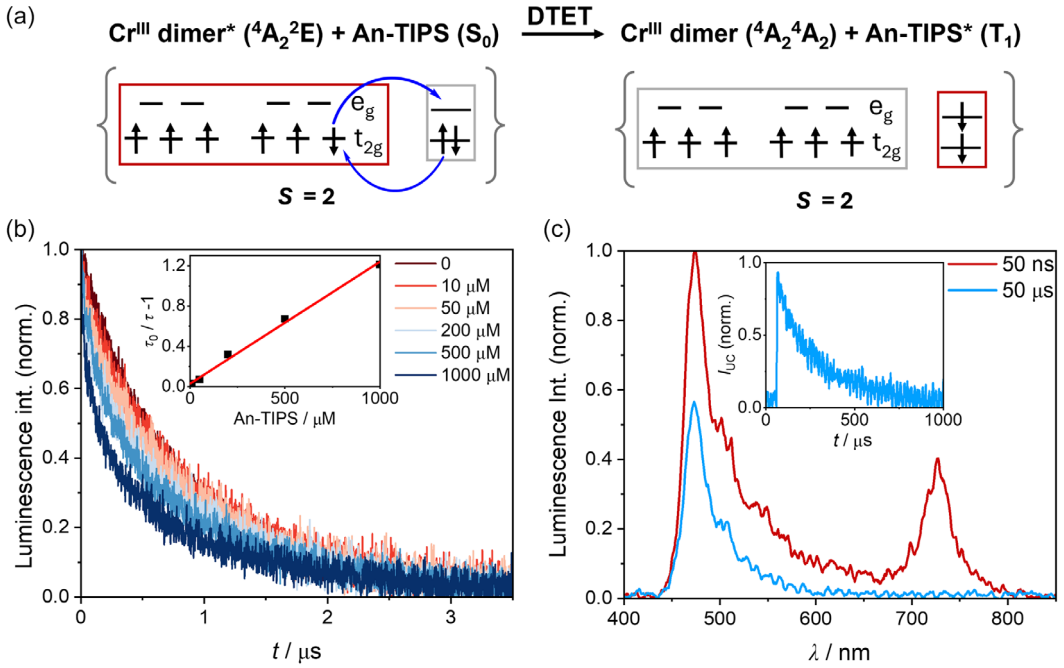

Figure 7. a) Reaction scheme of the luminescent dinuclear Cr^{III} complex and An-TIPS via DTET with their corresponding electronic microstates. b) Normalized luminescence lifetime quenching of $[Cr_2(dNinp)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)]^{3+}$ at 728 nm by An-TIPS with different concentrations in deaerated acetonitrile/toluene (1 : 1) at 20 °C. Excitation occurred at 532 nm with a ns-pulsed laser. Inset: Stern–Volmer plot based on lifetime quenching derived from the decays in the main plot. c) Luminescence spectra of the Cr^{III} dimer (100 µM)/An-TIPS (2.3 mM) pair in deaerated acetonitrile/toluene (1 : 1) at 20 °C recorded with different time delays and the luminescence decay at 470 nm (inset). Excitation occurred with a ns-pulsed laser at 532 nm (pulse energy of ≈50 mJ). Reproduced under the terms of the CC-BY license.[13] Copyright 2024, The Authors. Published by Wiley-VCH.

with doublet excited states for energy transfer-based applications, as recently investigated in photon upconversion with a mononuclear Cr^{III} complex,[41] Fe(III) complexes with a doublet ligand-to-metal charge transfer state,[47,60,105,106] and organic π-radicals with a doublet excited state.[107,108]

Exergonic DTET occurs from the dinuclear Cr^{III} complex to An-TIPS (9,10-bis((triisopropylsilyl)ethynyl)anthracene), a frequently used blue-emissive annihilator,[42,109,110] as evidenced with the quenched luminescence lifetime of the Cr^{III} dimer. This gives a rate constant k_{DTET} of 1.63×10^9 M^{-1} s^{-1} that is below the diffusion limit of the employed solvents.[13] For the Cr^{III} dimer/An-TIPS pair, selective excitation at 532 nm gives blue upconversion luminescence from An-TIPS maximized at 470 nm, which shows a delayed nature with a lifetime of 222 µs.[13] This study opens the door of using photoluminescent dinuclear Cr^{III} complexes for energy transfer-based applications.

3. Summary and Outlook

In this concept, we analyzed the recent methodologies for preparing ferromagnetically coupled dinuclear Cr^{III} complexes, reviewed the photophysical properties of dinuclear Cr^{III} complexes from the modern aspects of coordination chemistry, and provided a design strategy of developing dinuclear Cr^{III} complexes featuring both ferromagnetic exchange interactions and promising photoluminescence properties. To do so, the two Cr^{III} ions can be triply bridged with one carboxylate- and two hydroxo- or thiolato-groups to make ferromagnetic exchange interactions dominant.[12,71] To make dinuclear Cr^{III} complexes photoluminescent, multidentate chelating ligands with strong σ-donating/π accepting character are desired to generate a large ligand field splitting, which diminishes the back intersystem crossing.[31,81] Meanwhile, six-membered rings are expected to be formed with the metal center, leading to a nearly octahedral geometry with high molecular rigidity that suppresses the nonradiative decays of the excited states.[18,84] Following these guidelines, the obtained dinuclear Cr^{III} complex shows ferromagnetic coupling in the ground state and deep red luminescence from the excited states with sub-microsecond lifetime in solution at room temperature.[13] The exchange-coupled excited states in such dinuclear Cr^{III} complexes enable spin-allowed energy transfer to the triplet state of an organic chromophore, making them promising photosensitizers for energy transfer-based applications, such as photon upconversion and energy transfer catalysis. Such dinuclear Cr^{III} complexes, which feature ferromagnetic coupling and photoluminescence properties, could be attractive photomagnetic molecules for quantum data storage[89,111] or fundamentally novel photosensitizers that allow light energy conversion facilitated by magnetism.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: dinuclear chromium(III) complexes · doublet–triplet energy transfer · ferromagnetic coupling · photoluminescence · photon upconversion

[1] P. J. McCarthy, H. U. Güdel, *Coord. Chem. Rev.* **1988**, *88*, 69.
[2] A. Døssing, *Coord. Chem. Rev.* **2014**, *280*, 38.
[3] P. Andersen, *Coord. Chem. Rev.* **1989**, *94*, 47.
[4] J. Springborg, *Adv. Inorg. Chem.* **1988**, *32*, 55.
[5] P. W. Ball, *Coord. Chem. Rev.* **1969**, *4*, 361.
[6] E. Coronado, *Nat. Rev. Mater.* **2020**, *5*, 87.
[7] T. J. Morsing, J. Bendix, H. Weihe, A. Døssing, *Inorg. Chem.* **2014**, *53*, 2996.
[8] H. W. L. Fraser, G. S. Nichol, G. Velmurugan, G. Rajaraman, E. K. Brechin, *Dalton Trans.* **2017**, *46*, 7159.
[9] C. Reber, H. U. Güdel, L. Spiccia, W. Marty, *Inorg. Chem.* **1987**, *26*, 3186.
[10] R. Sanzenbacher, A. Böttcher, H. Elias, M. Hüber, W. Haase, J. Glerup, T. B. Jensen, M. Neuburger, M. Zehnder, J. Springborg, C. E. Olsen, *Inorg. Chem.* **1996**, *35*, 7493.
[11] T. J. Morsing, H. Weihe, J. Bendix, *Eur. J. Inorg. Chem.* **2014**, *35*, 5990.
[12] M. Börner, J. Klose, M. E. Gutierrez Suburu, C. A. Strassert, F. Yang, K. Y. Monakhov, B. Abel, B. Kersting, *Chem. Eur. J.* **2021**, *27*, 14899.
[13] S. Trippmacher, S. Demeshko, A. Prescimone, F. Meyer, O. S. Wenger, C. Wang, *Chem. Eur. J.* **2024**, *30*, e202400856.
[14] J. Ferguson, H. U. Güdel, *Aust. J. Chem.* **1973**, *26*, 505.
[15] S. Decurtins, H. U. Güdel, A. Pfeuti, *Inorg. Chem.* **1982**, *21*, 1101.
[16] S. Decurtins, H. U. Güdel, *Inorg. Chem.* **1982**, *21*, 3598.
[17] S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem., Int. Ed.* **2015**, *54*, 11572.
[18] S. Otto, M. Dorn, C. Förster, M. Bauer, M. Seitz, K. Heinze, *Coord. Chem. Rev.* **2018**, *359*, 102.
[19] S. Treiling, C. Wang, C. Förster, F. Reichenauer, J. Kalmbach, P. Boden, J. P. Harris, L. M. Carrella, E. Rentschler, U. Resch-Genger, C. Reber, M. Seitz, M. Gerhards, K. Heinze, *Angew. Chem., Int. Ed.* **2019**, *58*, 18075.
[20] F. Reichenauer, C. Wang, C. Förster, P. Boden, N. Ugur, R. Báez-Cruz, J. Kalmbach, L. M. Carrella, E. Rentschler, C. Ramanan, G. Niedner-Schatteburg, M. Gerhards, M. Seitz, U. Resch-Genger, K. Heinze, *J. Am. Chem. Soc.* **2021**, *143*, 11843.
[21] N. Sinha, C. Wegeberg, D. Häussinger, A. Prescimone, O. S. Wenger, *Nat. Chem.* **2023**, *15*, 1730.
[22] J. R. Jiménez, B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *J. Am. Chem. Soc.* **2019**, *141*, 13244.
[23] N. R. East, R. Naumann, C. Förster, C. Ramanan, G. Diezemann, K. Heinze, *Nat. Chem.* **2024**, *16*, 827.
[24] P. Herr, C. Kerzig, C. B. Larsen, D. Häussinger, O. S. Wenger, *Nat. Chem.* **2021**, *13*, 956.
[25] K. S. Kjær, N. Kaul, O. Prakash, P. Chábera, N. W. Rosemann, A. Honarfar, O. Gordivska, L. A. Fredin, K.-E. Bergquist, L. Häggström, T. Ericsson, L. Lindh, A. Yartsev, S. Styring, P. Huang, J. Uhlig, J. Bendix, D. Strand, V. Sundström, P. Persson, R. Lomoth, K. Wärnmark, *Science* **2019**, *363*, 249.
[26] J. D. Braun, I. B. Lozada, C. Kolodziej, C. Burda, K. M. E. Newman, J. van Lierop, R. L. Davis, D. E. Herbert, *Nat. Chem.* **2019**, *11*, 1144.
[27] J. Steube, A. Kruse, O. S. Bokareva, T. Reuter, S. Demeshko, R. Schoch, M. A. Arguello Cordero, A. Krishna, S. Hohloch, F. Meyer, K. Heinze, O. Kühn, S. Lochbrunner, M. Bauer, *Nat. Chem.* **2023**, *15*, 468.
[28] M. Gernert, L. Balles-Wolf, F. Kerner, U. Muller, A. Schmiedel, M. Holzapfel, C. M. Marian, J. Pflaum, C. Lambert, A. Steffen, *J. Am. Chem. Soc.* **2020**, *142*, 8897.
[29] D. Kim, M. C. Rosko, F. N. Castellano, T. G. Gray, T. S. Teets, *J. Am. Chem. Soc.* **2024**, *146*, 19193.
[30] R. Hamze, J. L. Peltier, D. Sylvinson, M. Jung, J. Cardenas, R. Haiges, M. Soleilhavoup, R. Jazzar, P. I. Djurovich, G. Bertrand, M. E. Thompson, *Science* **2019**, *363*, 601.
[31] C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, *49*, 1057.
[32] N. Sinha, O. S. Wenger, *J. Am. Chem. Soc.* **2023**, *145*, 4903.
[33] M. V. Appleby, R. A. Cowin, P. I. Djurovich, P. C. Ford, C. Förster, K. Heinze, M. Kato, W.-K. Kwok, A. J. Morris, J. S. Benjamin Thomas, M. E. Thompson, P. S. Wagenknecht, J. A. Weinstein, V. Wing-Wah Yam *Contributors for book Advances in Inorganic Chemistry*, Academic Press Inc, San Diego **2024**, pp. 1–314.
[34] X. L. Xin, M. Chen, Y. B. Ai, F. L. Yang, X. L. Li, F. Li, *Inorg. Chem.* **2014**, *53*, 2922.
[35] C. Wang, S. Otto, M. Dorn, K. Heinze, U. Resch-Genger, *Anal. Chem.* **2019**, *91*, 2337.
[36] S. Otto, J. P. Harris, K. Heinze, C. Reber, *Angew. Chem., Int. Ed.* **2018**, *57*, 11069.
[37] S. Otto, N. Scholz, T. Behnke, U. Resch-Genger, K. Heinze, *Chem. Eur. J.* **2017**, *23*, 12131.
[38] S. Dehnen, J. W. Steed, K. Lo, K. Heinze, O. S. Wenger, S. Singh, H.-B. Yang, S.-Q. Zang, *Inorg. Chem.* **2023**, *62*, 14823.
[39] L. P. Ravaro, K. P. S. Zanoni, A. S. S. de Camargo, *Energy Rep.* **2020**, *6*, 37.
[40] V. Ferraro, C. Bizzarri, S. Bräse, *Adv. Sci.* **2024**, *11*, e2404866.
[41] C. Wang, F. Reichenauer, W. R. Kitzmann, C. Kerzig, K. Heinze, U. Resch-Genger, *Angew. Chem., Int. Ed.* **2022**, *61*, e202202238.
[42] C. Wang, C. Wegeberg, O. S. Wenger, *Angew. Chem., Int. Ed.* **2023**, *62*, e202311470.
[43] F. Glaser, O. S. Wenger, *JACS Au* **2022**, *2*, 1488.
[44] K. M. Felter, M. C. Fravventura, E. Koster, R. D. Abellon, T. J. Savenije, F. C. Grozema, *ACS Energy Lett.* **2020**, *5*, 124.
[45] J. A. Kübler, B. Pfund, O. S. Wenger, *JACS Au* **2022**, *2*, 2367.
[46] Z. Mahmood, N. Rehmat, S. Ji, J. Zhao, S. Sun, M. Di Donato, M. Li, M. Teddei, Y. Huo, *Chemistry* **2020**, *26*, 14912.
[47] P. Jin, X. Xu, Y. Yan, H. Hammecke, C. Wang, *J. Am. Chem. Soc.* **2024**, *146*, 35390.
[48] W. R. Kitzmann, M. S. Bertrams, P. Boden, A. C. Fischer, R. Klauer, J. Sutter, R. Naumann, C. Förster, G. Niedner-Schatteburg, N. H. Bings, J. Hunger, C. Kerzig, K. Heinze, *J. Am. Chem. Soc.* **2023**, *145*, 16597.
[49] M. Yang, S. Sheykhi, Y. Zhang, C. Milsmann, F. N. Castellano, *Chem. Sci.* **2021**, *12*, 9069.
[50] B. M. Hockin, C. Li, N. Robertson, E. Zysman-Colman, *Catal. Sci. Technol.* **2019**, *9*, 889.
[51] P. A. Scattergood, *Recent Advances in Chromium Coordination Chemistry: Luminescent Materials and Photocatalysis*, Vol. *43*, Royal Society of Chemistry, Cambridge **2020**, pp. 1–34.
[52] M. D. Woodhouse, J. K. McCusker, *J. Am. Chem. Soc.* **2020**, *142*, 16229.
[53] A. Aydogan, R. E. Bangle, A. Cadranel, M. D. Turlington, D. T. Conroy, E. Cauët, M. L. Singleton, G. J. Meyer, R. N. Sampaio, B. Elias, L. Troian-Gautier, *J. Am. Chem. Soc.* **2021**, *143*, 15661.
[54] T. H. Bürgin, F. Glaser, O. S. Wenger, *J. Am. Chem. Soc.* **2022**, *144*, 14181.
[55] S. Sittel, R. Naumann, K. Heinze, *Front. Chem.* **2022**, *10*, 887439.
[56] J. Beaudelot, S. Oger, S. Peruško, T. A. Phan, T. Teunens, C. Moucheron, G. Evano, *Chem. Rev.* **2022**, *122*, 16365.
[57] L. H. M. de Groot, A. Ilic, J. Schwarz, K. Wärnmark, *J. Am. Chem. Soc.* **2023**, *145*, 9369.
[58] A. Y. Chan, A. Ghosh, J. T. Yarranton, J. Twilton, J. Jin, D. M. Arias-Rotondo, H. A. Sakai, J. K. McCusker, D. W. C. MacMillan, *Science* **2023**, *382*, 191.
[59] Y. Ye, P. Garrido-Barros, J. Wellauer, C. M. Cruz, R. Lescouëzec, O. S. Wenger, J. M. Herrera, J. R. Jiménez, *J. Am. Chem. Soc.* **2024**, *146*, 954.
[60] J. Wellauer, F. Ziereisen, N. Sinha, A. Prescimone, A. Velic, F. Meyer, O. S. Wenger, *J. Am. Chem. Soc.* **2024**, *146*, 11299.
[61] S. De Kreijger, A. Ripak, B. Elias, L. Troian-Gautier, *J. Am. Chem. Soc.* **2024**, *146*, 10286.
[62] C. Wang, H. Li, T. H. Bürgin, O. S. Wenger, *Nat. Chem.* **2024**, *16*, 1151.
[63] C. Wang, S. Otto, M. Dorn, E. Kreidt, J. Lebon, L. Srsan, P. Di Martino-Fumo, M. Gerhards, U. Resch-Genger, M. Seitz, K. Heinze, *Angew. Chem., Int. Ed.* **2018**, *57*, 1112.
[64] J. R. Jiménez, M. Poncet, S. Miguez-Lago, S. Grass, J. Lacour, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *Angew. Chem., Int. Ed.* **2021**, *60*, 10095.
[65] F. Reichenauer, R. Naumann, C. Förster, W. R. Kitzmann, A.-P. M. Reponen, S. Feldmann, K. Heinze, *Chem. Sci.* **2024**, *15*, 20251.
[66] S. Sittel, A. C. Sell, K. Hofman, C. Wiedemann, J. P. Nau, C. Kerzig, G. Manolikakes, K. Heinze, *ChemCatChem* **2023**, *15*, e202201562.
[67] F. A. Baptista, D. Krizsan, M. Stitch, I. V. Sazanovich, I. P. Clark, M. Towrie, C. Long, L. Martinez-Fernandez, R. Improta, N. A. P. Kane-Maguire, J. M. Kelly, S. J. Quinn, *J. Am. Chem. Soc.* **2021**, *143*, 14766.
[68] W. R. Kitzmann, K. Heinze, *Angew. Chem., Int. Ed.* **2022**, *62*, e202213207.
[69] C. Wang, K. Ebel, K. Heinze, U. Resch-Genger, I. Bald, *Chem. Eur. J.* **2023**, *29*, e202203719.
[70] O. Kahn, *Angew. Chem., Int. Ed.* **1985**, *24*, 834.
[71] H. W. L. Fraser, L. Smythe, S. Dey, G. S. Nichol, S. Piligkos, G. Rajaraman, E. K. Brechin, *Dalton Trans.* **2018**, *47*, 8100.

[72] R. H. Duncan Lyngdoh, H. F. Schaefer III, R. B. King, *Chem. Rev.* **2018**, *118*, 11626.
[73] F. S. Delgado, J. Sanchiz, T. López, F. Lloret, M. Julve, C. Ruiz-Pérez, *CrystEngComm* **2010**, *12*, 2711.
[74] L.-L. Wang, Y.-M. Sun, Z.-N. Qi, C.-B. Liu, *J. Phys. Chem. A* **2008**, *112*, 8418.
[75] A. Niemann, U. Bossek, K. Wieghardt, C. Butzlaff, A. X. Trautwein, B. Nuber, *Angew. Chem., Int. Ed.* **1992**, *31*, 311.
[76] H. Riesen, H. U. Güdel, *Mol. Phys.* **1987**, *60*, 1221.
[77] M. Morita, S. Shionoya, *J. Phys. Soc. Jpn.* **1970**, *28*, 134.
[78] C. D. Flint, P. Greenough, *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1469.
[79] R. Schenker, H. Weihe, H. U. Güdel, B. Kersting, *Inorg. Chem.* **2001**, *40*, 3355.
[80] A. D. Kirk, *Chem. Rev.* **1999**, *99*, 1607.
[81] E. M. S. Maçôas, R. Kananavicius, P. Myllyperkiö, M. Pettersson, H. Kunttu, *J. Am. Chem. Soc.* **2007**, *129*, 8934.
[82] V. Balzani, G. Bergamini, S. Campagna, F. Puntoriero, *Photochemistry and Photophysics of Coordination Compounds: Overview and General Concepts* (Eds: V. Balzani, S. Campagna), Vol. *280*, Springer, Berlin, Heidelberg **2007**, pp. 1–36.
[83] N. Serpone, M. A. Jamieson, M. S. Henry, M. Z. Hoffman, F. Bolletta, M. Maestri, *J. Am. Chem. Soc.* **1979**, *101*, 2907.
[84] O. Prakash, P. Chabera, N. Kaul, V. F. Hlynsson, N. W. Rosemann, I. B. Losada, Y. T. Hoang Hai, P. Huang, J. Bendix, T. Ericsson, L. Haggstrom, A. K. Gupta, D. Strand, A. Yartsev, R. Lomoth, P. Persson, K. Warnmark, *Inorg. Chem.* **2024**, *63*, 4461.
[85] L. S. Forster, *Coord. Chem. Rev.* **2002**, *227*, 59.
[86] N. Sinha, P. Yaltseva, O. S. Wenger, *Angew. Chem., Int. Ed.* **2023**, *62*, e202303864.
[87] F. Reichenauer, D. Zorn, R. Naumann, C. Förster, K. Heinze, *Inorg. Chem.* **2024**, *63*, 23487.
[88] Y. Ye, C. M. Cruz, B. Doistau, E. Colacio, C. Piguet, J. M. Herrera, J. R. Jimenez, *Inorg. Chem.* **2024**, *63*, 23886.
[89] T. J. Penfold, J. O. Johansson, J. Eng, *Coord. Chem. Rev.* **2023**, *494*, 215346.
[90] C. Förster, M. Dorn, T. Reuter, S. Otto, G. Davarci, T. Reich, L. Carrella, E. Rentschler, K. Heinze, *Inorganics* **2018**, *6*, 86.
[91] C. Förster, K. Mack, L. M. Carrella, V. Ksenofontov, E. Rentschler, K. Heinze, *Polyhedron* **2013**, *52*, 576.
[92] C. Förster, T. E. Gorelik, U. Kolb, V. Ksenofontov, K. Heinze, *Eur. J. Inorg. Chem.* **2015**, *2015*, 920.
[93] S. L. Dabb, N. C. Fletcher, *Dalton Trans.* **2015**, *44*, 4406.
[94] A. Squarcina, D. Fehn, L. Senft, J. Langer, I. Ivanović-Burmazović, *Z. Anorg. Allg. Chem.* **2021**, *647*, 809.
[95] A. Medina-Molner, M. Rohner, D. Pandiarajan, B. Spingler, *Dalton Trans.* **2015**, *44*, 3664.
[96] S. Tanase, I. A. Koval, E. Bouwman, R. de Gelder, J. Reedijk, *Inorg. Chem.* **2005**, *44*, 7860.
[97] G. A. Parada, L. A. Fredin, M. P. Santoni, M. Jäger, R. Lomoth, L. Hammarström, O. Johansson, P. Persson, S. Ott, *Inorg. Chem.* **2013**, *52*, 5128.
[98] A. Pfeil, *J. Am. Chem. Soc.* **1971**, *93*, 5395.
[99] B. Brunschwig, N. Sutin, *J. Am. Chem. Soc.* **1978**, *100*, 7568.
[100] L. Stein, C. Wang, C. Förster, U. Resch-Genger, K. Heinze, *Dalton Trans.* **2022**, *51*, 17664.
[101] A. M. M. Alazaly, G. J. Clarkson, M. D. Ward, A. A. Abdel-Shafi, *Inorg. Chem.* **2023**, *62*, 16101.
[102] E. Wigner, *Math Physik, Kl, IIa* **1927**, 375.
[103] A. R. Lee, C. S. Enos, A. G. Brenton, *Int. J. Mass Spectrom. Ion Processes* **1991**, *104*, 49.
[104] D. Guo, T. E. Knight, J. K. McCusker, *Science* **2011**, *334*, 1684.
[105] J. Wellauer, B. Pfund, I. Becker, F. Meyer, A. Prescimone, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, *147*, 8760.
[106] F. Glaser, S. De Kreijger, L. Troian-Gautier, *J. Am. Chem. Soc.* **2025**, *147*, 8559.
[107] J. Han, Y. Jiang, A. Obolda, P. Duan, F. Li, M. Liu, *J. Phys. Chem. Lett.* **2017**, *8*, 5865.
[108] Y. Wei, K. An, X. Xu, Z. Ye, X. Yin, X. Cao, C. Yang, *Adv. Optical Mater.* **2023**, *12*, 2301134.
[109] H. Tamura, *J. Phys. Chem. A* **2020**, *124*, 7943.
[110] H. Hammecke, D. Fritzler, N. Vashistha, P. Jin, B. Dietzek-Ivanšić, C. Wang, *Chem. Eur. J.* **2024**, *30*, e202402679.
[111] A. Stupakiewicz, K. Szerenos, D. Afanasiev, A. Kirilyuk, A. V. Kimel, *Nature* **2017**, *542*, 71.

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