

## Electronic Supplementary Information

### Early photochemical events of a ruthenium(II) molecular dyad capable of performing photochemical water oxidation and of its model compounds

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#### General procedures, equipment and methods

The NMR spectra were recorded on a JEOL ECX-400 or ECA-500 spectrometer operating at 400/500 MHz for protons. Chemical shifts were reported in parts per million (ppm) referenced to the residual solvent peak. Mass spectra were obtained on an Advion Mass Express ESI-MS spectrometer.

UV/Vis absorption spectra were taken on a Jasco V-560 spectrophotometer. For steady-state luminescence measurements, a Jobin Yvon-Spex Fluoromax 2 spectrofluorimeter was used, equipped with a Hamamatsu R3896 photomultiplier. The spectra were corrected for photomultiplier response using a program purchased with the fluorimeter.

Time-resolved transient absorption experiments were performed using a pump-probe setup based on the Spectra-Physics MAI-TAI Ti:sapphire system as the laser source and the Ultrafast Systems Helios spectrometer as the detector. The output of laser beam was split to generate pump and probe beam pulses with a beam splitter (85 and 15%). The pump pulse (400 nm, 1-2  $\mu$ J) was generated with a Spectra-Physics 800 FP OPA and was focused onto the sample cuvette. The probe beam was delayed with a computer controlled motion controller and then focused into a 2-mm sapphire plate to generate a white light continuum (spectral range 450–800 nm). The white light is then overlapped with the pump beam in a 2-mm quartz cuvette containing the sample. The effective time resolution was ca. 200 fs, and the temporal chirp over the white-light 450–750 nm range ca. 150 fs; the temporal window of the optical delay stage was 0–3200 ps. Please note that all the transient spectra shown in the present paper are chirp corrected. The chirp correction was done by using the pump-induced absorption signals themselves in the same conditions (same cuvette, solvent, temperature, stirring frequency...) used for each single experiment. The time-resolved data were analyzed with the Ultrafast Systems Surface Explorer Pro software.

Electrochemical measurements were carried out in the dry and argon-purged stated acetonitrile, at r.t. with an Autolab multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon (8 mm<sup>2</sup>, Amel) electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using the redox couple ferrocene/ferrocinium as internal reference (395 mV *vs* SCE in acetonitrile). The concentration in analyte was about 0.5 mM, unless otherwise stated. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rates between 50 and 500 mV/s and were stated in each case. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons reported in the main text was established using the areas of the peaks in differential pulse voltammetry (DPV).

UV–vis–NIR spectroelectrochemical measurements were obtained with a SPECAC Omni Cell System: an optically transparent thin-layer electrode (OTTLE) cell with the working Pt-mesh, twinned Ag-wire reference and Pt-mesh auxiliary electrodes melt-sealed into a polyethylene spacer –CaF<sub>2</sub> windows and 0.25 mm path length. The UV–vis–NIR spectra were registered with a JASCO V570 spectrophotometer concurrently applying a potential by using an Autolab multipurpose equipment interfaced to a PC. TBAPF<sub>6</sub>, (+99%) supporting electrolyte and acetonitrile solvent (anhydrous, 99.8%) were supplied by Aldrich.

Experimental uncertainties are as follows: absorption maxima, 2 nm; molar absorption, 15%; luminescence maxima, 4 nm; luminescence lifetimes, 10%; transient absorption decay and rise rates, 10%; redox potentials, 20 mV.

## Synthesis

The mononuclear complex [Ru(bpy)<sub>2</sub>(BL)](PF<sub>6</sub>)<sub>2</sub> (**1**) where BL = 2,6-di-(1',8'-naphthyridyl-2'-yl)pyrazine<sup>1</sup> and the heteroleptic dinuclear complex **2**, [(bpy)<sub>2</sub>Ru(BL)Ru(ttbt)(I)](PF<sub>6</sub>)<sub>3</sub> where ttbt = 4,4',4''-tri-*tert*-butyltpy, were prepared as previously described.<sup>2</sup> ESI-MS [M-(PF<sub>6</sub>)<sub>2</sub>]<sup>2+</sup> 727.

The homoleptic dinuclear complex  $[(bpy)_2Ru(BL)Ru(bpy)_2](PF_6)_4$  (**3**) was prepared by treating BL with two equivalents of  $[Ru(bpy)_2Cl_2]$  in refluxing EtOH/H<sub>2</sub>O (3:1) overnight. After cooling and filtering NH<sub>4</sub>PF<sub>6</sub> (58 mg) was added to the filtrate and the solution was evaporated to afford 0.245 g of a black solid that was purified by chromatography on silica gel using CH<sub>3</sub>CN/H<sub>2</sub>O/K<sub>2</sub>NO<sub>3</sub> (sat) (5:4:1) as the eluent. A green fraction was collected and the solid material obtained from this fraction was dissolved in H<sub>2</sub>O and the product precipitated by the addition of saturated NH<sub>4</sub>PF<sub>6</sub> to afford **3** (100 mg).

The homoleptic dinuclear complex  $[(ttbt)Ru(Cl)(BL)Ru(ttbt)(Cl)](PF_6)_2$  was prepared by treating the bridging ligand BL with two equivalents of  $[Ru(ttbt)Cl_3]$  in the manner described for **3**: <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 11.73 (s, 2H), 8.63 (6H), 8.40 (4H), 8.31 (d, 2H), 8.24 (d, 2H), 8.17 (d, 2H), 7.85 (4H), 7.45 (dd, 2H), 7.23 (4H), 1.73 (18 H), 1.33 (36 H). This material was then treated with excess KI to convert the dichloride to the diiodide **4**. ESI-MS:  $[M-(PF_6)_2]^{2+}$  798.

## References

1. Brown, D.; Muranjan, S.; Thummel, R. P. *Eur. J. Inorg. Chem.* **2003**, 3547-3553.
2. Kaveevivitchai, N.; Chitta, R.; Zong, R.; El Ojaimi, M.; Thummel, R. P. *J. Am. Chem. Soc.* **2012**, *134*, 10721-10724.