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Supporting Information

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Femtosecond Isomerization in a Photochromic Molecular Switch

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Materials. The compound *cis*-$Ru(bpy)_2Cl_2 \cdot xH_2O$ was either synthesized using published methods (*Inorg. Chem.* **1978** *17*, 3334-3341), or purchased from Strem and used as received. The complex silver hexafluorophosphate ($AgPF_6$) was purchased from Strem and used without further purification. The reagent 3-chloroperbenzoic acid (*m*-cpba) was purchased from Aldrich and used as received. The dithioether ligand, $(CH_3)_2Si(CH_2SCH_3)_2$ (SS) was obtained from Dr. Rabinovich at UNC-Charlotte, typically prepared by reaction of dimethyldichlorosilane ($(CH_3)_2SiCl_2$) with two equivalents of $LiCH_2SMe$ in the presence of base. Tetra *n*-butyl ammonium hexafluorophosphate ($TBAPF_6$), for use in electrochemical measurements, was purchased from Fluka and recrystallized from hot ethanol three times. Acetonitrile and methanol for electrochemical experiments were of spectroscopic grade and purchased from Burdick and Jackson. All other reagents and solvents were used without further purification.

$[Ru(bpy)_2(SS)](PF_6)_2$. (SS is dimethyl bis(dimethylthiomethylene)silane) Dark purple *cis*-$Ru(bpy)_2Cl_2$ (250.6 mg, .482 mmol), dithioether (100μL, .543mmol) and 2 equivalents of $AgPF_6$ (260.7 mg, 1.03 mmol) are dissolved in 100 mL 1,2-dichloroethane. The reaction was refluxed for 2.5 hours under argon. The solution changed from purple to deep red as the reaction progressed during which time solid AgCl precipitated. The solution was cooled to -30 °C to ensure precipitation of all AgCl and was then filtered to collect 2 equivalents of AgCl. The filtrate volume was reduced to dryness and reconstituted in ethanol. Diethyl ether was added to precipitate the product as a red solid. The product was isolated via vacuum filtration, washed with ether (3 x 15mL), and air-dried. Yield: 314.4 mg (74%). UV-Vis (MeOH) λ_{max}= 425 nm (5100 $M^{-1}cm^{-1}$). ^1H NMR ($CDCl_3$, 300 MHz) δ: 9.72 (d, bpy, 2 H), 8.77 (d, bpy, 2 H), 8.63 (d, bpy, 2 H), 8.38 (t, bpy, 2 H), 8.09 (t, bpy, 2 H), 8.02 (t, bpy, 2 H), 7.55 (d, bpy, 2 H), 7.40 (t, bpy, 2 H), 2.09 (d, CH_2, 2 H), 1.97 (d, CH_2, 2 H), 1.25 (s, SCH_3, 6 H), 0.45 (s, $SiCH_3$, 6 H). Anal. Calc'd. (found) for $C_{26}H_{32}F_{12}N_4P_2RuS_2Si$: C, 35.33 (35.69); H, 3.65 (3.79); N, 6.34 (6.50); S, 7.26 (6.98).

Instrumentation. Cyclic voltammetry was performed on a CH Instruments CH1730A Electrochemical Analyzer. This workstation contains a digital simulation package as part of the software package to operate the workstation (CHI version 2.06). The working electrode was a glassy-carbon electrode (BAS) or Pt disk electrode where the electrode surface is 2.0mm^2. The counter and reference electrodes were Pt wire and Ag/AgCl, respectively. Electrochemical measurements were typically performed in acetonitrile or propylene carbonate solutions containing 0.1 M $TBAPF_6$ electrolyte in a one compartment cell. Electronic absorption spectra were collected on an Agilent 8453 spectrophotometer. Kinetic analyses of O→S rates determined in solution were performed on this same spectrometer. Goodness-of-fit for monoexponential plots was determined qualitatively by inspection of residual plots. Proton nuclear magnetic resonance (^1H NMR) spectra were collected on both a 300 MHz Bruker AG spectrometer and a 500 MHz Varian spectrometer in deuterated acetonitrile (CD_3CN). Emission spectra were collected at room temperature in propylene carbonate solution on a PTI C-60 Fluorimeter equipped with a Hamamatsu R928 PMT (185-900 nm). Fluorescence lifetimes were determined by the time-correlated single photon counting method. A home built Ti:sapphire laser (KMLabs) was pumped by a Millenia VS. the Ti;Sapphire laser was mode locked to yield a 100fs pulse-width with a rep-rate of 100MHz. the output was frequency doubled to yield 400nm laser light used to excite the sample. Luminescence was focused into a 0.1m monochrometer (Edmund Scientific) onto a fast PMT (Becker & Hickl GmbH, PMH100-1). Data collection electronics were integrated on a single PC card (Becker & Hickl, Germany). The instrument response function FWHM was 200ps.

Transient Absorption Spectroscopy. Picosecond transient absorption spectra were acquired at the Ohio Laboratory for Kinetic Spectrometry (OLKS) as part of Bowling Green State University's (BGSU) Center for Photochemical Studies. The experimental details were described previously, and only a brief discussion is provided here.(*J. Phys. Chem. A* **1999**, *103*, 7587-7596. *J. Phys. Chem. A* **2001**, *105*, 1757-1766. *J. Phys. Chem. A* **2005**, *109*, 7653-7656.) Spectra-Physics Hurricane Evolution and Ti:sapphire were combined to yield 800 nm pulses of 130 fs in duration at a rate of 1 kHz. The excitation wavelength of 400 nm (~2 μJ/pulse) was obtained from frequency-doubling the Ti:sapphire fundamental. A portion of the 800 nm fundamental was employed to generate the white light continuum probe source by focusing the light through either an ethylene glycol flow-through cell or a 3 mm thick sapphire plate. Detection from ~450 to 750 nm was achieved with a double CCD spectrograph. Transient spectra at a particular delay time represent the average of 4000 excitation pulses. The instrument is operated through an in-house (BGSU) LabVIEW software routine. Kinetic analysis of the data was performed at Ohio University (OU) with the SPECFIT (version 3.0.37, Spectrum Software Associates) program, a global analysis routine based on single value decomposition. Goodness-of-fit was evaluated qualitatively by inspection of the residual plots.

Quantum Yield of Isomerization. Quantum yields of isomerization were obtained by irradiating degassed solutions of $[Ru(bpy)_2(OSSO)]^{2+}$ in methanol and propylene carbonate at 298 K. Photoconversion was achieved using either a 75 W Xenon-arc lamp employing a monochromator to select the appropriate wavelength or Nd:YAG laser. Incident radiation intensities were monitored by potassium ferrioxalate actinometry. A detailed explanation of the quantum yield procedure may be found elsewhere but are based on the procedure for determination of photosubstitution quantum yields (*Inorg. Chem.* **2005**, *44*, 8065-8075).

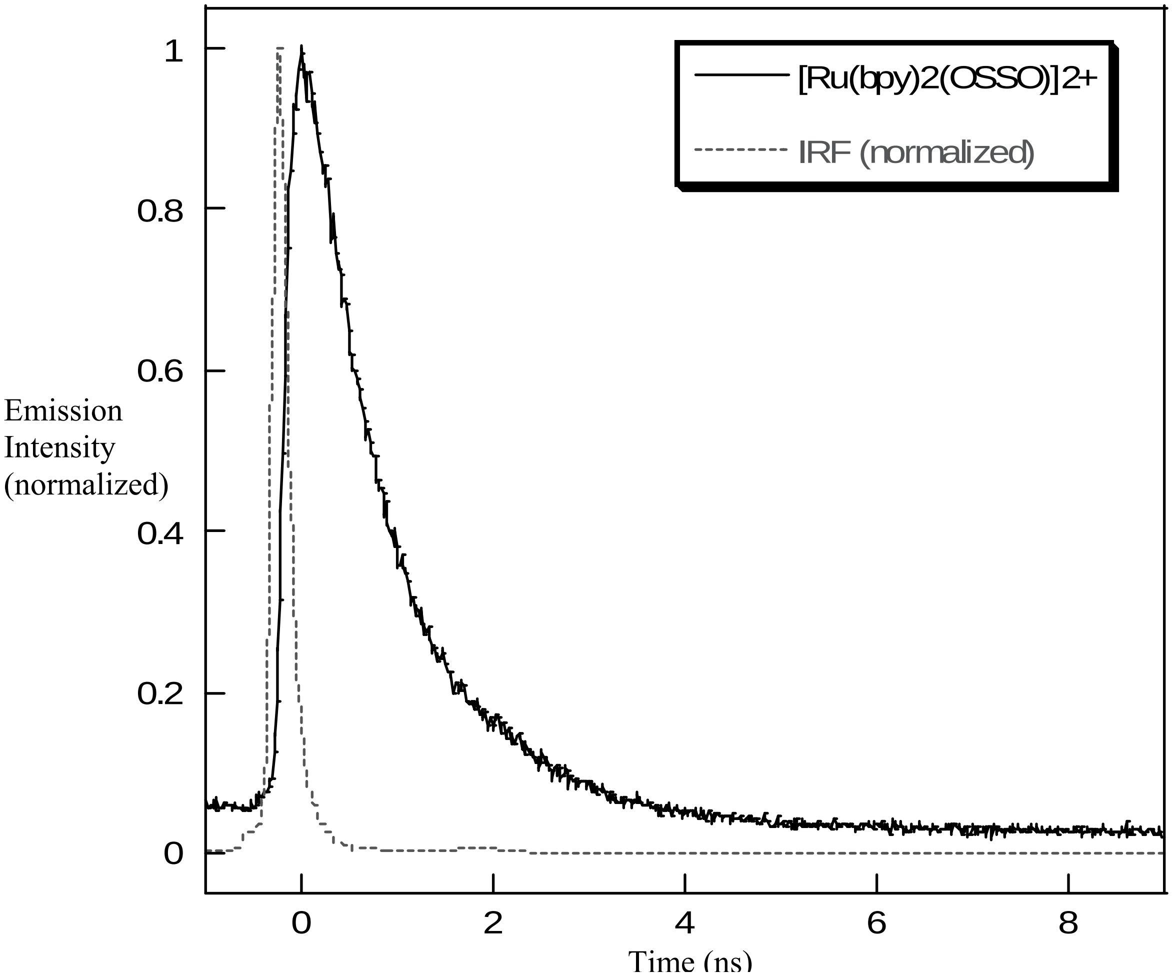

Figure S1. Emission lifetime Spectrum of [S,O]-[Ru(bpy)$_2$(OSSO)]$^{2+}$ in propylene carbonate. λ_{exc} = 400nm; λ_{obs} = 565nm.