

## ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

### Electron Injection into Titanium Dioxide by Panchromatic Dirhodium Photosensitizers with Low Energy Red Light

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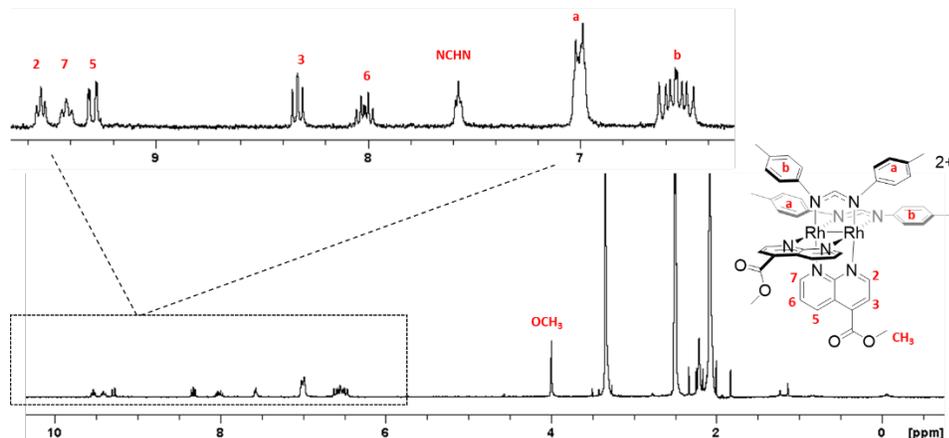
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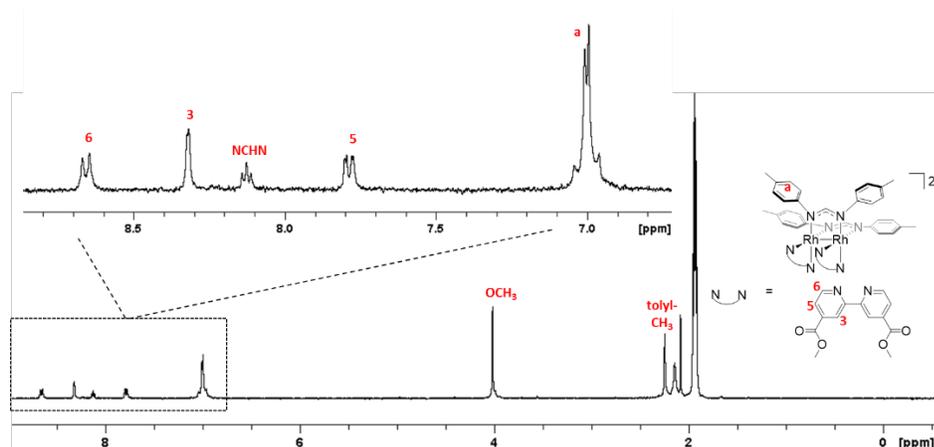
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## Materials

All materials were used as received unless stated otherwise. The ligand 4-methoxycarbonyl-1,8-naphthyridine was synthesized by refluxing 25 mg (0.14 mmol) 1,8-naphthyridine-4-carboxylic acid in 2.0 mL MeOH with 0.2 mL H<sub>2</sub>SO<sub>4</sub>. MeOH was evaporated, the acid was neutralized with NaHCO<sub>3</sub>, and the ligand was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The ligand 2,2'-bipyridine-4,4'-methoxycarbonyl was synthesized following the procedure described by Meyer et al.<sup>S1</sup> The synthesis of **1** and **2** proceeds similarly to other naphthyridine-bridged and polypyridyl-chelated Rh<sub>2</sub>(II,II) complexes.<sup>S2,S3</sup>



**Figure S1.** <sup>1</sup>H NMR of **1** in DMSO-d<sub>6</sub> (250 MHz): δ 2.21 (12 H, s, tolyl CH<sub>3</sub>), 3.99 (6 H, s, OCH<sub>3</sub>), 6.55 (8 H, m, tolyl), 7.01 (8 H, m, tolyl), 7.57 (2 H, dd, NCHN), 8.02 (2 H, ddd, 6), 8.33 (2 H, dd, 3), 9.29 (2 H, dd, 5), 9.42 (2 H, dd, 7), 9.54 (2 H, dd, 2).



**Figure S2.** <sup>1</sup>H NMR of **2** in CH<sub>3</sub>CN-d<sub>3</sub> (250 MHz): δ 2.25 (12 H, s, tolyl CH<sub>3</sub>), 4.02 (12 H, s, OCH<sub>3</sub>), 7.00 (16 H, m, tolyl), 7.79 (2 H, d, 5), 8.13 (2 H, t, NCHN), 8.32 (2 H, s, 3), 8.66 (2 H, d, 6).

### Preparation of **1@TiO<sub>2</sub>** and **2@TiO<sub>2</sub>**

Complex **1** (~6 mg) was added to 1 mL CH<sub>3</sub>CN and the electronic absorption spectrum was taken in a 1 mm pathlength cuvette (Figure S6a). P25 TiO<sub>2</sub> nanoparticles (~50mg) was added to the solution subsequently to prepare sensitizer-TiO<sub>2</sub> (**1@TiO<sub>2</sub>**). Upon mixing, TiO<sub>2</sub> quickly changed to a blue color, indicating anchoring of the dye to TiO<sub>2</sub>. The nanoparticles were centrifugated, and the supernatant was removed and examined by electronic absorption spectroscopy (Figure S6a). A decrease of 0.02 OD was observed at 630 nm. **1@TiO<sub>2</sub>** was washed with CH<sub>3</sub>CN until the supernatant was colorless.

### Methods and Instrumentation.

<sup>1</sup>H NMR spectra were measured in DMSO-d<sub>6</sub> or CH<sub>3</sub>CN-d<sub>3</sub> using a Bruker DPX 250 MHz spectrometer at 298 K and the spectra collected for **1** and **2** are shown in Figs. S1 and S2, respectively.

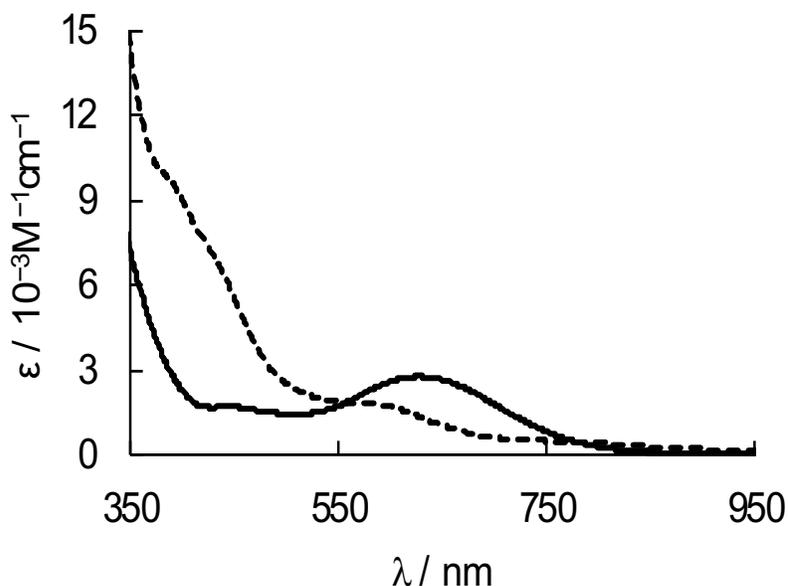
Electronic absorption spectra were collected on a Hewlett-Packard 8453 diode array spectrometer; extinction coefficients were obtained by serial dilution in CH<sub>3</sub>CN of 1-2 mg of complex massed on a Mettler-Toledo XSE105 DualRange balance and values agreed within 6% of one another.

Electrochemistry measurements were conducted on a BASi model CV-50W potentiostat (Bioanalytical Systems, Inc.; West Lafayette, IN, USA). Cyclic voltammetry experiments were recorded under inert N<sub>2</sub> atmosphere at 200 mV/s with three electrodes consisting of a glassy carbon disc working electrode (3 mm), a Pt wire counter electrode and a Ag/AgCl (3 M NaCl) reference electrode. The measured potentials were standardized to ferrocene ( $E_{1/2} = +0.44$  V vs Ag/AgCl in CH<sub>3</sub>CN). Approximately 0.5 mM of sample were dissolved in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> CH<sub>3</sub>CN electrolyte solution. Spectroelectrochemical measurements were performed in a homemade H-cell under inert gas where the Ag/AgCl reference and glassy carbon rod were kept in a working compartment under continuous flow N<sub>2</sub> and the carbon mesh counter electrode in the auxiliary compartment. Complexes were dissolved in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile electrolyte solution in the working compartment.

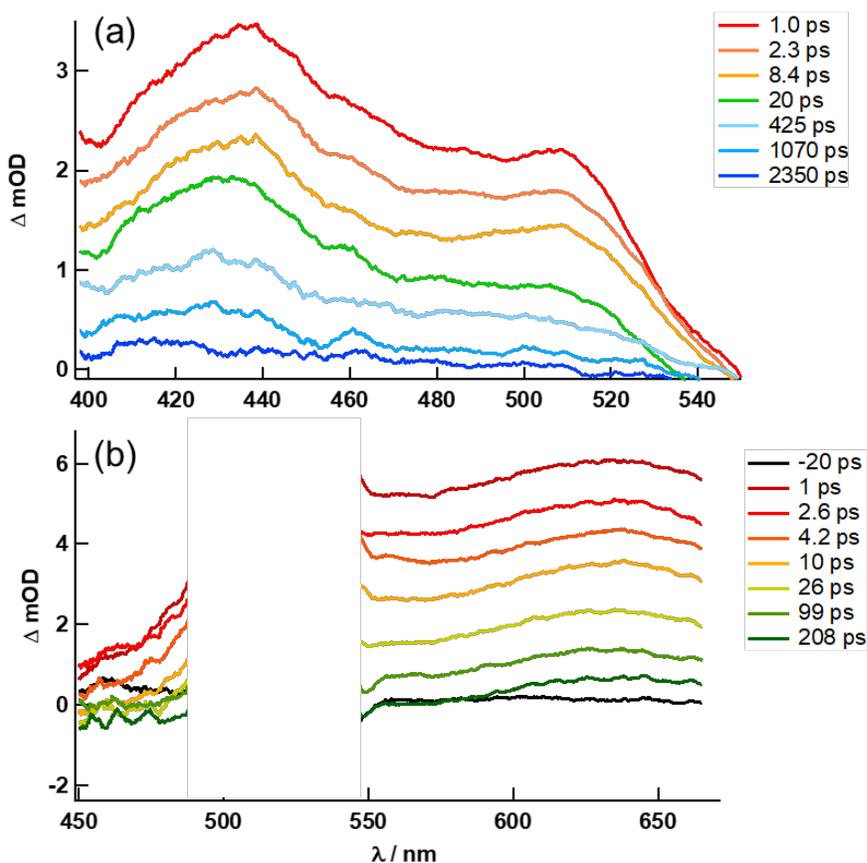
Femtosecond transient absorption (fsTA) spectroscopy was performed using a previously reported setup using a Ti:Sapphire laser system oscillator and amplifier (Astrella, Coherent).<sup>S4</sup> The pump beam (2 μJ) was generated from the signal output of an optical parametric amplifier (OPerA Solo, Coherent) and the white light probe and reference was generated using CaF<sub>2</sub> crystal. The probe and reference spectra were collected on a thermoelectrically cooled CCD camera (Princeton Instrument, 1340 x 100 pixels) and home-built software written in LabVIEW 2015. The instrument response was determined to be 85 fs through Kerr effect in cyclohexane. A 1 mm path length Harrick Scientific flow cell was equipped with 1 mm CaF<sub>2</sub> windows and the

samples were prepared at an optical density of  $\sim 0.5$  OD at the pump wavelength. The polarization of the pump and probe was set to magic angle to minimize the effect of rotational diffusion. The electronic absorption spectra of the sample before and after the experiment were examined to make sure no degradation during the experiment.

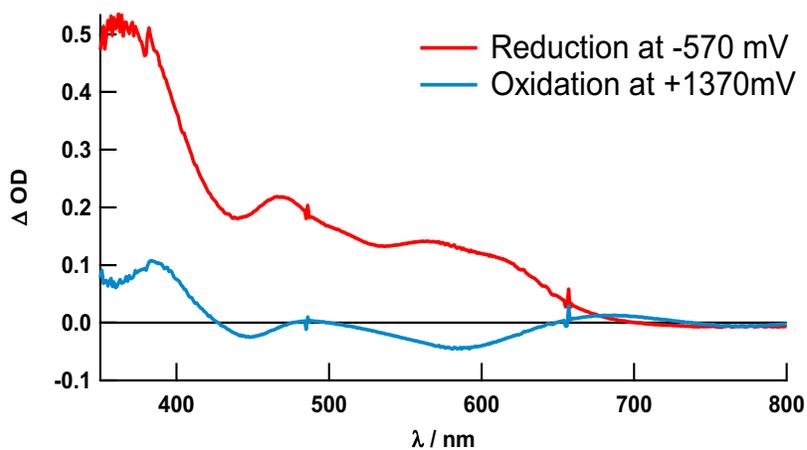
Time-resolved infrared spectroscopy (fsTRIR) was conducted using a previously reported setup with modification.<sup>S3</sup> A short pulse oscillator (Coherent, Mantis) was used to seed a Ti:Sapphire regenerative amplifier (Coherent Legend, 1 kHz, 300 fwhm). The excitation wavelength was obtained from an optical parametric amplifier (OPerA, Coherent) with either a UV/Vis or sum frequency generation (SFG) attachment which is then filtered and focused onto an optical delay stage. The probe was generated from a difference frequency generation (DFG) module in front of another OPerA optical parametric amplifier, which output radiation from  $2500 - 800 \text{ cm}^{-1}$ . A Ge beam splitter is used to produce a probe and a reference IR beam that passed through the sample with  $\sim 5 \text{ mm}$  apart vertically. The probe is overlapped with the pump at the sample. Probe and reference spectra were collected on a Triax 320 spectrograph and imaged on a HgCdTe CCD chip ( $32 \times 2$ ) with  $4 \text{ cm}^{-1}$  resolution for each window. All TRIR were performed under an  $\text{N}_2$  inert gas positive pressure and at room temperature.



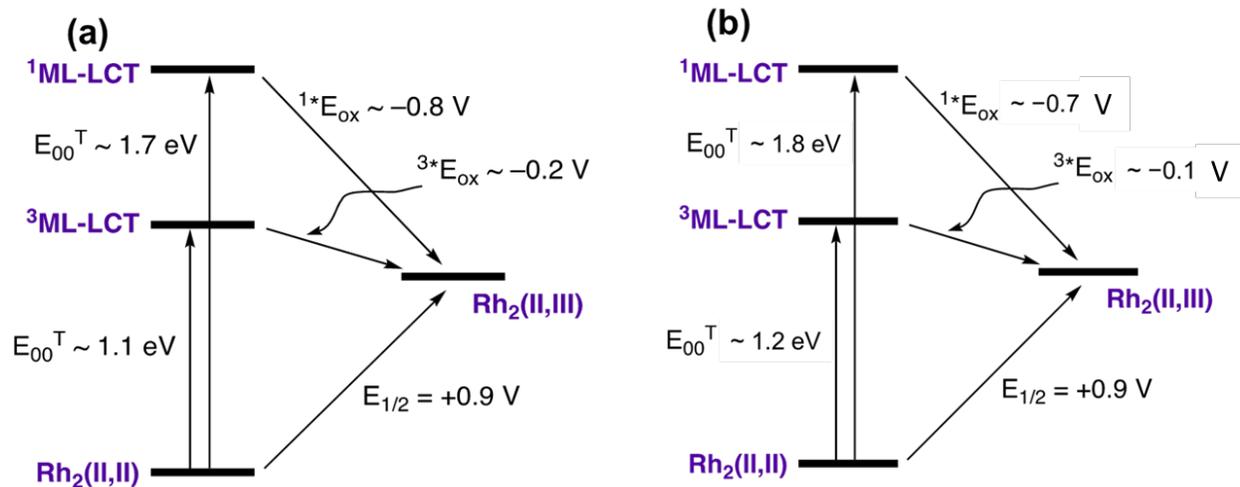
**Figure S3.** Electronic absorption spectra of **1** (solid) and **2** (dashed) in  $\text{CH}_3\text{CN}$ .



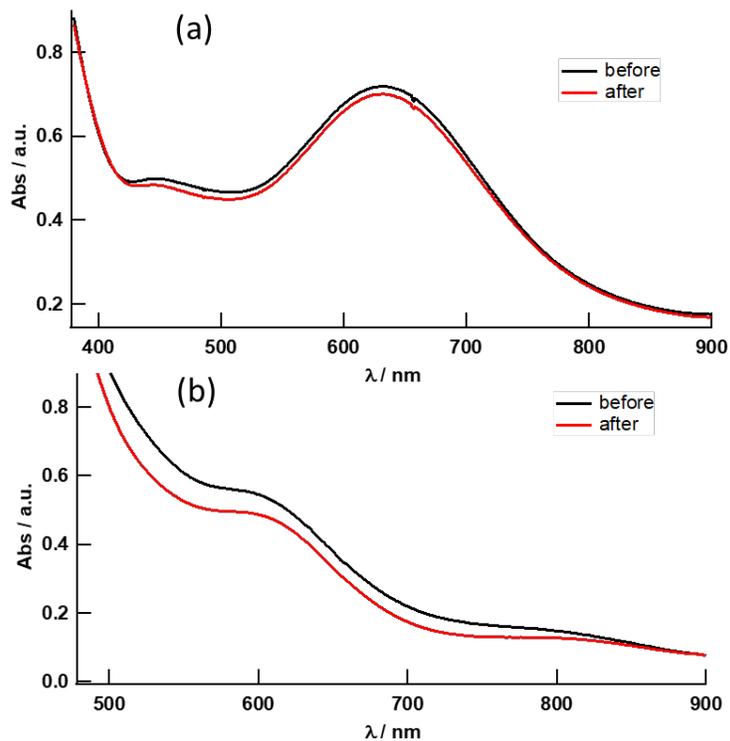
**Figure S4.** FsTA spectra of (a) **1** ( $\lambda_{\text{exc}} = 600 \text{ nm}$ ,  $2 \mu\text{J}$ ) (b) **2** ( $\lambda_{\text{exc}} = 520 \text{ nm}$ ,  $2 \mu\text{J}$ ) in  $\text{CH}_3\text{CN}$ .



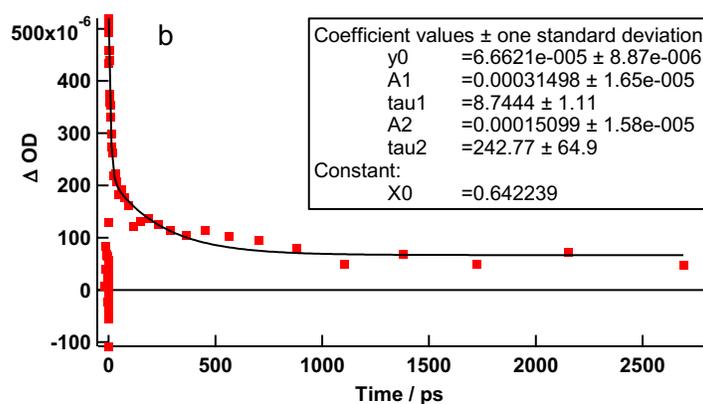
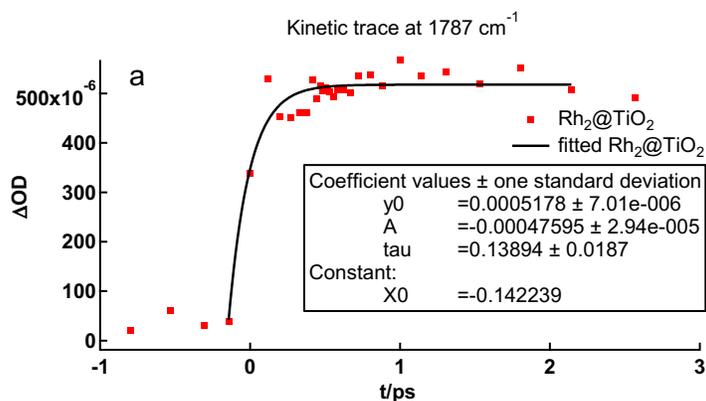
**Figure S5.** Spectroelectrochemistry of **2** at applied potentials of  $+1.37 \text{ V}$  (blue) and  $-0.57 \text{ V}$  (red) in  $\text{CH}_3\text{CN}$  ( $0.1 \text{ M Bu}_4\text{NPF}_6$ ).



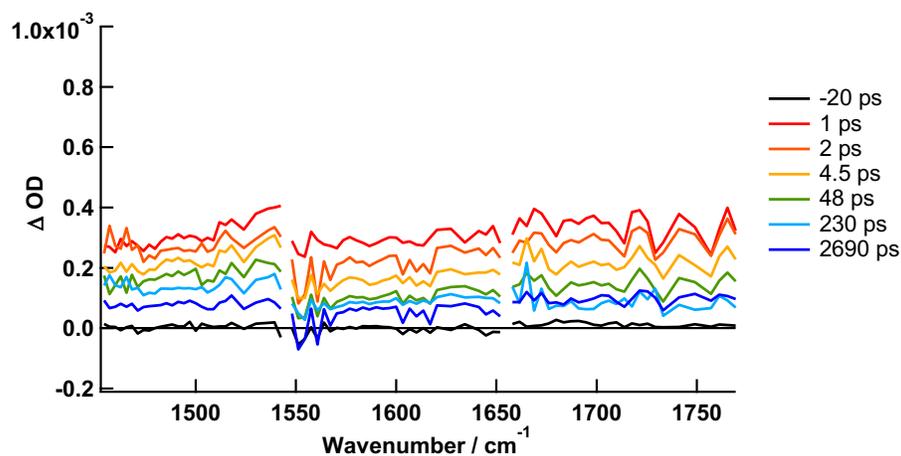
**Figure S6.** Modified Latimer diagrams of (a) **1** and (b) **2**.



**Figure S7.** Electronic absorption spectra collected before (black) and after (red) anchoring of (a) **1** and (b) **2** to TiO<sub>2</sub> nanoparticles.



**Figure S8.** Kinetic traces of **1**@TiO<sub>2</sub> measured (a) at 1787  $\text{cm}^{-1}$  within 5 ps after excitation (b) at 1610  $\text{cm}^{-1}$  with long decay components.



**Figure S9.** TRIR spectra of **2**@TiO<sub>2</sub> in CD<sub>3</sub>CN (2  $\mu\text{J}$ ,  $\lambda_{\text{ex}} = 520 \text{ nm}$ ).

The electron injection efficiency was calculated as follows:

$$\varphi_{inj} = \frac{k_{inj}}{k_{inj} + k_d}$$

where  $k_{inj}$  and  $k_d$  represent the rates of electron injection and excited state decay (radiative and nonradiative), respectively.<sup>S5</sup> Ultrafast electron injection was observed for both **1** and **2**, within the instrument response time <130 fs ( $k_{inj} > 7.69 \times 10^9 \text{ s}^{-1}$ ). The singlet excited state decay rate constant  $k_d$  is  $2.5 \times 10^8 \text{ s}^{-1}$  and  $4 \times 10^8 \text{ s}^{-1}$  for **1** and **2**, respectively. Thus, the electron injection efficiency is determined as 97% and 95%, respectively for **1** and **2**.

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