

Excited-state annihilation in a homodinuclear Ru-metal complex

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Supporting Information ESI:

For the investigation of the photoinduced excited-state dynamics of $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{Ru}(\text{tbbpy})_2]^{4+}$ (**Ru**) several transient absorption measurements are performed. The setup used to collect this data is published elsewhere in detail.^[S1] As pump source within the pump-probe differential absorption experimental layout a laser pulse centered at 510 nm is used, while a white-light continuum serves as probe pulse. Both pulses were arranged in a magic-angle polarization geometry in order to selectively monitor the photoinduced population dynamics. The energy of the pump pulse was tuned employing a Berek compensator in concert with a linear polarizer. The concentrations of the samples were controlled via measuring the optical densities of the samples in the cuvette directly used in the differential absorption experiment. To ensure that no sample degradation occurs during the pump-probe experiments all samples were checked with UV/Vis-spectroscopy before and after measurement. As solvent acetonitrile (ACN) of high purity (spectroscopic grade) was used. Due to strong coherent artifact signals observed in the probe region, the temporal resolution of the experiment is restricted to roughly 350 fs.

The steady-state absorption spectrum was recorded with a Jasco V-670 spectrophotometer and the emission spectrum with a Jasco FP-6200 spectrofluorimeter. The solution was diluted (optical density < 0.05) for recording the emission spectra.

This supporting information presents the set of differential absorption spectra in detail including the so-called *decay associated spectra* (DAS – for details see below). The transient data is presented for high and low concentration of **Ru** as well as for the high and low pump power regime. The high (low) concentration of **Ru** employed in the measurements is $5.06 \cdot 10^{-4}$ mol/l ($1.01 \cdot 10^{-4}$ mol/l).

For analysis of the transient absorption data the complete data set, i.e. differential absorption amplitudes as a function of the probe wavelength λ_{pr} and the delay time t between pump and probe pulse, is treated with a global fit routine, which uses a sum of exponentials as fit function:

$$\Delta A(t, \lambda_{pr}) = \phi(\lambda_{pr}) + \sum_{i=1}^n A_i(\lambda_{pr}) \cdot e^{-t/\tau_i}$$

To simulate long-lived pump-induced absorption changes, which decay on a time-scale longer than the range covered by our experiment, the constant offset $\phi(\lambda_{pr})$ is introduced. The DAS correspond to the wavelength-dependent preexponential factor $A_i(\lambda_{pr})$, which contain spectral characteristics from each individual kinetic component associated with τ_i . Beforehand each data-set was numerically chirp corrected. The pulse-overlap region was ignored during the fitting procedure in order to avoid contributions from coherent artifacts.^[S2] In fitting the high-intensity data it is assumed that the spectral signatures dominantly stem from doubly excited molecular species. Otherwise the fitting would have taken into account the dynamics of both singly and doubly excited species. However, as the dynamics in the high-intensity regime is qualitatively different from the data recorded in the low-intensity regime (see below and main text of the communication), this assumption is justified.

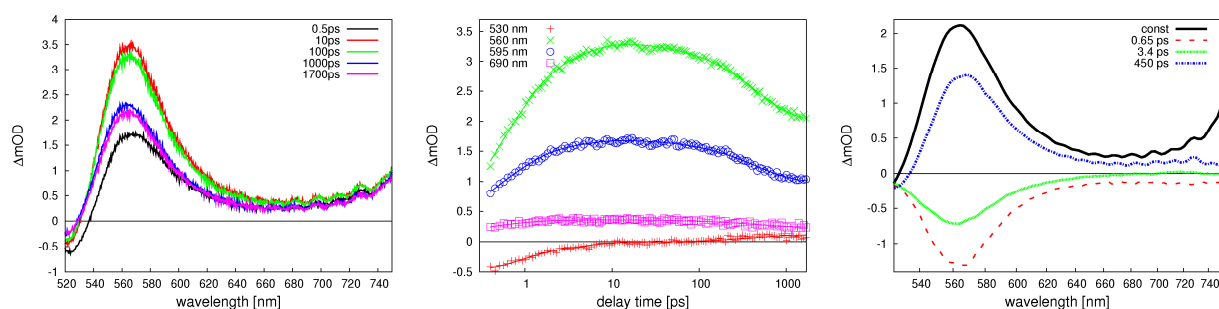


Figure 1: Differential-absorption spectra (left), transient kinetics and DAS of **Ru** at high concentration and high excitation density.

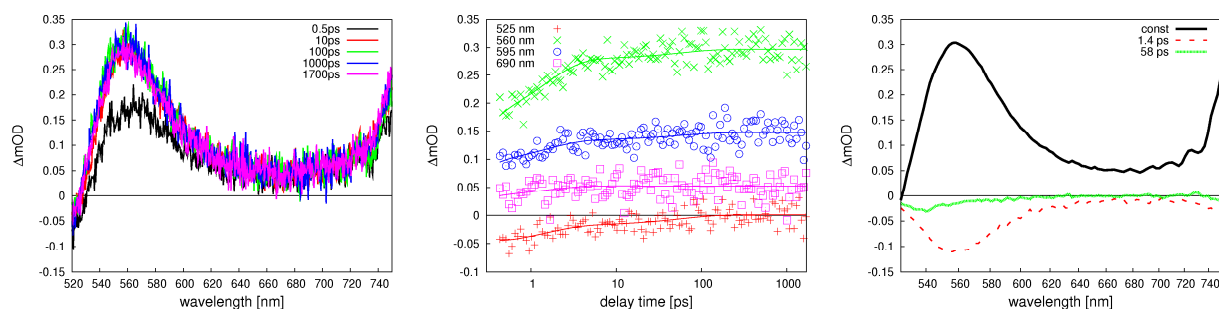


Figure 2: Differential-absorption spectra (left), transient kinetics and DAS of **Ru** at high concentration and low excitation density.

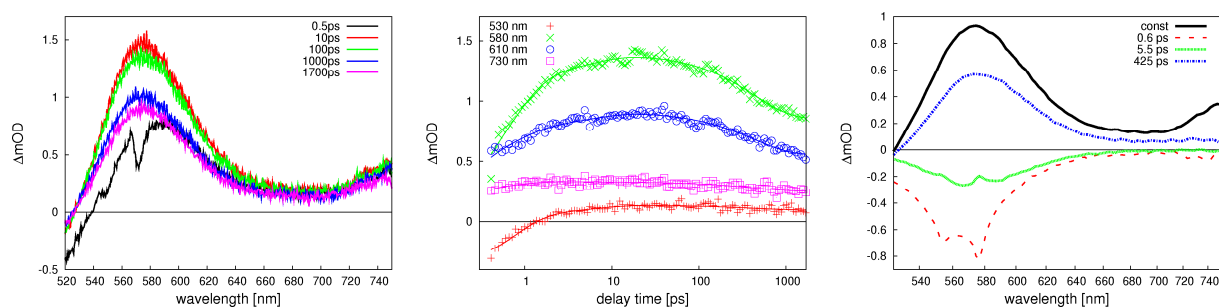


Figure 3: Differential-absorption spectra (left), transient kinetics and DAS of **Ru** at low concentration and high excitation density.

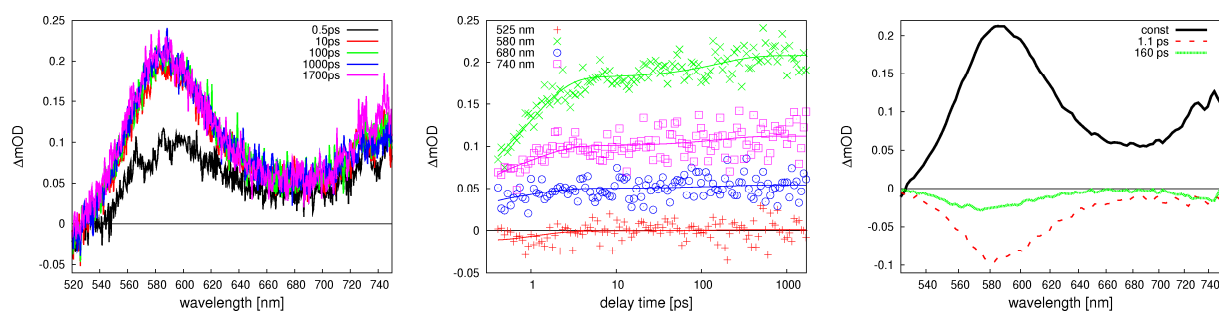


Figure 4: Differential-absorption spectra (left), transient kinetics and DAS of **Ru** at low concentration and low excitation density.

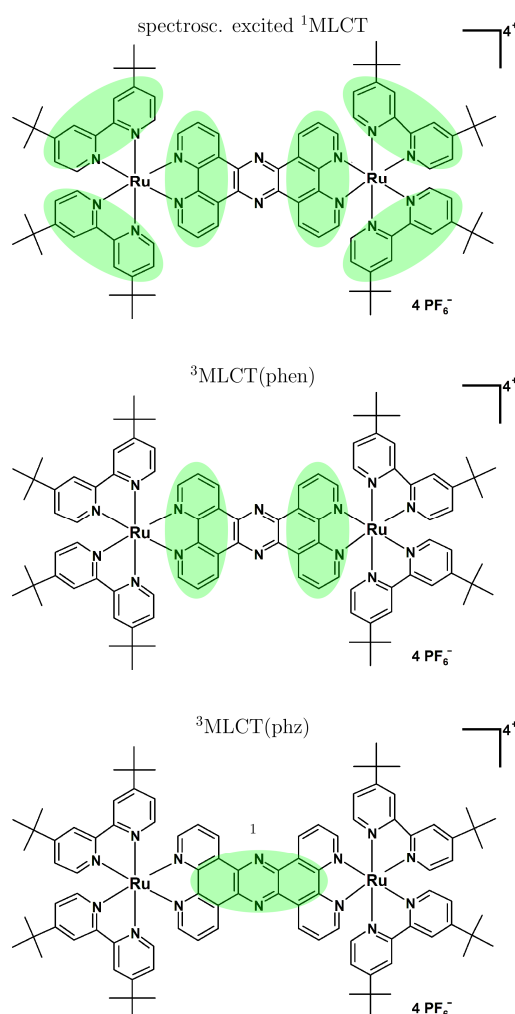


Figure 5 Schematic visualization of the excited states of Ru which are involved in the intensity-dependent photophysics. The upper panel shows the spectroscopically excited $^1\text{MLCT}$ state, which bares contributions from all different ligands. The nomenclature $^3\text{MLCT}(\text{phen})$ and $^3\text{MLCT}(\text{phz})$ refers to the text of the communication.

Information regarding synthesis and structural characterization:

All solvents and reagents were of commercial grade, purchased from Aldrich, Fluka or Merck and used without further purification. $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{Ru}(\text{tbbpy})_2](\text{PF}_6)_4$ ^[S3,S4] and $(\text{tbbpy})_2\text{RuCl}_2$ ^[S5] were prepared according to literature methods. This compound has been characterized by elemental analysis, mass spectrometry, 1D and 2D $^1\text{H}/^{13}\text{C}$ -NMR spectroscopy and IR spectroscopy.

^1H -NMR and ^{13}C -NMR spectra were recorded at ambient temperature on a Bruker AC 400 Spektrometer (^1H : 400.25 MHz, ^{13}C : 100.64 MHz). All spectra were referenced to TMS or deuterated solvent as an internal standard.

Electrospray-Mass spectra (MS) were recorded on a Finnigan MAT 95 XL. The positive ES mass spectra were achieved with voltages of 3-4kV applied to the electrospray needle.

Elemental analyses (EA) were performed by the Microanalytical Laboratory of the University Jena. IR spectroscopy was performed using a FT-IR spectrometer Perkin-Elmer System 2000 employing KBr pellets. The microwave-assisted reactions were carried out by using the Microwave Laboratory Systems MLS EM-2 microwave system.

References:

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