Supporting Information for

Detection of a charge-separated catalyst precursor state in a linked photosensitizer-catalyst assembly

Anusree Mukherjee,¹ Oleksandr Kokhan,¹ Jier Huang,¹ Jens Niklas,¹ Lin X. Chen,^{*1,2} David M. Tiede,¹ Karen L. Mulfort^{*1}

¹Division of Chemical Sciences and Engineering, Argonne National Laboratory, 9700 South Cass Avenue, Argonne IL 60439; ²Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston IL 60208

Synthesis of RuL1, RuL2 and assemblies 1 and 2.



Figure S1. Synthesis scheme of the photosensitizer $[Ru(bpy)_2L1 \cdot 2PF_6]$

$Ru(bpy)_2Ll\cdot 2PF_6(RuL1)$

Ru(by)₂(5,6-diamino-1,10-phenanthroline)·2PF₆ (0.051 g, 0.05 mmol) was dissolved in absolute ethanol (20 mL). Solid NaHCO₃ (0.0105 g, 0.125 mmol) was added with stirring to the solution at room temperature. In a separate vial dichloroglyoxime (0.008 g, 0.05 mmol) was dissolved in ethanol (5 mL). The solution of dichloroglyoxime was added dropwise to the solution of Ru(bpy)₂(5,6-diamino-1,10-phenanthroline)·2PF₆ at room temperature with stirring. The temperature of the solution was then raised to 60°C and it was stirred at that temperature for 90 minutes. The hot solution was then filtered and the filtrate was concentrated under rotary evaporation. Petroleum ether was added to the concentrated solution to precipitate a brown solid (0.020 g, 0.02 mmol, 40% yield). ESI-MS: $[M-2PF_6^-]^{2+}$ calculated 354.06; observed 354.1. UV-Vis $[\lambda_{max}, nm, (\varepsilon, M^{-1} cm^{-1})$ in CH₃CN]: 244(23570), 286(43750), 450 (18750). ¹H-NMR (500 MHz, CD₃CN), δ , ppm: 9.07 (s, 1H, OH); 9.03 (s, 1H, OH); 8.68 (m, 4H, Ar-CH); 7.63 (m, 6H, Ar-CH); 8.38 (d, 4H, Ar-CH); 8.20 (d, 2H, Ar-CH); 7.93 (t, 4H, Ar-CH); 6.99 (t, 2H, Ar-CH); 4.75 (s, 2H, NH).

Synthesis of assembly 1

To a solution of **RuL1** (0.020 g, 0.02 mmol) in acetone (3 mL), $CoCl_2.H_2O$ (0.0024 g, 0.01 mmol) was added at once. The resulting solution was agitated at room temperature for 10 minutes. The solvent was removed under reduced pressure to isolate 1 as brown solid (0.016 mg, 0.007 mmol, 70% yield).



Figure S2. Synthesis scheme of the photosensitizer $[Ru(bpy)_2L2 \cdot 2PF_6]$

Chloro-methylglyoxime

Chloro-methylglyoxime was prepared by slight modification of a published procedure.¹ In a 2neck round bottom flask, methylglyoxime (1g, 0.01 mmol) was suspended in water (20 mL) and concentrated HCl (5 mL). This solution was then cooled to 0 °C in an ice bath and upon stirring the suspension dissolved to give a clear solution. To this pre-cooled solution, Cl_2 gas was slowly bubbled for 15 minutes and then with medium flow for 2 hours (caution, rapid bubbling was never done). The solution, initially changed color to blue and later a white precipitate appeared. The solution was immediately filtered and the precipitate was allowed to air dry. Chloromethylglyoxime was isolated as an off-white solid (0.169 g, 1.2 mmol, 12% yield). ¹H-NMR (500 MHz, CDCl₃), δ , ppm: 2.41 (s, 3H, CH₃); 1.98 (s, 2H, NOH).

Ligand L2.

The ligand **L2** was synthesized by modifying a published procedure.² 5-amino-1,10phenanthroline (0.054 g, 0.28 mmol) was added to a round bottom flask, cooled to -15°C in a $CO_2(s)/THF$ bath and triethanolamine (0.028 g, 0.28 mmol) was added in one aliquot. To this solution, chloro-methylglyoxime (0.0379 g, 0.28 mmol) in THF (5 mL) was added dropwise, while maintaining the temperature at -15°C. The solution was then stirred for 1 hour and then the temperature was raised to room temperature. ESI-MS of the reaction mixture confirmed complete conversion to product, the solvent was removed by rotary evaporation and the solid was used without further purification to give **L2** as a red solid (0.040 g, 0.135 mmol, 48% yield). ESI-MS: $[M+H^+]^+$ calculated 296.11; observed 296.3. ¹H-NMR (500 MHz, CD₃CN), δ , ppm: 10.86 (s, 1H, OH); 9.58 (s, 1H, OH); 5.53 (s, 1H, NH); 8.93 (d, 2H, Ar-CH); 8.60 (d, 2H, Ar-CH); 7.60 (2H, Ar-CH); 6.84 (s, 1H, Ar-CH); 3.59 (s, 3H, CH₃).

$Ru(bpy)_2L2 \cdot 2PF_6(RuL2)$

Ru(bpy)₂Cl₂ (0.056 g, 0.108 mmol) was added in one portion to a solution of L2 (0.040 g, 0.135 mmol) in absolute ethanol (30 mL). The resulting solution was refluxed for 4 hours under N₂. After concentration in vacuo, followed by dissolution of the residue in a minimum volume of water, the complex was precipitated by addition of saturated aqueous KPF₆. The precipitate was filtered, washed with water, and dried in air. The product was obtained as a brown solid (0.072 g, 0.072 mmol, 68% yield). ESI-MS: $[M-2PF_6^-]^{2+}$ calculated 354.5; observed 354.3. UV-Vis [λ_{max} , nm, (ε, M⁻¹ cm⁻¹) in CH₃CN]: 242 (33750), 288 (46250), 456 (24250). ¹H-NMR (500 MHz, CD₃CN), δ , ppm: 10.07 (s, 1H, OH); 10.09 (s, 1H, OH); 8.73 (d, 2H, Ar-CH); 8.38 (d, 4H, Ar-CH); 8.20 (d, 4H, Ar-CH); 7.99 (t, 4H, Ar-CH); 6.99 (t, 2H, Ar-CH); 7.60 (m, 6H, Ar-CH); 6.84 (s, 1H, Ar-CH); 5.53 (s, 1H, NH); 3.59 (s, 3H, CH₃).

Synthesis of assembly 2

To a solution of **RuL2** (0.035 g, 0.035 mmol) in acetone (5 mL), $CoCl_2 \cdot H_2O$ (0.004 g, 0.017 mmol) was added as a solid. The resulting solution was agitated at room temperature for 10 minutes. The solvent was removed under reduced pressure to isolate **2** as reddish-brown solid (0.034 mg, 0.016 mmol, 90% yield).

Ground state absorbance and emission spectroscopy

Figure S3. UV-Vis absorbance spectra of RuL1 (red) and assembly 1 (black) in CH_3CN normalized to MLCT absorbance band.



Figure S4. UV-Vis absorbance spectra of **RuL2** (red) and assembly **2** (black) in CH₃CN, normalized to MLCT absorbance band.



Figure S5. Normalized emission spectral overlay of RuL1 (black) and RuL2 (red) following excitation at 450 nm.



Ground state electrochemistry

Figure S6. Cyclic voltammograms of **RuL1**(black) and **RuL2** (gray) in 0.1M TBAPF₆ / CH₃CN, ferrocene used as internal standard.



Ground state EPR spectroscopy





Ground state Co K-edge X-ray absorption spectroscopy

Figure S8. X-ray absorption near edge structure of assembly 1 (red), 2 (blue) and $[Co^{III}(dmgH)(dmgH_2)Cl_2]$ (green, used as a standard). The observed pre-edge feature and the edge-energy shift in the assembly 1 as compared to the Co(III) standard strongly support the Co(II) oxidation state of the assembly. It appears that the oxidation state in assembly 2 lies at an intermediate value between Co(II) and Co(III), and is a mixture of Co(II) and Co(III). Inset: XAFS of the respective assemblies with the Co(III) standard.



Figure S9. Fourier-transformed XAFS spectra (left) and partial molecular structures (right) of Co(III) standard (A), assembly **1** (B), and assembly **2** (C). The symbols represent the original data and the solid lines represent the best fitting. The dashed vertical lines are intended to show that assembly **2** lies at an oxidation state intermediate between Co(II) and Co(III). The fitting parameters for Co(III) standard and assembly **1** are shown in Table S1.



Table S1. Structural parameters from EXAFS fit of the first shell bond distances using a model with 4 Co-N bonds and 2 Co-Cl bonds at different distances. The model input distances were based on the crystal structure of $[Co(dmgH)(dmgH_2)Cl_2]$.³

	vector	Ν	R(Å)	$\sigma^2(\text{\AA})^2$
assembly 1	Co-N	4	2.05	0.009
-	Co-Cl	2	2.29	0.003
Co ^{III} (dmgH)(dmgH ₂)Cl ₂	Co-N	4	1.86	0.004
	Co-Cl	2	2.16	0.009

Ground state solution-phase X-ray scattering

Figure S10. Solvent subtracted SAXS/WAXS of **RuL1** (black) and assembly 1 (gray), 5mM in CH₃CN. Discontinuity in scattering at 0.78 < q < 0.88Å⁻¹ is due to change between small-angle and wide-angle detector. Scattering of CH₃CN alone (dashed) is shown for comparison.



Figure S11. Guinier analysis of small-angle X-ray scattering of **RuL1** (A) and assembly **1** (B). Black squares are experimental data; blue circles are energy-minimized model data; red lines are fits to Guinier equation.



Table S2. Complete Guinier fitting parameters of small angle X-ray scattering of **RuL1** and assembly **1**.

		I ₀	R _g (Å)	R^2
RuL1	model	$6.772e5 \pm 8.055e2$	6.58 ± 0.01	0.9999
	experiment	$2.79e-3 \pm 1.60e-5$	6.57 ± 0.08	0.9856
assembly 1	model	$3.091e6 \pm 2.811e3$	10.70 ± 0.12	0.9969
	experiment	$4.19e-3 \pm 6.66e-5$	10.65 ± 0.18	0.9697

Figure S12. Solvent subtracted SAXS/WAXS of **RuL2** (black) and assembly **2** (gray), 5mM in CH₃CN. Discontinuity in scattering at 0.78 < q < 0.88Å⁻¹ is due to change between small-angle and wide-angle detector. Scattering of CH₃CN alone (dashed) is shown for comparison.



Figure S13. Guinier analysis of small-angle X-ray scattering of **RuL2** (A) and assembly **2** (B). Black squares are experimental data; blue circles are energy-minimized model data; red lines are fits to Guinier equation.



Table S3. Complete Guinier fitting parameters of small angle X-ray scattering of **RuL2** and assembly **2**.

		I ₀	$R_{g}(A)$	R^2
RuL2	model	$6.507e5 \pm 5.914e1$	6.12 ± 0.01	0.9999
	experiment	$3.11e-3 \pm 1.99e-5$	6.10 ± 0.11	0.9765
assembly 2	model	$2.996e6 \pm 3.761e2$	10.33 ± 0.02	0.9996
	experiment	$6.37e-3 \pm 7.37e-5$	10.09 ± 0.16	0.9810

Spectroelectrochemistry of model cobaloxime compound

Figure S14. Spectroelectrochemistry of 1 mM [Co(dmgH)(dmgH₂)Cl₂] at Co(III/II) potential (**A**) and Co(II/I) potential (**B**) in CH₃CN/H₂O mixture (1:1) using 0.1M KCl as a supporting electrolyte.



Ultrafast and nanosecond transient optical spectroscopy of assembly 1 and related analyses

Figure S15. Comparison of excitation and decay associated with charge separation and excited state of RuL1 (black) and assembly 1 (red), blue lines are best fit to data (~0.25mM solutions in CH₃CN, pump 420 nm, probe 570 nm). Response from ultrafast (~1 ps to ~3 ns) and nanosecond (~1 ns to 5 μ s) measurements were combined to obtain complete decay and enable comprehensive fitting.



Table S4. Summary of fit parameters to 570 nm decay of transient absorption of **RuL1** and assembly **1**. Amplitude of fitting constant is reported as percent of total decay; remainder that does not total to 100% results from sub-picosecond decay attributed to fast singlet-to-triplet intersystem crossing.

	τ_1	$ au_2$	$ au_3$
D.,I 1			558 ± 6 ns
KULI			98%
assembly 1	$26 \pm 1 \text{ ps}$	3.0 ± 0.6 ns	246 ± 9 ns
	27%	23%	24%

Figure S16. Proposed energy level diagram for photoinduced electron transfer and charge recombination pathways for assembly 1 in CH_3CN . Chemical structures and observed decay times of **RuL1** and assembly 1 (right). The energy levels were measured or calculated as described below.



Ru(II)-L1-Co(II), ground state of assembly 1.

The measured Ru(II/III) potential of **RuL1** in 0.1M TBAPF₆/CH₃CN by cyclic voltammetry (1.36V vs. SCE, see Figure S6).

MLCT₁, ligand-based excited state.

Calculated according to equation S1:

$$E(MLCT_1) = E(Ru^{3+} / Ru^{2+}) - E^{0-0}$$
(S1)

 $E(Ru^{3+}/Ru^{2+})$ is the ground state potential measured from cyclic voltammetry of **RuL1**, E^{0-0} is zero-zero excitation energy calculated from the absorption maxima of **RuL1** in CH₃CN (450nm, 2.75eV, see Figure S3).

 $MLCT_0$, ligand-based excited state.

Calculated according to equation 1, where E^{0-0} is calculated from the measured emission wavelength of **RuL1** (608nm, 2.04eV, see Figure S5).

Co(II/I), ground state of cobaloxime module.

The Co(II/I) potential is taken from the literature value of the Co(dmgH)(dmgH₂)Cl₂ model compound in 0.1M TBAPF₆/CH₃CN (-0.79V vs SCE).⁴

Figure S17. A) Proposed five-state model which describes the multi-exponential decay observed following visible excitation of assembly **1** and correlates with the relevant donor-acceptor energy levels proposed in Figure S16. B) Overlay of experimental decay at 570 nm of assembly **1** following 420 nm excitation (red), experimental fit to data (blue), and MATLAB solution to system of linear differential equations (gray). Inputs to MATLAB fitting routine were rate constants obtained from fitting experimental data:

$$\begin{split} k_{GS1} &= 0.004 \text{ x } 10^9 \text{ s}^{-1} \\ k_{CR0} &= 38.6 \text{ x } 10^9 \text{ s}^{-1} \\ k_{GS0} &= 0.32 \text{ x } 10^9 \text{ s}^{-1} \end{split}$$





Control ultrafast transient optical spectroscopy experiments for assembly 1

Figure S18. Ultrafast transient absorption spectrum of RuL1 [panel A] and a 2:1 mixture of RuL1 and ZnCl₂, respectively [panel B] in CH₃CN, following excitation at 420 nm. The Zn analogue of assembly 1 was prepared by adding 0.05 mM of ZnCl₂ to a solution of 0.1 mM of RuL1 in MeCN.



Figure S19. Ultrafast transient absorption spectrum of $[Ru(bpy)_2(5\text{-amino-phen})]\cdot 2PF_6$ [panel **A**] and a 2:1 mixture of $[Ru(bpy)_2(5\text{-amino-phen})]\cdot 2PF_6$ and CoCl₂, respectively [panel **B**] in CH₃CN following excitation at 420 nm.



Ultrafast and nanosecond transient optical spectroscopy of assembly 2 and related analyses

Figure S20. Ultrafast transient absorption spectra of RuL2 (A) and assembly 2 (B) in CH_3CN following excitation at 420 nm.



Figure S21. Comparison of excitation and decay associated with charge separation and excited state of RuL2 (black) and assembly 2 (red), blue lines are best fit to data (~0.25mM solutions in CH₃CN, pump 420 nm, probe 600 nm). Response from ultrafast (~1 ps to ~3 ns) and nanosecond (~1 ns to 5 μ s) measurements were combined to obtain complete decay and enable comprehensive fitting.



Table S2. Summary of kinetic parameters of excited state absorption of **RuL2** and assembly **2.** Amplitude of fitting constant is reported as percent of total decay; remainder that does not total to 100% results from sub-picosecond decay attributed to fast singlet-to-triplet intersystem crossing.

	τ_1	$ au_2$	$ au_3$
RuL2	$17 \pm 0.7 \text{ ps}$	8 ± 0.18 ns	$606 \pm 16 \text{ ns}$
	38%	42%	18%
assembly 2	$16 \pm 0.7 \text{ ps}$	2 ± 0.06 ns	$177 \pm 14 \text{ ns}$
	44%	40%	15%

References

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