Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Excited State Investigation of a New Ru(II) Complex for Dual Reactivity with Low Energy Light

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Experimental Section

Materials. All materials were used as received without further purification unless otherwise noted. Solvents were of reagent grade quality. Pyridine was acquired from Mallinckrodt Chemicals, ammonium hexafluorophosphate and deuterated acetone were purchased from Aldrich, diethyl ether and acetonitrile were obtained from Fisher Scientific, and 200 proof ethanol was purchased from Decon Laboratories. [Ru(tpy)Cl_3],[S1] dppn, [S2] Me_2dppn, [S3] **3**, [S4] and **4** [S5] were prepared by literature methods.

Synthesis of [Ru(tpy)(Me_2dppn)(py)](PF_6)$_2$ (1). [Ru(tpy)Cl_3] (0.050 g, 0.11 mmol), Me_2dppn (0.048 g, 0.13 mmol), LiCl (0.020 g, 0.5 mmol), and TEA (0.2 mL) in 30 mL 2:1 EtOH/H_2O was heated at reflux for 4 hours. The reaction mixture was cooled to room temperature and stirred with 0.1 g NH_4PF_6. The solid was collected by vacuum filtration and washed with H_2O and Et_2O. Purification was achieved by dissolving the resulting solid in CH_2Cl_2 and filtering to remove solid impurities. The solvent was removed from the purple-red solution of $[Ru(tpy)(NN)Cl]^{2+}$. [Ru(tpy)(Me_2dppn)Cl](PF_6) (0.025 g, 0.029 mmol) and excess pyridine (1 mL) in 20 mL of 2:1 EtOH/H_2O were heated at reflux overnight. The resulting orange solution was cooled to room temperature. EtOH was removed under vacuum and excess NH_4PF_6 was added to precipitate $[Ru(tpy)(dppn)(py)]^{2+}$. The solid was collected by vacuum filtration and washed with H_2O and Et_2O. Yield: 0.029 g (0.028 mmol, 95 %). ^{1}H NMR (400 MHz) of [Ru(tpy)(Me_2dppn)(py)](PF_6)$_2$ in $(CD_3)_2CO$, δ ppm (splitting, integration): 9.96 (d, 1H), 9.46 (d, 1H), 9.19 (s, 1H), 9.11 (s, 1H), 8.90 (d, 2H), 8.79 (d, 2H), 8.47 (d, 2H), 8.40 (m, 4H), 8.22 (td, 2H), 8.04 (m, 2H), 7.89 (m, 1H), 7.77 (dt, 2H), 7.61 (d, 1H), 7.55 (ddd, 2H), 7.30 (t, 2H), 2.46 (s, 3H), 1.96 (s, 3H). ESI(+) MS: $[M-PF_6]^+$, $m/z = 919.1$; $[M-2PF_6]^{2+}$, $m/z = 387.1$; $[M-py-2PF_6]^{2+} = 347.4$.

Synthesis of [Ru(tpy)(dppn)(py)](PF_6)$_2$ (2). The method described for **1** was followed for the preparation of **2** by substituting the Me_2dppn for dppn (0.043 g, 0.13 mmol) to produce the $[Ru(tpy)(dppn)Cl]^{2+}$ intermediate, of which 0.030 g (0.035 mmol) were reacted with excess pyridine (1 mL) to form the product. Purification was carried out as described above. Yield: 0.032 g (0.033 mmol, 94 %). ^{1}H NMR (400 MHz) of [Ru(tpy)(dppn)(py)](PF_6)$_2$ in $(CD_3)_2CO$, δ ppm (splitting, integration): 10.03 (dd, 1H), 9.54 (dd, 1H), 9.46 (dd, 1H), 9.25 (s, 1H), 9.15 (s, 1H), 8.93 (d, 2H), 8.80 (d, 2H), 8.54 (ddd, 1H), 8.45 (m, 3H), 8.19 (m, 7H), 7.99 (tt, 1H), 7.79 (m, 3H), 7.47 (m, 4H). ESI(+) MS: $[M-PF_6]^+$, $m/z = 891.1$; $[M-2PF_6]^{2+}$, $m/z = 373.1$.

Instrumentation. ^{1}H NMR spectra were collected with a Bruker 400 MHz DPX spectrometer. Steady-state absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrometer. Emission data for $^1O_2$ experiments were collected on a Horiba Fluoromax-4 spectrometer. Photolysis and ligand exchange quantum yield experiments were performed with a 150 W Xe arc lamp (USHIO) in a Miliarch lamp housing unit that was powered by an LPS-220 power supply equipped with an LPS-221 igniter (all from PTI). Bandpass filters (Thorlabs) and long pass filters (CVI Melles Griot) were used to select the appropriate excitation wavelengths. Nanosecond transient absorption experiments were performed using a home-built instrument previously reported [S6] equipped with a frequency-tripled (355 nm) Spectra Physics GCR-150 Nd:YAG laser (fwhm ~ 8 ns) excitation source. Ultrafast transient absorption measurements were performed with previously reported laser and detection systems. [S7] The sample was excited with 568nm (1.5 mW at the sample) by the output of optical parametric amplifier with a sum frequency generator. A Harrick Scientific flow cell equipped with 1 mm CaF_2 windows (path length = 1 mm) was used for the sample with a total volume of 10 mL upon irradiation. A polarization angle between the pump and the probe beams of 54.7° was used to avoid rotational diffusion effects. The measurements were repeated four times at each time delay and the spectra were corrected for the chirp in the white light probe continuum. [S8]

Methods. ^1H NMR was performed in acetone-d_6 and chemical shifts were referenced to the residual acetone peak (2.05 ppm). Electrospray ionization (ESI) mass spectrometry was performed using a Bruker micrOTOF instrument with CH_3OH as the eluent. Quantum yield of $^1O_2$ produced were measured with $[Ru(bpy)_3]^{2+}$ as a standard ($\Phi = 0.81$ in CH_3OH) and 1,3-diphenylisobenzofuran (DPBF) as a $^1O_2$ trap. Samples were measured in CH_3OH in a 1 × 1 cm quartz cuvette. The samples were absorption matched at the irradiation wavelength (A = 0.01 at 460 nm). [S9] The samples were irradiated in the presence of 1.0 μM DPBF and the decreased emission of DPBF was monitored as a function of time (λ_{exc} = 405 nm and λ_{em} = 479 nm). A plot of the emission intensity vs irradiation time provided a linear trend. The slope for samples **1** and **2** were compared to that of $[Ru(bpy)_3]^{2+}$ to afford the quantum yields. The ligand exchange quantum yields were measured with an irradiation wavelength of 500 nm in deaerated CH_3CN. Potassium tris(ferrioxalate) was used as the chemical actinometer to determine the photon flux of the lamp. [S10] The nanosecond and ultrafast transient absorption decays were fit to mono- or biexponential decays as needed.[S11]

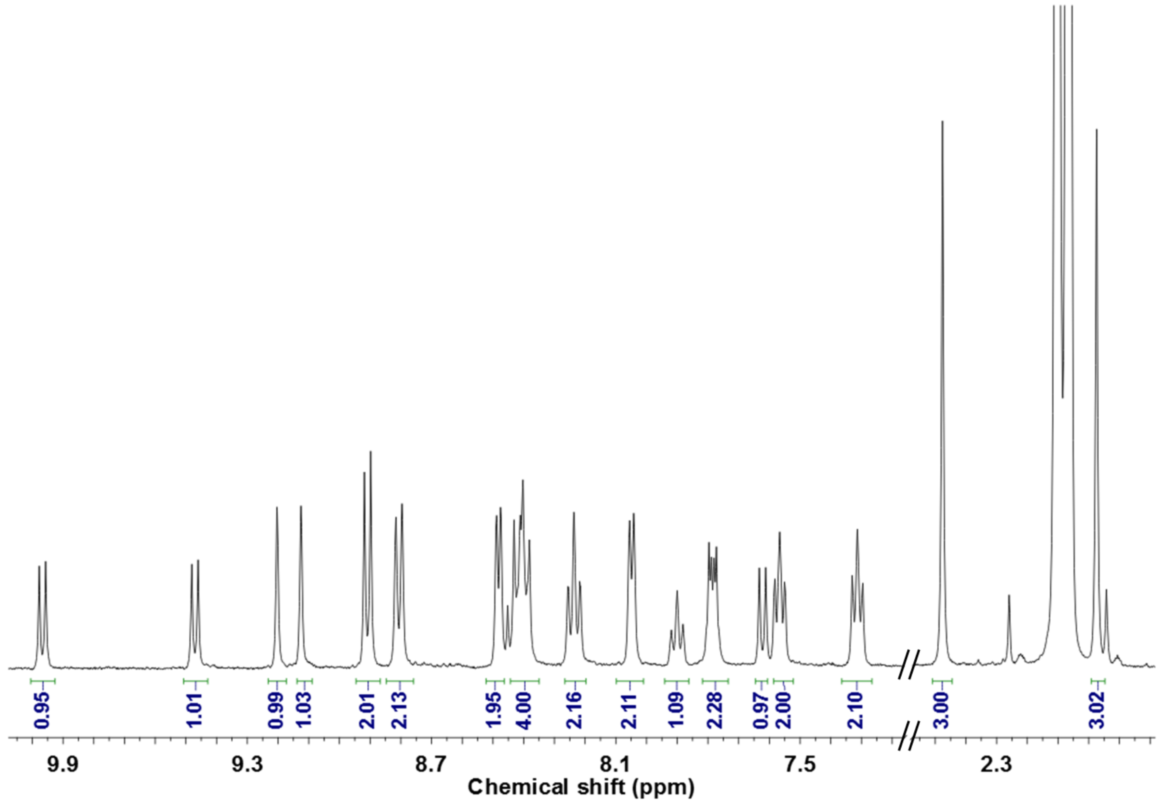

Figure S1. ^{1}H NMR spectrum of **1** in $(CD_3)_2CO$.

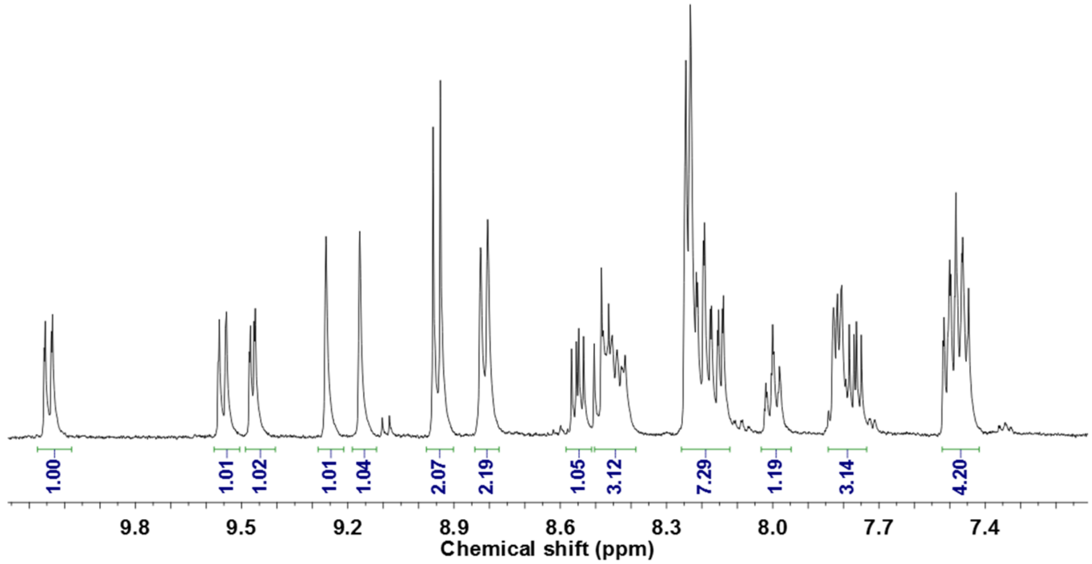

Figure S2. ^{1}H NMR spectrum of **2** in $(CD_3)_2CO$.

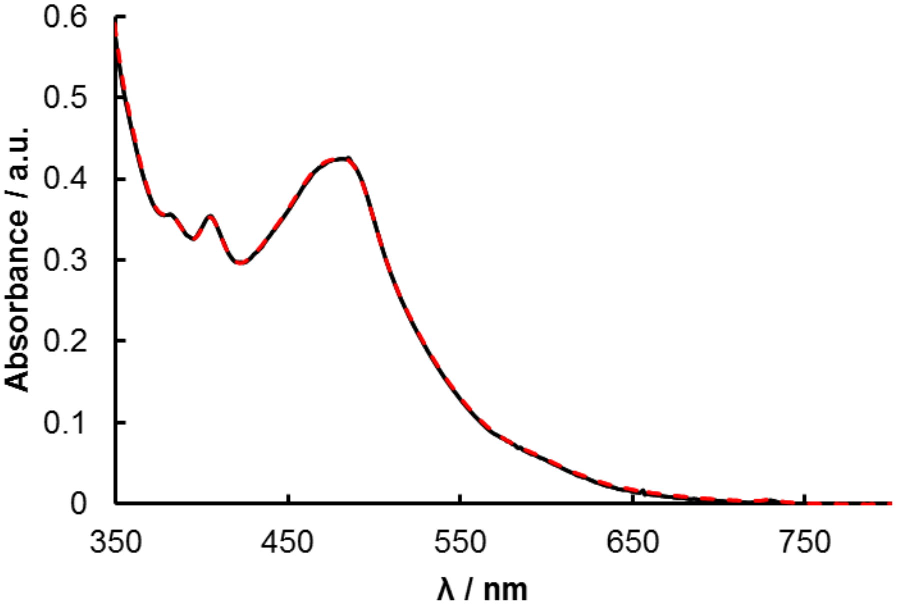

Figure S3. Electronic absorption spectrum of **1** in CH_3CN in the dark initially (black) and after 24 hours (red).

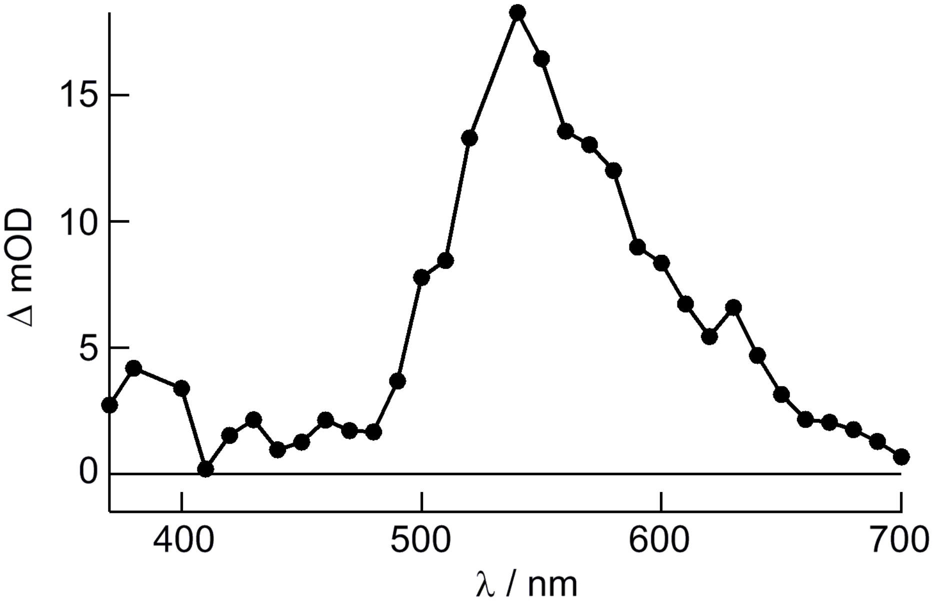

Figure S4. Transient absorption spectrum of **2** in pyridine collected 50 ns after the laser pulse (λ_{ex} = 355 nm, fwhm = 8 ns)

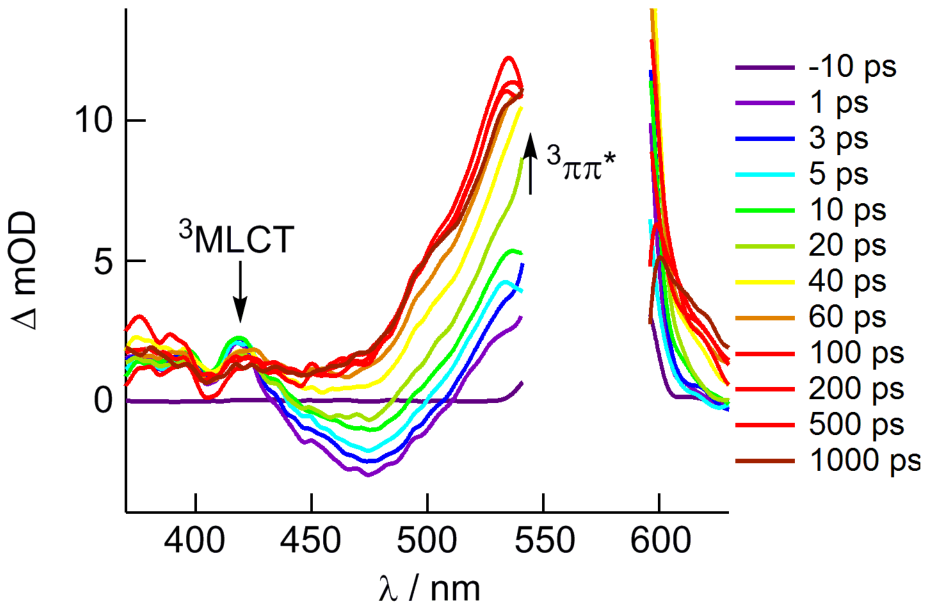

Figure S5. Ultrafast transient absorption spectra of **2** in CH_3CN with λ_{exc} = 568 nm (fwhm = 300 fs).

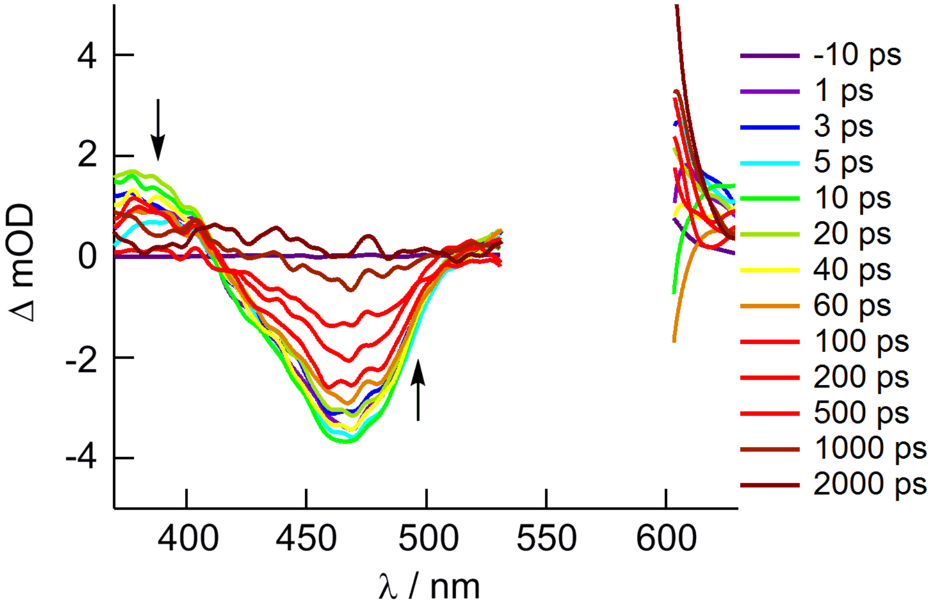

Figure S6. Ultrafast transient absorption spectra of **4** in CH_3CN with λ_{exc} = 568 nm (fwhm = 300 fs).

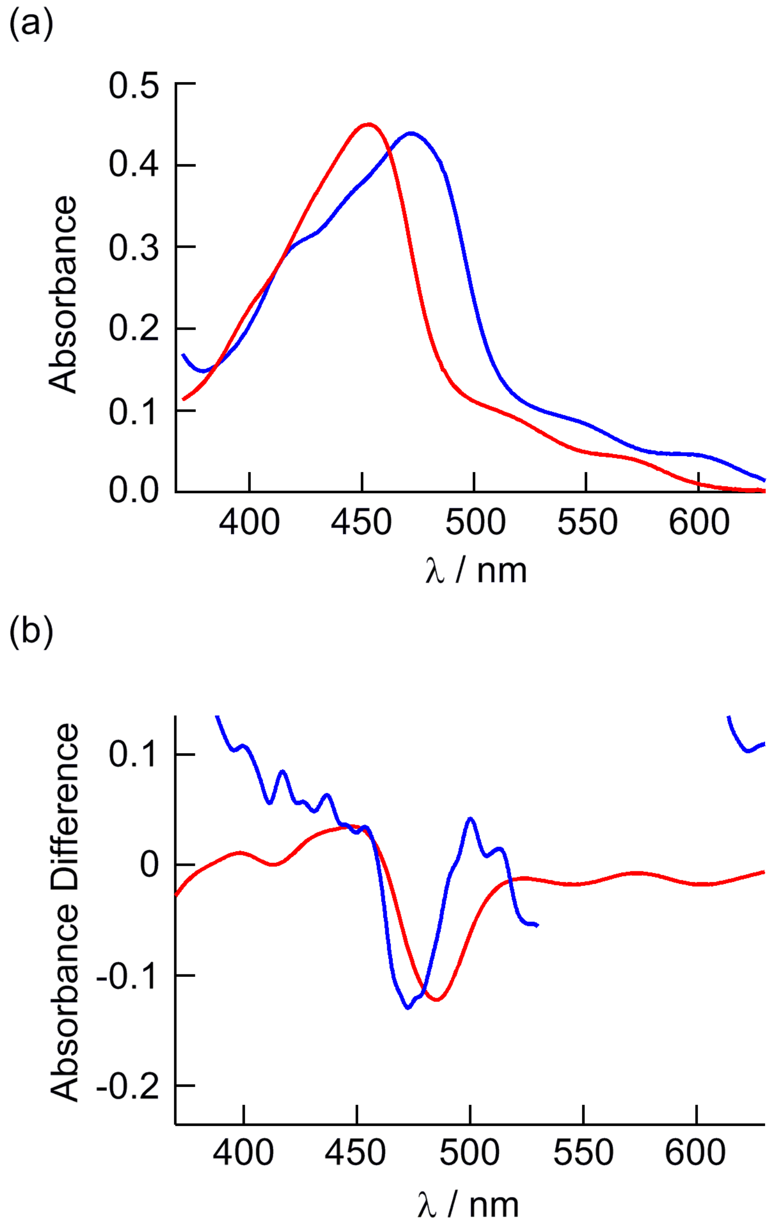

Figure S7. (a) Electronic absorption spectra of **3** (blue) and [Ru(tpy)(Me$_2$bpy)(CH$_3$CN)]$^{2+}$ (red) and (b) differential absorption spectrum of **3** and [Ru(tpy)(Me$_2$bpy)(CH$_3$CN)]$^{2+}$ (red) and 2 ns time delay trace from transient absorption of **3** in CH$_3$CN (blue).

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