## An Excited State Dynamics Driven Reaction:

## Wavelength-Dependent Photoisomerization

# Quantum Yields in [Ru(bpy)<sub>2</sub>(dmso)<sub>2</sub>]<sup>2+</sup>

### Supplementary Information

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#### 1) Instrumentation

All of the transient spectra presented in the manuscript were collected at either Ohio University or University of New Mexico.

a) Ultrafast Systems Helios (Ohio University)

A Spectra Physics Solstice (one-box regenerative amplifier containing a Mai Tai femtosecond oscillator and Empower pump laser) was used to produce 800 nm pulses at a repetition rate of 1 kHz at 3.5 W average power and a pulse width of ~100 fs. From this unit, the beam is split (50:50) with one beam directed to an optical parametric amplifier (TOPAS-C, Light Conversion) and the other to the Helios spectrometer (HE-vis-3200) to create the pump (TOPAS) and probe (Helios) sources, respectively. The 355 - 400 nm pump beam was generated by fourth harmonic generation of the signal pulse from the TOPAS. The 800 nm probe beam is split from a second beamsplitter (95:5) with the 95% dumped and 5% passed through a CaF<sub>2</sub> plate to generate a white light continuum ( $\sim$ 330 to 650 nm). The 400 nm repump beam was generated by passing the 95% dumped 800 nm beam through a Second Harmonic Generation (SHG) BBO crystal. The OPA pump and white light beam path are nearly collinear with  $<10^{\circ}$  angle overlap. The SHG repump has a third beam path with  $\sim 25^{\circ}$  angle overlap with the white light beam. The spectrum was integrated for 2 s for each measurement. A bulk sample solution of  $\sim 60$  mL was prepared of the SS-bonded isomer in propylene carbonate, which was flowed through a 2 mm path length by a fluid pump (Lab Pump Jr., model RHSY by Fluid Metering, Inc, Syosset, NY) at a flow rate of 12 mL/min to provide a fresh portion of solution for each spectrum collected. Transient absorption data were corrected by subtracting spectral background features that persisted from the previous pulse and appeared prepulse as well as applying chirp correction using Surface Xplorer Pro 1.1.5 software (Ultrafast Systems). All kinetics were fit using global analysis function as well as single wavelength functions in Surface Xplorer Pro 1.1.5 software.

#### b) Newport Transient Absorption Spectrometer (TAS) (University of New Mexico)

A Spectra Physics Solstice ACE (one-box regenerative amplifier containing a Mai Tai Short Pulls femtosecond oscillator and Accend pump laser) was used to produce 800 nm pulses at a repetition rate of 1 kHz at 7.1 W average power and a pulse width of ~60 fs. From this unit, the beam is split twice (80:20) and (85:15) with ~4.7 W directed to an optical parametric amplifier (TOPAS-Prime, Light Conversion) and the other to the TAS spectrometer to create the pump (TOPAS) and probe (TAS) sources, respectively. The 355 - 400 nm pump beam was generated by fourth harmonic generation of the signal pulse from the TOPAS. The 800 nm probe beam is split from a second beamsplitter (95:5) with the 95% dumped and 5% passed through a CaF<sub>2</sub> plate to generate a white light continuum (~330 to 750 nm). The 400 nm repump beam was generated by passing the 95% dumped 800 nm beam through a Second Harmonic Generation (SHG) BBO crystal. The OPA pump is collinear with the SHG repump and white light beam path are nearly collinear with  $<10^{\circ}$  angle overlap. The spectrum was integrated for 2 s for each measurement. A bulk sample solution of  $\sim 60$  mL was prepared of the SS-bonded isomer in propylene carbonate, which was flowed through a 2 mm path length by a fluid pump (Lab Pump Jr., model RHSY by Fluid Metering, Inc, Syosset, NY) at a flow rate of 12 mL/min to provide a fresh portion of solution for each spectrum collected. The 60 mL bulk solution is submerged in a slush bath for low temperature experiments. The O<sub>2</sub>O-bonded isomer was generated by continues irradiation of the S<sub>2</sub>S-bonded solution stirred in a 250ml erlenmeyer with 405 nm Blue laser diode. The O,O-bonded isomer was also flowed with the same conditions as the S,S- isomer. Transient absorption data were corrected by subtracting spectral background features that persisted from the previous pulse and appeared prepulse as well as applying chirp correction using Surface Xplorer Pro 4.1 software (Ultrafast Systems). All kinetics were fit using global analysis function as well as single wavelength functions in Surface Xplorer Pro 4.1 software.

#### Pulse-shaping experiments were performed in Germany.

#### c) Laser System at Würzburg, Germany

Our experimental setup for fs time-resolved transient-absorption spectroscopy was described in detail in previous publications.<sup>1,2</sup> In essence, a Ti:Sa oscillator and regenerative amplifier laser system (Solstice, Spectra Physics, 800 nm, 100 fs, 1 kHz) served as the light source. Part of the output was used as a pump for a noncollinear optical parametric amplifier (NOPA, Topas White, Light Conversion). To obtain UV pump pulses centered at 355 and 375 nm. All pulses were characterized via frequency-resolved optical gating<sup>3,4</sup>. Pulse durations below 50 fs were achieved for the UV pump pulses. The pump pulses were compressed using either a commercially available acousto-optic pulse shaper for the UV pulses (DAZZLER, Fastlite)<sup>5–7</sup> or a home-built frequency domain pulse shaper making use of a liquid-crystal display placed in the Fourier plane of a 4f setup<sup>2,8,9</sup> for pulses in the visible spectral range.

As a probe, a white-light continuum was generated by focusing a small part of the 800 nm pulses into a continuously moving CaF<sub>2</sub> plate yielding spectra that cover the spectral range between 330 nm up to the near infrared region. The pump–probe delay was varied by changing the optical path length of the probe using a mechanical translation stage with a maximum delay of about 3 ns. Every second pump pulse was blocked by an optical chopper working at half of the repetition rate of the laser system (500 Hz). Pump and probe beam were focused into a flow cell with a path length of 200  $\mu$ m and spatially overlapped at the position of the sample. The change of the optical density as a function of probe wavelength and pump–probe delay was determined for consecutive probe pulses with a spectrometer (Acton SP2500i, Princeton Instruments) and a two-dimensional CCD chip (Pixis 2K, Princeton Instruments) at a data acquisition rate of 1 kHz. In all measurements, the angle between the polarization directions of pump and probe was adjusted to the magic angle of 54.7° to avoid polarization anisotropy effects.

Global data analysis<sup>10</sup> of the time-resolved spectra was performed using the software interface Glotaran<sup>11</sup> based on the R-package TIMP<sup>12</sup>. A multiexponential fitting model resulted in decay-associated difference spectra (DADS) as well as evolutionary-associated difference spectra (EADS).

#### d) Quantum Yield Procedure

The Quantum Yield data was collected on an Agilent 8453 UV-Vis with Chemstation Ver. B.04.01. A Ti:Sapphire Amplifier (Solstice, Spectra-Physics) was used to generate 795 nm pulses (150 fs, 4.2mJ, 1 kHz) which passes through a 50/50 beamsplitter into an optical parametric amplifier (TOPAC-C, Light Conversion) to generate the desired wavelength for sample irradiation.

Individual S,O-bonded complex and O,O-bonded complex quantum yields of isomerization measurements were determined by irradiating solutions of the S,S-bonded complex in propylene carbonate at room temperature. Incident radiation intensity,  $I_0$  (Equation 1), was determined using potassium ferrioxalate actinometry. In Equation 1,  ${}^{n}Fe^{2+}$  is moles of Fe<sup>2+</sup> produced upon irradiation,  $\Phi_{\lambda}$  is the quantum yield at the irradiation wavelength,  $t_i$  is the time in seconds the actinometer was irradiated and  $A_{\lambda}$  is the absorbance of the actinometer at the excitation wavelength during irradiation. Individual quantum yields of isomerization ( $\Phi_{S,S\to S,O}$  and  $\Phi_{S,S\to O,O}$ ) were calculated using Equation 2, where  $[S,S]_0$  is the concentration of the S,S-bonded isomer at the start of the experiment,  $[PP]_t$  is the concentration of photoproduct (the S,O- and O,O-bonded isomers for  $\Phi_{S,S\to S,O}$  and  $\Phi_{S,S\to O,O}$  respectively) at time t, V is the volume of the solution, t is irradiation time in seconds and  $A_{irr}$  is the absorbance of the solution at the irradiation time in seconds and  $A_{irr}$  is the absorbance of the solution at the start 180 seconds and averaged to yield the reported quantum yield of isomerization.

$$I_{0} = \frac{n_{Fe^{2}}}{\Phi_{\lambda}t_{i}(1-10^{-A_{\lambda}})}$$
Equation 1
$$\Phi_{S,S \to PP} = \frac{[S,S]_{0}V[\ln([S,S]_{0}) - \ln([S,S]_{0} - [PP]_{t})]}{tI_{0}(1-10^{A_{irr}})}$$
Equation 2

The concentration of photoproducts (the S,O- and O,O-bonded isomers) at time t,  $[PP]_t$ , was obtained by sequential calculations performed in absorption regions where only one isomer is found. The  $[O,O]_t$  was determined by linear regression of absorption spectrum from 510 nm to 570 nm and the extinction spectra in that region to gather the concentration. The  $[S,O]_t$  was determined by first subtraction of the [O,O] isomer contribution at time *t*, second a subtraction of the [O,O] isomer contribution, third a linear regression of absorption spectra at 415 nm and the extinction spectra at that wavelength to gather the concentration.



2) SIMPLISMA analysis of [S,S] [Ru(bpy)2(DMSO)2]OTf2 photolysis at 405 nm excitation

Figure S1 SIMPLISMA deconvolution of of [S,S] [Ru(bpy)2(DMSO)2]OTf2 photolysis at 405 nm excitation where blue is [S,S] [Ru(bpy)2(DMSO)2]OTf2, green is [O,S] [Ru(bpy)2(DMSO)2]OTf2 and red is [O,O] [Ru(bpy)2(DMSO)2]OTf2 from 325 to 700 nm. This measurement is collected in propylene carbonate.

3) Pump Probe Transient Map for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> excitation at 355 nm



Figure S2a) Raw pump-probe map at 355 nm excitation; x-axis = wavelength, y-axis = delay step, color map corresponds to  $\Delta A$ 



Figure S2b) Corrected linear time pump-probe map at 355 nm excitation; x-axis = wavelength, y-axis = delay time, color map corresponds to  $\Delta A$  for the first 500 ps of the experiment



4) Pump Probe Transient Map for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> excitation at 375 nm

Figure S3a) Raw pump-probe map at 375 nm excitation; x-axis = wavelength, y-axis = delay step, color map corresponds to  $\Delta A$ 



Figure S3b) Corrected linear time pump-probe map at 375 nm excitation; x-axis = wavelength, y-axis = delay time, color map corresponds to  $\Delta A$  for the first 500 ps of the experiment

5) Pump Probe Transient Map for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> excitation at 390 nm



Figure S4a) Raw pump-probe map at 390 nm excitation; x-axis = wavelength, y-axis = delay step, color map corresponds to  $\Delta A$ 



Figure S4b) Corrected linear time pump-probe map at 390 nm excitation; x-axis = wavelength, y-axis = delay time, color map corresponds to  $\Delta A$  for the first 500 ps of the experiment



6) Pump Probe Transient Map for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> excitation at 400 nm

Figure S5a) Raw pump-probe map at 400 nm excitation; x-axis = wavelength, y-axis = delay step, color map corresponds to  $\Delta A$ 



Figure S5b) Corrected linear time pump-probe map at 400 nm excitation; x-axis = wavelength, y-axis = delay time, color map corresponds to  $\Delta A$  for the first 500 ps of the experiment

7) Select Pump Probe Transient Spectra for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> excitation at 355 nm



Figure S6 a)Electronic absorbance spectra for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>](OTf)<sub>2</sub> S,S (black), O,O (red), O,O-S,S (blue). b) Pump-probe excitation 355 nm transient spectra at 0.7 (black), 2 (red), 6 (blue), 12 (green), 20 (orange) ps. c) Pump-probe excitation 355 nm transient spectra at 20 (black), 100 (red), 250 (blue), 1000 (green), 3000 (orange) ps.



Figure S7 Single wavelength kinetic fitting of pump probe transient absorption of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  excitation at 355 nm.



Figure S8. SVD global fitting spectral components from pump-probe transient absorption of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 355 nm excitation. The black spectrum is correlated to the  $1.8 \pm 0.1$ , red is correlated to  $236 \pm 5$  ps and blue is the residual spectral signature.



Figure S9. SVD global kinetic components from pump-probe transient absorption of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 355 nm excitation. The black line is the real signal and the red line is the kinetic fitting.



8) Select Pump Probe Transient Spectra for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> excitation at 375 nm

Figure S10. a) Electronic absorbance spectra for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>](OTf)<sub>2</sub> S,S (black), O,O (red), O,O-S,S (blue). b) Pump-probe excitation 375 nm transient spectra at 0.7 (black), 2 (red), 6 (blue), 12 (green), 20 (orange) ps. c) Pump-probe excitation 375 nm transient spectra at 20 (black), 100 (red), 250 (blue), 1000 (green), 3000 (orange) ps.



Figure S11. Single wavelength kinetic fitting of pump probe transient absorption of  $[Ru(bpy)_2(DMSO)_2]OTf_2$  excitation at 375 nm.



Figure S12. SVD global fitting spectral components from pump-probe transient absorption of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 375 nm excitation. The black spectrum is correlated to the 1.5 Fixed , red is correlated to  $220 \pm 20$  ps and blue is the residual spectral signature.



Figure S13. SVD global kinetic components from pump-probe transient absorption of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 375 nm excitation. The black line is the real signal and the red line is the kinetic fitting.





Figure S14. a) Electronic absorbance spectra for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>](OTf)<sub>2</sub> S,S (black), O,O (red), O,O-S,S (blue). b) Pump-probe excitation 390 nm transient spectra at 0.7 (black), 2 (red), 6 (blue), 12 (green), 20 (orange) ps. c) Pump-probe excitation 390 nm transient spectra at 20 (black), 100 (red), 250 (blue), 1000 (green), 3000 (orange) ps.



Figure S15. Single wavelength kinetic fitting of pump probe transient absorption of  $[Ru(bpy)_2(DMSO)_2]OTf_2$  excitation at 390 nm.



Figure S16. SVD global fitting spectral components from pump-probe transient absorption of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 390 nm excitation. The black spectrum is correlated to the 2.5 ± 0.3, red is correlated to 200 ± 10 ps and blue is the residual spectral signature.



Figure S17. SVD global kinetic components from pump-probe transient absorption of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 390 nm excitation. The black line is the real signal and the red line is the kinetic fitting.

10) Select Pump Probe Transient Spectra for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> excitation at 400 nm



Figure S18. a) Electronic absorbance Spectra for [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>](OTf)<sub>2</sub> S,S (black), O,O (red), O,O-S,S (blue). b) Pump-probe excitation 400 nm transient spectra at 0.7 (black), 2 (red), 6 (blue), 12 (green), 20 (orange) ps. c) Pump-probe excitation 400 transient spectra at 20 (black), 100 (red), 250 (blue), 1000 (green), 3000 (orange) ps.



Figure S19. Single wavelength kinetic fitting of pump probe transient absorption of  $[Ru(bpy)_2(DMSO)_2]OTf_2$  excitation at 390 nm.



Figure S20. SVD global fitting spectral components from pump-probe transient absorption of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 400 nm excitation. The black spectrum is correlated to the 2.1 ± 0.7, red is correlated to 240 ± 50 ps and blue is the residual spectral signature.



Figure S21. SVD global kinetic components from pump-probe transient absorption of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 400 nm excitation. The black line is the real signal and the red line is the kinetic fitting.





	365 nm	526 nm	704 nm
A <sub>1</sub>	$0.00029 \pm 7E-5$	$-0.00036 \pm 5E-5$	$1E-4 \pm 4E-5$
$\tau_1$ (ps)	$3300 \pm 1390$	$8470\pm5000$	$3020 \pm 2850$
A <sub>2</sub>	$0.00094 \pm 3E-5$	$-0.00038 \pm 7E-5$	$0.00014 \pm 9E-5$
$\tau_2(ps)$	$1.9 \pm 0.2$	$94 \pm 50$	$95 \pm 80$
A <sub>3</sub>	$0.00036 \pm 7E-5$	$-0.00118 \pm 6E-5$	$0.00028 \pm 9E-5$
$\tau_3(ps)$	$240 \pm 100$	$2.9 \pm 0.3$	$2.8 \pm 1.5$

Figure S22. Pump-probe single wavelength kinetic fitting of [O,O] bonded  $[Ru(bpy)_2(DMSO)_2](OTf)_2$  at 365, 526 and 704 nm.



Figure S23. SVD global fitting spectral components from pump-probe transient absorption of O,O  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 495 nm excitation. The black spectrum is correlated to the  $3.3 \pm 0.2$ , red is correlated to  $83 \pm 28$  ps and blue is the residual spectral signature with a lifetime of over 7000 ps.



Figure S24. SVD global fitting spectral components from pump-probe transient absorption of O,O  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at a 495 nm excitation. The black line is the real signal and the red line is the kinetic fitting.





Figure S25. S,O and O,O isomer product distribution following excitation at 355 nm (black), 375 nm (red), 390 nm (blue) and 400 (green) of  $S_1S_2(DMSO_2)_2(DMSO_2)_2$  at room temperature in propylene carbonate.



Figure S26. S,O and O,O isomer product distribution following excitation at 355 nm in pure ethylene glycol (black), 75% ethylene glycol 25% propylene carbonate (red), 50% ethylene glycol 50% propylene carbonate (blue), and 25% ethylene glycol 75% propylene carbonate (green) of S,S- $[Ru(bpy)_2(DMSO)_2]OTf_2$  at room temperature.



Figure S27. S,O and O,O isomer product distribution following excitation in propylene carbonate solution at 355 nm (black), 375 nm (red), 390 nm (blue) and 400 (green) of S,S- $[Ru(bpy)_2(DMSO)_2]OTf_2$  at -19°C in a carbon tetrachloride dry ice slush bath.



Figure S28. S,O and O,O isomer product distribution following excitation in propylene carbonate solution at 355 nm (black), 375 nm (red), 390 nm (blue) and 400 (green) of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  at -38°C in an acetonitrile dry ice slush bath.

13) Quantum Control Experiments using a Genetic Algorithm



Figure S29. Excitation at 375 nm of S,S- $[Ru(bpy)_2(DMSO)_2]OTf_2$  with optimization goal of increasing the ratio between [O,O]-photoinduced absorption (at 500 nm) and [S,O]-photoinduced absorption (at 416 nm) at 3 ns pump-probe delay



Figure S30. Excitation at 375 nm of S,S [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> with optimization goal of increasing the ratio between [S,O]-photoinduced absorption (at 416 nm) and [O,O]-photoinduced absorption (at 500 nm) at 3 ns pump-probe delay



Figure S31. Excitation at 355 nm of S,S  $[Ru(bpy)_2(DMSO)_2]OTf_2$  with optimization goal of increasing the ratio between [O,O]-photoinduced absorption (at 500 nm) and [S,O]-photoinduced absorption (at 416 nm) at 3 ns pump-probe delay.



14) Coherence Oscillations in [S,S] [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> at 355 nm excitation

Figure S32. Signal oscillations with  $\tau \approx 80$  fs (420 cm<sup>-1</sup>) observed strongly at 342 nm single-wavelength kinetics and partially at 371 nm single-wavelengths kinetics



Figure S33. Transient absorption map of [S,S] [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> at 355 nm excitation coherence experiment.

15) Pump-RePump-Probe Transient Absorption (PRPTA)



Figure S34. PRPTA with a  $\Delta t = 500$  fs between pump1 (355 nm) and pump2 (400 nm) of S,S [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>. Shown on the left are the transient kinetics and on the right is the S,O and O,O isomer product formation ratios.



Figure S35. PRPTA with a  $\Delta t = 4$  ps between pump1 (355 nm) and pump2 (400 nm) of S,S [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>. Shown on the left are the transient kinetics and on the right is the S,O and O,O isomer product formation ratios.



Figure S36. PRPTA with a  $\Delta t = 675$  ps between pump1 (355 nm) and pump2 (400 nm) of S,S [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>. Shown on the left are the transient kinetics and on the right is the S,O and O,O isomer product formation ratios.



Figure S37. PRPTA with a  $\Delta t = 500$  fs between pump1 (390 nm) and pump2 (400 nm) of S,S [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>. Shown on the left are the transient kinetics and on the right is the S,O and O,O isomer product formation ratios.



Figure S38. PRPTA with a  $\Delta t = 3$  ps between pump1 (390 nm) and pump2 (400 nm) of S,S [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>. Shown on the left are the transient kinetics and on the right is the S,O and O,O isomer product formation ratios.



Figure S39. PRPTA with a  $\Delta t = 675$  ps between pump1 (390 nm) and pump2 (400 nm) of S,S [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>. Shown on the left are the transient kinetics and on the right is the S,O and O,O isomer product formation ratios.



Figure S40. PRPTA with a  $\Delta t = 3$  ps between pump1 (500 nm) and pump2 (400 nm) of O,O [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>. Shown on the left are the transient kinetics and on the right is the S,O and O,O isomer product formation ratios.

16) Select  $\Delta(\Delta A)$  PRPTA kinetics



Figure S41.  $\Delta(\Delta A)$  PRPTA kinetics with a  $\Delta t = 4$  ps between pump1 (355 nm) and pump2 (400 nm) of S,S [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>.



Figure S42.  $\Delta(\Delta A)$  PRPTA with a  $\Delta t = 3$  ps between pump1 (390 nm) and pump2 (400 nm) of S,S [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>.The kinetics are on the left while the spectra are on the right



Figure S43.  $\Delta(\Delta A)$  PRPTA with a  $\Delta t = 3$  ps between pump1 (500 nm) and pump2 (400 nm) of O,O [Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub>. The kinetics are on the left while the spectra are on the right



16) 77K Emission of an irradiated S,S Ru(bpy)<sub>2</sub>(DMSO)<sub>2</sub>]OTf<sub>2</sub> solution

Figure S44. 77K emission spectra of an irradiated solution of  $[Ru(bpy)_2(DMSO)_2]OTf_2$  Lamp excitations are at 355 (black), 400 (red), 450 (blue), 500 (green), 550 (brown), and 600 (orange) nm. The orange spectrum is assigned to the O,O isomer emission while the red spectrum is assigned to predominantly O,S isomer emission.

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