



Review

Understanding and exploiting long-lived near-infrared emission of a molecular ruby



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ABSTRACT

Enabling strong and long-lived NIR emission from complexes with earth-abundant metal ions is exemplified by embedding chromium(III) in a very strong ligand field yielding the molecular ruby $[\text{Cr}(\text{ddpd})_2]^{3+}$. This review aims at illustrating the main non-radiative decay pathways for electronically excited chromium(III) complexes, namely back-intersystem crossing, excited state distortion and multiphonon relaxation and at controlling these pathways by molecular design. The case study of $[\text{Cr}(\text{ddpd})_2]^{3+}$ highlights recent successful design strategies and discusses first applications of the highly emissive 3d metal complex as optical sensor molecule and as photosensitizer.

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1. Introduction

Near-infrared (NIR) luminescence is a strongly growing research field due to its increasing importance in cutting-edge technological applications such as photovoltaic spectral conversion

[1], optical telecommunication [2], light upconverting materials [3], chemical sensors, or bioimaging [4]. Triplet metal-to-ligand charge transfer (³MLCT) emitters based on d⁶, d⁸ or d¹⁰ metal ions such as ruthenium(II), gold(III) or copper(I) can suffer from strong excited state distortions [5]. This can lead to efficient non-radiative relaxation via direct surface crossing of the ³MLCT and the ground state and hence to low photoluminescence quantum yields [5]. In the excited states of emissive lanthanoid complexes, such as

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europium(III) or neodymium(III) complexes, excited state distortions are typically absent, leading to long-lived emission with sharp emission bands [6].

Transition metal ions with d^3 electron configuration, e.g., chromium(III) [8] or manganese(IV) [9], experience a comparable electronic situation enabling sharp emission bands as exemplified by the famous 694 nm emission of ruby (Cr^{III} in Al_2O_3) [10]. After excitation in the ligand field bands of chromium(III) in an octahedral field (${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$; ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$), intersystem crossing (ISC) leads to population of the emissive doublet states (${}^2\text{E}_g$, ${}^2\text{T}_{1g}$; Fig. 1). For typical molecular chromium(III) complexes, such as $[\text{Cr}(\text{tpy})_2]^{3+}$ or $[\text{Cr}(\text{urea})_6]^{3+}$ however, the ligand field splitting is not as strong as in ruby (Scheme 1) [4,11]. This enables back-ISC processes (k_{BISC}) from the doublet states to the ${}^4\text{T}_{2g}$ state followed by fluorescence, dissociation/substitution (k_{chem}) or non-radiative relaxation via the Jahn–Teller distorted ${}^4\text{T}_{2g}$ state (Fig. 1b) [8]. Consequently, the photoluminescence quantum yields of chromium(III) complexes are not particularly high [4]. Prior to our work, the highest quantum yield has been reported for $[\text{Cr}(\text{phen})_3]^{3+}$ with $\Phi = 0.15\%$ [4]. Other deactivation pathways of tris(bidentate) complexes such as $[\text{Cr}(\text{bpy})_3]^{3+}$, $[\text{Cr}(\text{phen})_3]^{3+}$ or $[\text{Cr}(\text{en})_3]^{3+}$ could be enabled by the trigonal distortion of these complexes as has also been suggested for some trigonally distorted cage complexes of chromium(III) (Fig. 1b; k_{trig}) [12]. In these trigonally distorted complexes, the ${}^4\text{A}_{2g}(\text{O}_h)$ ground state and the ${}^4\text{T}_{2g}(\text{O}_h)$ ligand field excited state mix to give a higher energy ${}^4\text{E}'(\text{D}_{3h})$ ground state and a ${}^4\text{E}''(\text{D}_{3h})$ excited state with a reduced energy difference according to angular overlap calculations (Fig. 1b; k_{trig}) [12]. A further relevant excited

state decay of the low-energy doublet states of chromium(III) complexes is a multiphonon relaxation pathway provided by high-energy oscillators such as CH, NH or OH of the ligand or solvents similar to the situation encountered for NIR-emissive lanthanoid complexes (Fig. 1b, k_{nr}) [13,14].

This review summarizes the efforts on the design of the strongly NIR-emissive chromium(III) complex $[\text{Cr}(\text{ddpd})_2]^{3+}$ (molecular ruby) (Scheme 1), on the understanding of its electronic structure and its excited state dynamics and on initial applications of this NIR luminophor.

2. Tuning of the chelate ligand for photoluminescence

With the back-ISC process to the ${}^4\text{T}_{2g}$ state being one of the most important deactivating pathways of excited chromium(III) complexes, ligand design should increase the energy gap between the ${}^4\text{T}_{2g}$ and the ${}^2\text{E}_g$ states prohibiting the back-ISC (Fig. 1b). As the energy of the ${}^4\text{T}_{2g}$ state increases with increasing ligand field strength Δ_o while the energy of the ${}^2\text{E}_g$ and ${}^2\text{T}_{1g}$ doublet states is essentially independent from Δ_o , a strong ligand field is required delivering a system far to the right side of the ${}^2\text{E}_g/{}^4\text{T}_{2g}$ crossing point in the Tanabe–Sugano diagram (Fig. 1a; $\Delta_o/B > 20$).

To optimize the poor metal–ligand orbital overlap in $[\text{Cr}(\text{tpy})_2]^{3+}$ with the small 79° N–Cr–N bite angle, a ligand forming six-membered chelate rings and $\sim 90^\circ$ bite angles is employed, namely ddpd with a “N–CH₃” unit formally inserted between the pyridine rings of tpy (Scheme 1) [15]. Treatment of CrCl_2 with

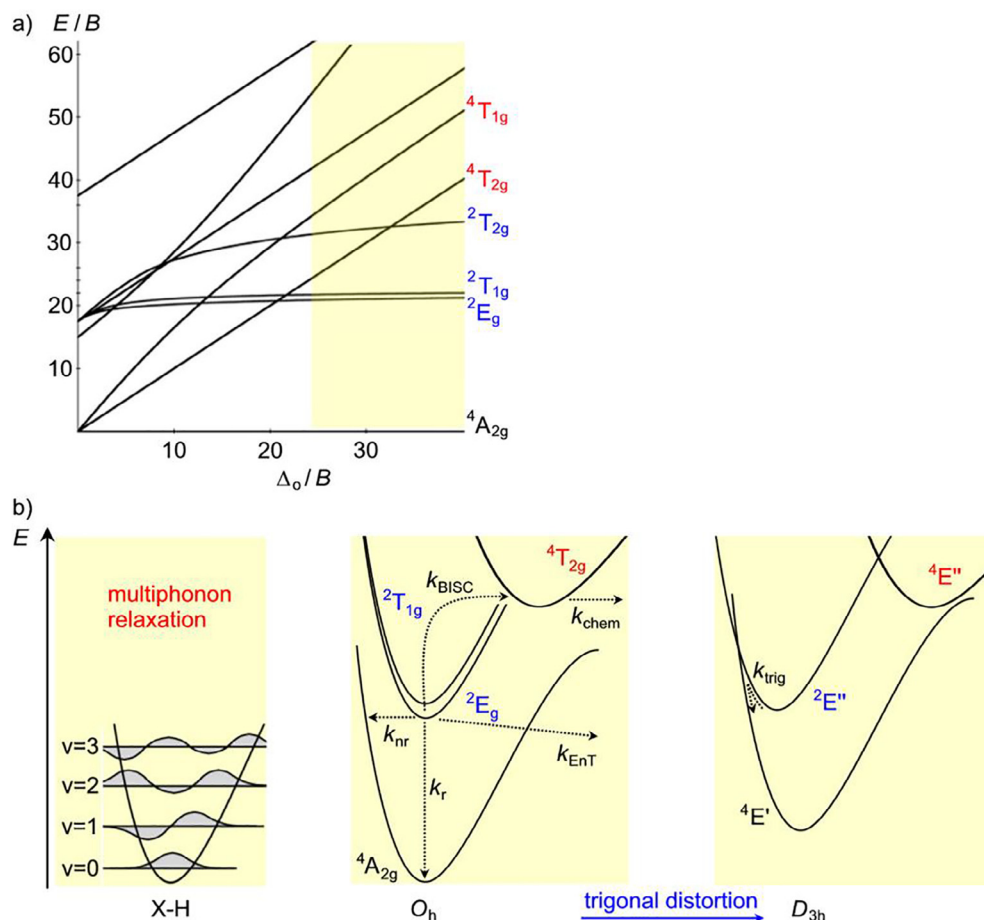


Fig. 1. (a) Tanabe–Sugano diagram [7] of the d^3 electron configuration ($C/B = 4$) with the important doublet and quartet states indicated and with the high-field region ($\Delta_o/B > 20$) highlighted and (b) schematic illustration of decay pathways of electronically excited chromium(III) complexes (radiative decay k_r ; back-ISC k_{BISC} ; chemical reaction k_{chem} ; electronic energy transfer k_{EnT}) (center); non-radiative decay via electronic-to-vibrational energy transfer to high-energy XH oscillators (k_{nr}) (left) and surface crossing in trigonally distorted complexes (k_{trig}) (right).

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