

A Co(II)-Ru(II) dyad relevant to light-driven water oxidation catalysis.

Alejandro Montellano López,^{a‡} Mirco Natali,^{b‡} Erica Pizzolato,^a Claudio Chiorboli,^c Marcella Bonchio,^a Andrea Sartorel^{*a} and Franco Scandola^{*b}

^a*ITM-CNR* and Department of Chemical Sciences, University of Padova, via Marzolo 1, 35131 Padova, Italy Fax: +39 049 8275300; Tel: +39 049 8275252; E-mail: andrea.sartorel@unipd.it.

^bDepartment of Chemical and Pharmaceutical Sciences, University of Ferrara, and Centro Interuniversitario per la Conversione Chimica dell'Energia Solare (sez. Ferrara), via Fossato di Mortara 17-27, 44121 Ferrara, Italy Fax: +39 0532 240709; Tel: +39 0532 455160; E-mail: snf@unife.it.

^cISOF-CNR c/o Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Via Luigi Borsari 46, 44121 Ferrara, Italy.

[‡]These authors contributed equally to the paper.

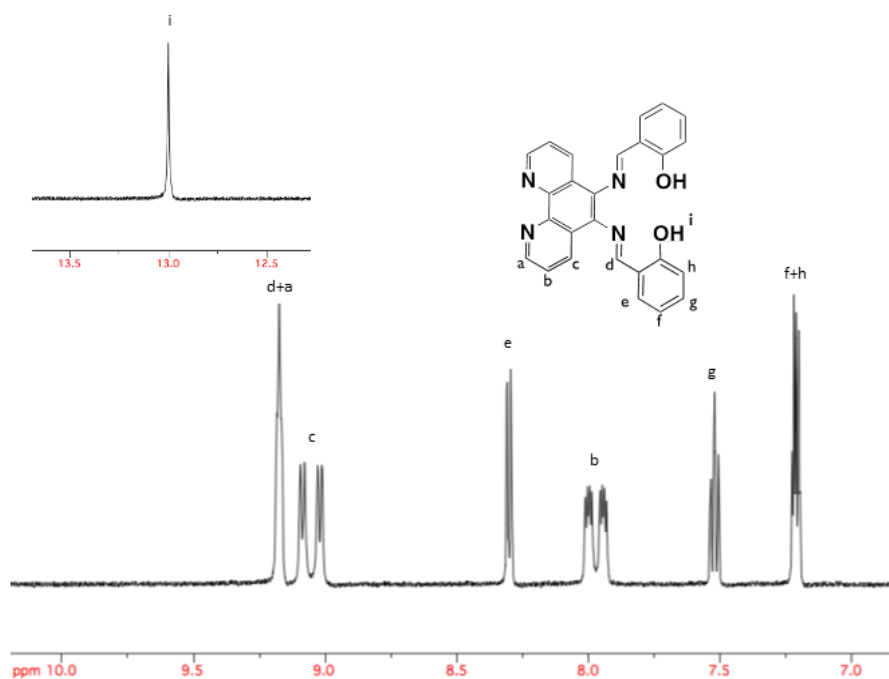


Figure S1. ¹H-NMR (500 MHz) spectra of (2) d⁶-DMSO.

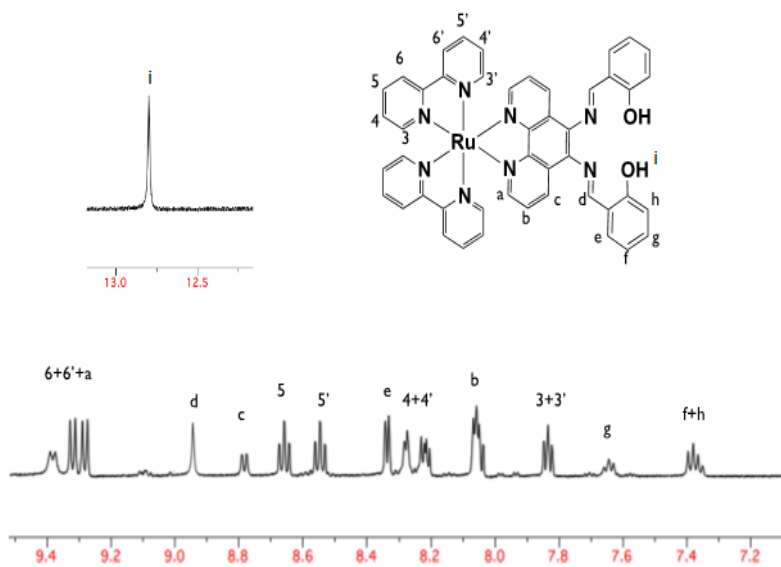


Figure S2. ¹H-NMR (500 MHz) spectra of (3) d⁶-DMSO.

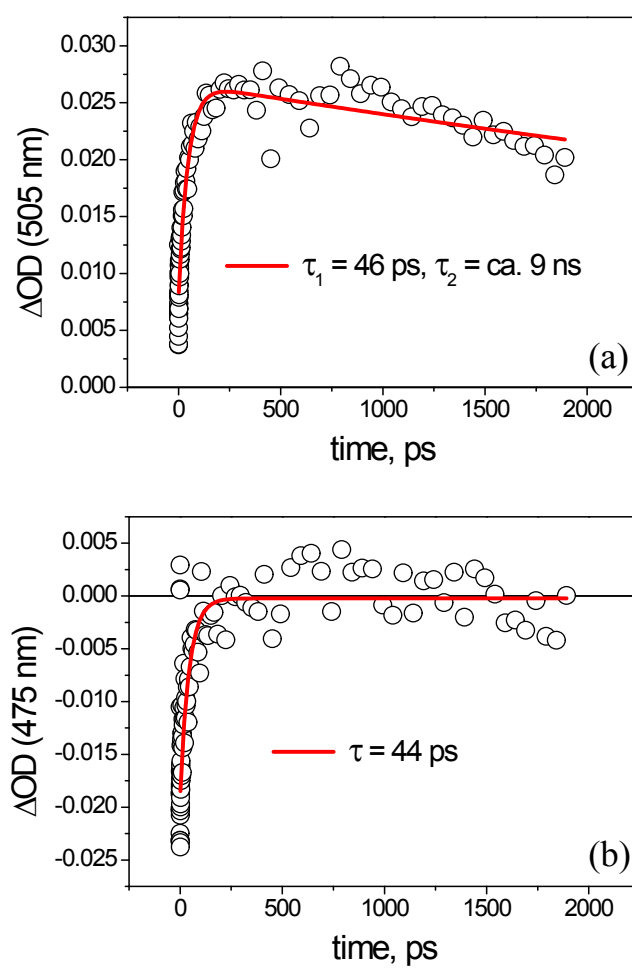


Figure S3. Kinetic analysis obtained by UFS (excitation at 400 nm) on **3** (a) at 505 nm and (b) at 475 nm.

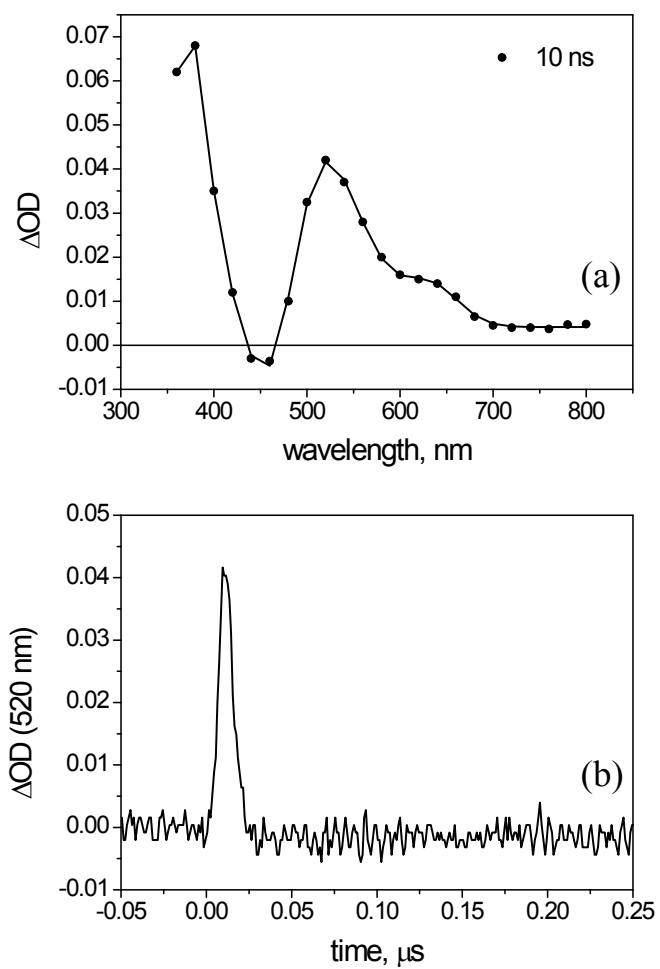


Figure S4. (a) Transient spectrum of **3** in acetonitrile at 10 ns time-delay obtained by laser flash photolysis (excitation at 355 nm); (b) kinetic profile of the transient recorded at 520 nm.

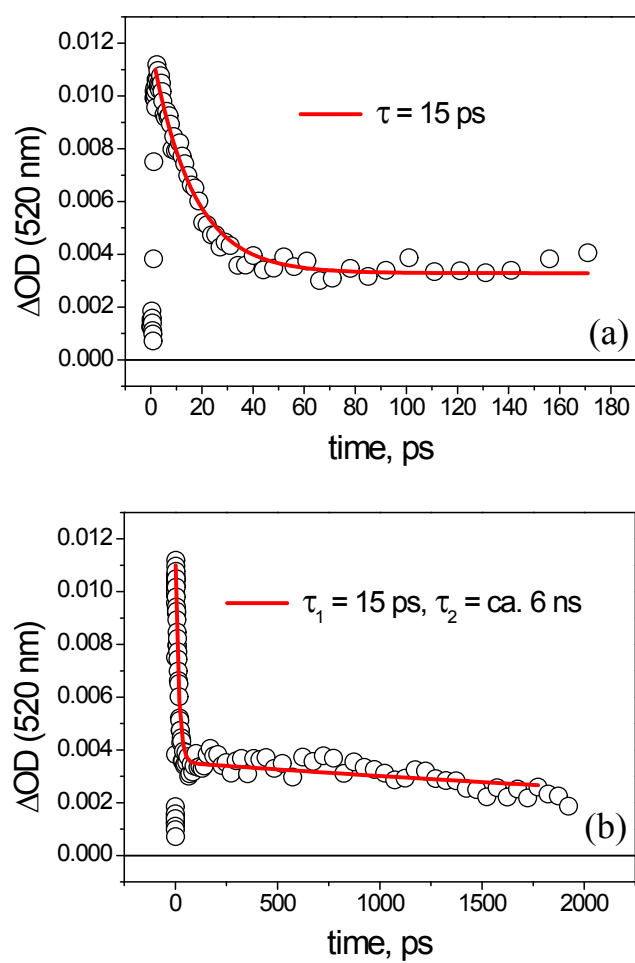


Figure S5. Kinetic analysis obtained by UFS (400-nm excitation) on **1** in acetonitrile at 520 nm: (a) 0-200 ps and (b) 0-2000 ps.

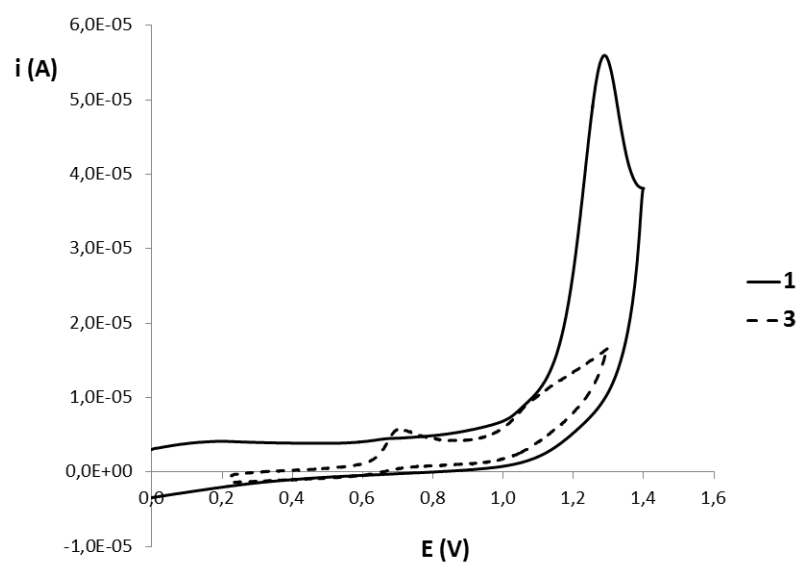


Figure S6. Cyclic voltammograms of 0.5 mM **1** and **3** under anodic scans in 0.2 M phosphate buffer, pH 7. Working electrode glassy carbon, counter electrode: platinum wire, reference electrode: Ag/AgCl (3 M NaCl); scan rate 20 mVs^{-1} .

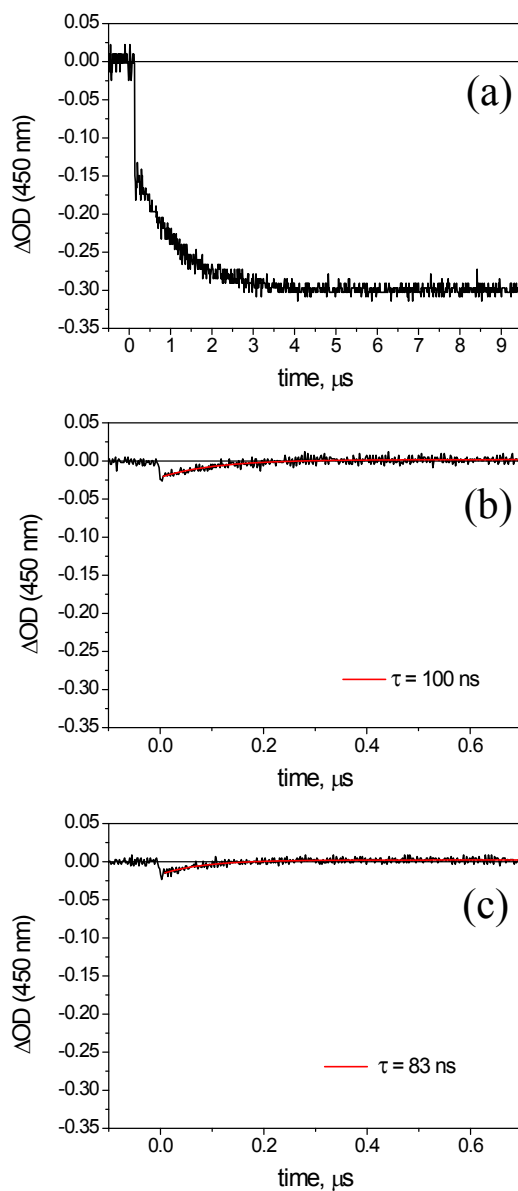


Figure S7. Kinetic analysis at 450 nm obtained by laser flash photolysis (355-nm excitation) in pH 7 phosphate buffer solutions (optically matched at the excitation wavelength) containing (a) $Ru(bpy)_3^{2+}$ and 5 mM $Na_2S_2O_8$, (b) **3** and 5 mM $Na_2S_2O_8$, and (c) **1** and 5 mM $Na_2S_2O_8$. The efficiency of the bimolecular excited-state quenching by persulfate, as determined by emission measurements, is comparable ($\geq 90\%$) in the three cases.