

Molecular Ruby: Exploring the Excited State Landscape

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Supporting Information

Experimental Details

Absorption spectra were recorded using a JASCO V770 spectrometer. Emission and excitation spectra were recorded using an FLS1000 (Edinburgh Instruments) spectrofluorometer with a xenon lamp (Xe2) as excitation source and the photomultipliers N-G11 PMT-980 (250–980 nm) as well as the liquid nitrogen cooled Hamamatsu N-G09 PMT-1700 (500–1700 nm) were used for detection. The absolute fluorescence quantum yield of $[\text{Cr}(\text{ddpd})_2]^{3+}$ was determined using the FLS1000 spectrofluorometer and an integrating sphere setup. Deconvolution of the absorption and emission spectra was performed using the software OriginPro 9.0.

Fs-Transient absorption spectra were measured using a Helios-Fire pump-probe setup (Ultrafast Systems) paired with a regeneratively amplified 1030 nm laser (Pharos, Light Conversion, 1030 nm, 200 fs, 200 μJ). The effective laser repetition rate of 1 kHz was set via an internal pulse picker. A small portion of the 1030 nm fundamental is directed to the optical delay line and is subsequently used to generate broadband probe light by focusing onto a sapphire (visible range) or YAG (NIR range) crystal. The pump pulse is generated with an optical parametric amplifier (Orpheus-F, Light Conversion). The pump fluence at the sample was 1 $\mu\text{J}/\text{pulse}$. Samples were measured in 1 mm path length cuvettes, with an OD of 0.4 at 500 nm. Global analysis of the TA data was done using the R-package TIMP software with the graphical interface Glotaran 1.5.1.¹

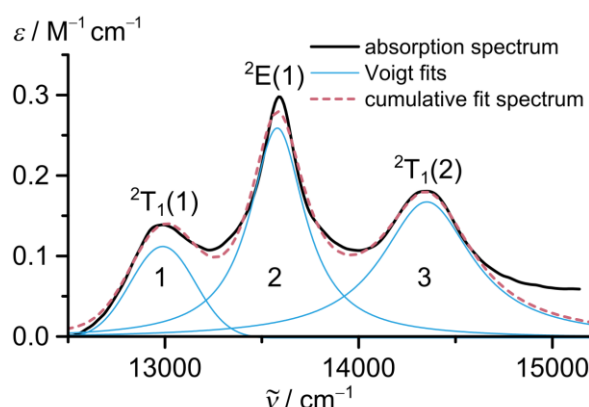


Figure S1: Experimental absorption spectrum of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in CD_3CN (120 mM) in the region of the spin-forbidden ${}^4\text{A}_2 \rightarrow {}^2\text{T}_1/{}^2\text{E}$ transitions with Voigt fits.

Table S1: Parameters of the Voigt fits of the absorption spectrum of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in CD_3CN (120 mM) in the region of the spin-forbidden ${}^4\text{A}_2 \rightarrow {}^2\text{T}_1/{}^2\text{E}$ absorptions. The assignment is based on CASSCF(7,12)-FIC-NEVPT2 calculations.²

Fit	Peak position / cm^{-1} (in nm)	$\epsilon_{\text{max}} / \text{M}^{-1} \text{cm}^{-1}$	FWHM / cm^{-1}	Norm. area	Assignment
1	12989 (770)	0.11	395	1.00	${}^4\text{A}_2 \rightarrow {}^2\text{T}_1(1)$
2	13580 (736)	0.26	346	2.96	${}^4\text{A}_2 \rightarrow {}^2\text{E}(1)$
3	14352 (697)	0.17	572	3.17	${}^4\text{A}_2 \rightarrow {}^2\text{T}_1(2)$

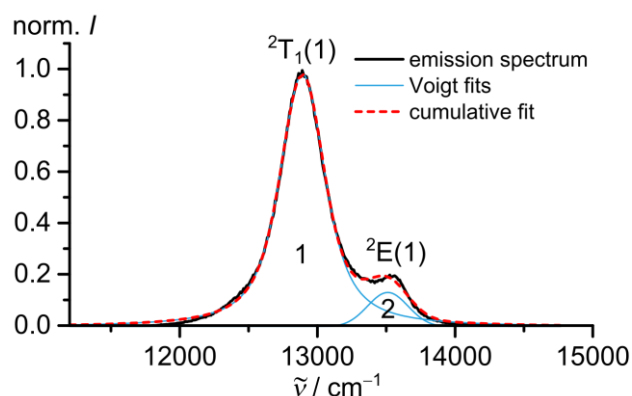


Figure S2: Phosphorescence spectrum of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in acetonitrile at 293 K fitted with two Voigt functions.

Table S2: Parameters of the Voigt fits of the phosphorescence spectrum of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in acetonitrile at 293 K. The assignment is based on CASSCF(7,12)-FIC-NEVPT2 calculations.²

Fit	Peak position / cm^{-1} (in nm)	FWHM / cm^{-1}	Norm. area	
1	12889 (776)	392	1.00	${}^2\text{T}_1(1) \rightarrow {}^4\text{A}_2$
2	13509 (740)	345	0.091	${}^2\text{E}(1) \rightarrow {}^4\text{A}_2$

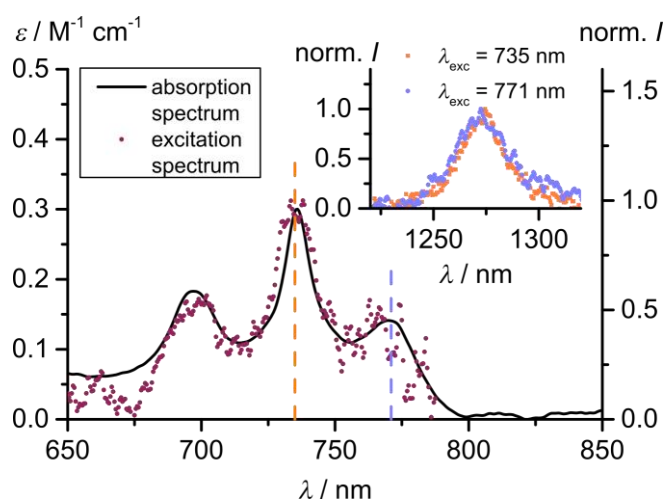


Figure S3: Absorption and excitation spectrum ($\lambda_{\text{em}} = 1274 \text{ nm}$) of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in aerated CD_3CN (120 mM) in the region of spin-forbidden ${}^4\text{A}_2 \rightarrow {}^2\text{T}_1/{}^2\text{E}$ transitions. Inset: ${}^1\text{O}_2$ phosphorescence spectra sensitized by $[\text{Cr}(\text{ddpd})_2]^{3+}$ with excitation at 735 and 771 nm, respectively.

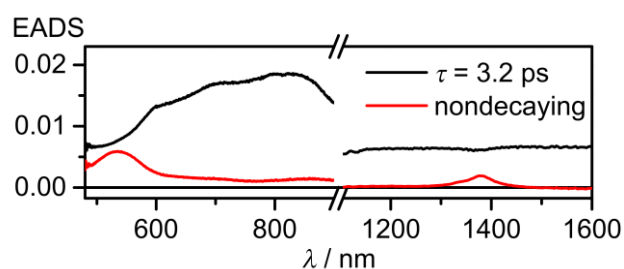


Figure S4: Evolution-associated difference spectrum (EADS) obtained from fs-transient absorption data of $[\text{Cr}(\text{ddpd})_2]^{3+}$ in CH_3CN ($\lambda_{\text{exc}} = 435 \text{ nm}$).

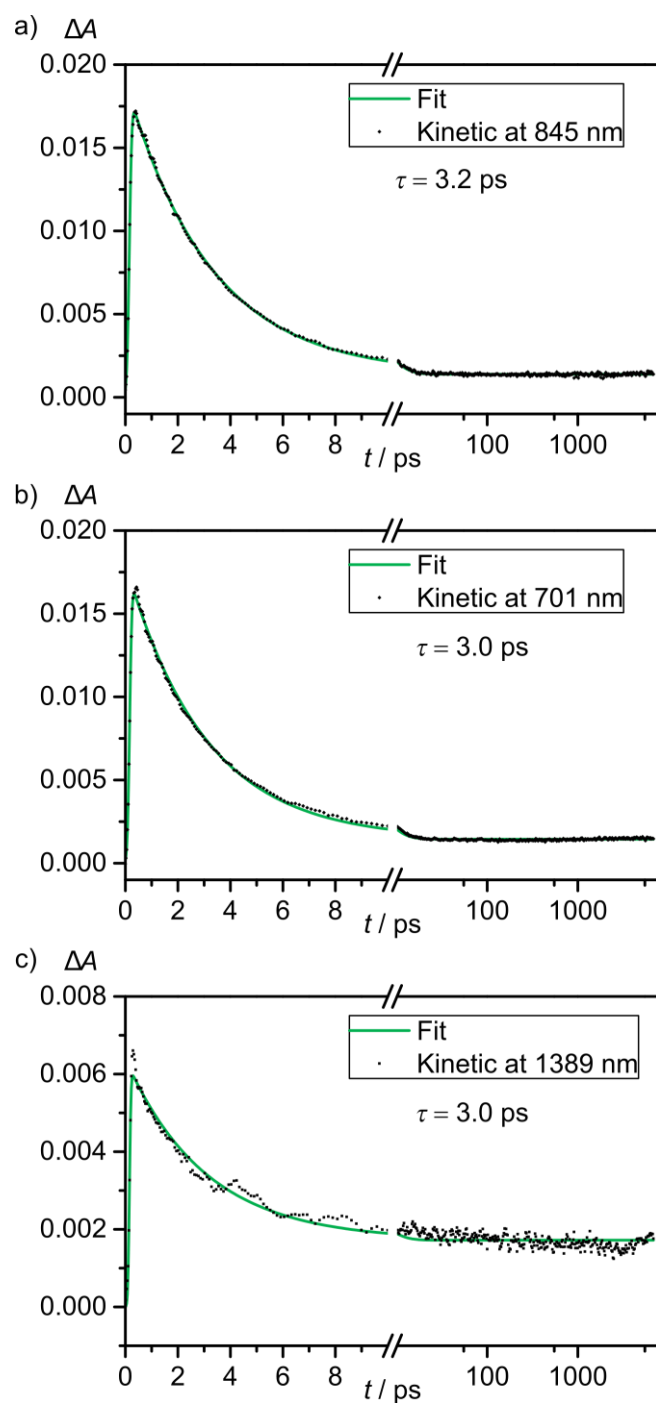


Figure S5: Decay traces of the TA signal of $[\text{Cr}(\text{ddpd})_2]^{3+}$ ($\lambda_{\text{exc}} = 435$ nm) in CH_3CN with monoexponential fits.

References

- 1 J. J. Snellenburg, S. P. Laptinok, R. Seger, K. M. Mullen and I. H. M. van Stokkum, *J. Stat. Soft.*, 2012, **49**.
- 2 S. Otto, J. P. Harris, K. Heinze and C. Reber, *Angew. Chem. Int. Ed.*, 2018, **57**, 11069–11073.