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**Experimental**

**Materials.** All chemicals were used as received unless noted otherwise. RuCl$_3$$\cdot$3H$_2$O, RhCl$_3$$\cdot$3H$_2$O, 4,7-diphenyl-1,10-phenanthroline (Ph$_2$Phen) and 4,7-diphenyl-1,10-phenanthroline 4',4''-disulfonate sodium salt (NaSO$_3$Ph$_2$phen) were purchased from Alfa Aesar. 2,3-Bis(2-pyridyl)pyrazine (dpp), ascorbic acid, sodium ascorbate, tetrabutylammonium chloride (TBACl) and tetrabutylammonium hexafluorophosphate (TBAPF$_6$) were purchased from Aldrich Chemical Company. Spectral grade acetonitrile was purchased from Burdick & Jackson. Ammonium hexafluorophosphate (NH$_4$PF$_6$) was purchased from Oakwood Products Inc. HPLC grade diethyl ether and methylene chloride were purchased from Fisher Scientific. Absolute ethanol was purchased from Decon Laboratories. Sephadex® LH-20 was purchased from GE Healthcare. Silica gel (SiliaFlash® P60) was purchased from SiliCycle Inc. Ultrapure water was obtained from a Millipore Milli-Q® water purification system. Ultrapure argon and breathing air were purchased from Praxair Inc. The unsulfonated photocatalyst [(Ph$_2$phen)$_2$Ru(dpp)]$_2$RhCl$_2$Cl$_3$ was synthesized using previously reported procedures.$^1$

**Synthesis.** K$_3$[(SO$_3$Ph$_2$phen)$_2$Ru(dpp)]$_2$RhCl$_2$. The ligand NaSO$_3$Ph$_2$phen (2.82 g, 4.80 mmol) was dissolved in 50 mL of DMF and added dropwise to a solution containing RuCl$_3$$\cdot$3H$_2$O (0.62 g, 2.40 mmol) and tetrabutylammonium chloride hydrate (5.00 g) while stirring.$^2$ The reaction was refluxed for 6 h, cooled to RT, added to a separatory funnel containing 300 mL of water, extracted with chloroform (4 × 100 mL) and dried under vacuum. The complex was then purified using column chromatography having a silica gel stationary phase and a 10:1 acetone/methanol (v/v) mobile phase. The unreacted NaSO$_3$Ph$_2$phen ligand eluted first as a yellow band, followed by the dark purple product [(SO$_3$Ph$_2$phen)$_2$RuCl]$_4$ and finally the [(SO$_3$Ph$_2$phen)$_3$Ru]$^4$− eluted last with the majority of the emissive impurity remaining on the column. Next, dpp (0.07 g, 0.30 mmol) was combined with (Bu$_4$N)$_4$[(SO$_3$Ph$_2$phen)$_2$RuCl]$_2$ and the reaction refluxed for 4 h in 2:1 ethanol/water. The resulting product was then added dropwise to a saturated solution of KPF$_6$ in acetonitrile to induce precipitation and purified using silica gel chromatography having a 10:2:0.5 acetonitrile/methanol/water (v/v) mobile phase (Yield = 56%). (˗)ESI-MS: [M−2K]$^2$, m/z = 658.03.
Next, K₂[[(SO₃Ph:phen)₂Ru(dpp)]RhCl₃] (0.37 g, 0.27 mmol) of was combined with RhCl₃·3H₂O (0.04 g, 0.14 mmol) and refluxed in 2:1 ethanol:water (50 mL) for 4 h. The product was then added dropwise to a saturated solution of KPF₆ in acetone to induce precipitation, collected using vacuum filtration and purified using LH-20 size exclusion chromatography having a 2:1 acetonitrile/water (v/v) mobile phase (Yield = 83%). (-)ESI-MS: [M−3K]⁻, m/z = 935.65.
**Synthesis.** \( \text{K}_4[(\text{SO}_3\text{Ph}_2\text{phen})_2\text{Ru}]_2(\text{dpp})] \).

\( \text{K}_2[(\text{SO}_3\text{Ph}_2\text{phen})_2\text{Ru}]_2(\text{dpp})] \) (0.26 g, 0.19 mmol) was combined with \((\text{Bu}_4\text{N})_4[(\text{SO}_3\text{Ph}_2\text{phen})_2\text{RuCl}_2]\) (0.40 g, 0.18 mmol) and refluxed in 2:1 ethanol:water (30 mL) for 4 h. The product was then added dropwise to a saturated solution of KPF\(_6\) in acetone to induce precipitation, collected using vacuum filtration and purified using LH-20 size exclusion chromatography having a 2:1 acetonitrile/water (v/v) mobile phase (Yield = 70%). \(-\text{ESI-MS: } [\text{M}−4\text{K}]^{4−}, m/z = 599.75\).  

![Synthetic scheme for \( \text{K}_4[(\text{SO}_3\text{Ph}_2\text{phen})_2\text{Ru}]_2(\text{dpp})] \).](image)

**Methods.**

**Mass spectrometry.** Negative ion electrospray ionization mass spectroscopy (ESI\(^−\)) was carried out using an Agilent 6220 accurate mass time-of-flight (TOF) instrument. Samples were dissolved in HPLC grade water prior to analysis.

**Electrochemistry.** Cyclic voltammetry and square wave voltammetry were measured using a Bioanalytical Systems, Inc. (BASi) Epsilon potentiostat with a three-electrode configuration having a glassy carbon working electrode, Pt auxiliary electrode, and Ag/AgCl (3 M NaCl) as reference electrode using ferrocene as an internal standard \((\text{FeCp}_2^+/\text{FeCp}_2 = 0.46 \text{ V})\). All measurements were performed under argon containing 0.1 M TBAPF\(_6\) in spectrophotometric dimethylformamide with a 100 mV/s scan rate. Electrochemical oxidation in dimethylformamide was measured at −78°C using dry ice:isopropanol bath prior to analysis in order to increase the solvent potential window. Cyclic voltammetry was measured with a scan rate of 100 mV/s. Square wave voltammetry was measured having a frequency of 15 Hz, pulse time = 30 ms, fixed pulse potential = 25 mV, and a 4 mV potential step.
Figure S3. Cyclic voltammogram of (Bu$_4$N)$_3$[((SO$_3$Ph)$_2$phen)$_2$Ru(dpp)$_2$RhCl$_2$] (solid) and [((Ph$_2$phen)$_2$Ru(dpp)$_2$RhCl$_2$](PF$_6$)$_5$ (dotted) under an argon atmosphere using glassy carbon working electrode, platinum wire auxiliary electrode and Ag/AgCl reference electrode in 0.1 M Bu$_4$NPF$_6$ dimethylformamide solution. Anodic scans measured at -78°C. SO$_3$Ph$_2$phen = 4,7-diphenyl-1,10-phenanthroline 4',4''-disulfonate, Ph$_2$phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine).

Figure S4. Cyclic voltammogram of (Bu$_4$N)$_4$[((SO$_3$Ph$_2$phen)$_2$Ru]dpp] under an argon atmosphere using glassy carbon working electrode, platinum wire auxiliary electrode and Ag/AgCl reference electrode in 0.1 M Bu$_4$NPF$_6$ dimethylformamide solution. Anodic scans measured at -78°C. SO$_3$Ph$_2$phen = 4,7-diphenyl-1,10-phenanthroline 4',4''-disulfonate, dpp = 2,3-bis(2-pyridyl)pyrazine).
**Electronic Absorption Spectroscopy.** Electronic absorption was measured using a Hewlett-Packard 8453 diode array spectrophotometer with 1 nm resolution. Spectra were collected in 1 cm quartz cuvettes (Starna Cells Inc.) in ultrapure water. Extinction coefficients were prepared gravimetrically and calculated from the average of three samples.

![Figure S5. Electronic absorbance spectra of SO₃Ph₂phenRu₂.](image)

**Luminescence Spectroscopy.** Steady state luminescence spectroscopy was measured in screw-top 1 cm quartz cuvettes (Starna Cells Inc.). Emission spectra were measured at room temperature in ultrapure water following deoxygenation with argon. Spectra were measured using a Quanta Master QM-200-45E fluorimeter from Photon Technologies International Inc. employing a Czerny-Turner monochromator having a grating blazed at 750 nm. Samples were excited using a water-cooled 150 W xenon arc lamp and emission was measured at a 90° angle using a thermoelectrically cooled Hamamatsu R2658 photomultiplier tube operating in photon counting mode. Emission quantum yields were referenced to \([\text{Os(bpy)}_3]^{2+} (\Phi = 4.62 \times 10^{-3})\) and calculated using the method of Winfield and Williams,\(^4\)\(^5\) using the same instrument settings and correcting for PMT response. The rate of electron transfer \(k_{et}\) from the \(^3\)MLCT excited state was calculated using the following equations.

![Figure S6. Simplified Jablonski-type state diagram for SO₃Ph₂phenRu₂.](image)
\[ \tau_{\text{model}} = \frac{1}{k_r + k_{nr}} \] 

\[ \tau_{\text{trimetallic}} = \frac{1}{k_r + k_{nr} + k_{et}} \] 

\[ k_{et} = \frac{1}{\tau_{\text{trimetallic}}} - \frac{1}{\tau_{\text{model}}} \]

**Stern-Volmer Quenching.** Steady state luminescence was measured in screw-top 1 cm quartz cuvettes (Starnes Cells Inc.). Emission spectra were measured at room temperature in ultrapure water following deoxygenation with argon. Deoxygenated solutions of ascorbate were injected into the sealed cuvettes and the steady state luminescence measured using a Quanta Master QM-200-45E fluorimeter from Photon Technologies International Inc. Samples were excited using a water-cooled 150 W xenon arc lamp and emission was measured at a 90° angle using a thermoelectrically cooled Hamamatsu R2658 photomultiplier tube operating in photon counting mode and correcting for PMT response. Quenching rate constants \(k_q\) were calculated from the slope of a plot of \(\Phi_0/\Phi\) vs. ascorbate concentration and the excited state lifetime of the photocatalyst in the absence of quencher (Formula S10).

\[ k_q = K_{sv} / \tau_0 \]

Figure S11. Stern-Volmer analysis of \(K_3[[(\text{SO}_3\text{Ph}_{2}\text{phen})_2\text{Ru(dpp)}]_2\text{RhCl}_2]\) in deoxygenated aqueous solutions. \(\text{SO}_3\text{Ph}_{2}\text{phen} = 4,7\)-diphenyl-1,10-phenanthroline 4',4''-disulfonate, dpp = 2,3-bis(2-pyridyl)pyrazine, \(\Phi_0 = \) quantum yield of emission in the absence of quencher, \(\Phi = \) quantum yield of emission in the presence of quencher.
**Excited-State Lifetime Measurements.** Time-resolved emission spectroscopy of K₃[{(SO₃Ph₂phen)₂Ru(dpp)}₂RhCl₂] (10 µM) was measured in screw-top 1 cm quartz cuvettes (Starnes Cells Inc.). Time-resolved emission was measured using a PL-2300 nitrogen laser equipped with a PL-201 dye laser. The dye used was coumarin 500 and excitation monochromator was set to 520 nm. The emission was detected at 90° after passing through a monochromator set to 790 nm and measured using a Hamamatsu R928 PMT operating in direct output mode. The emission decay was recorded on a Techtronix TDS3052C oscilloscope. The lifetime was calculated from the average of 300 sweeps. Data was fitted to mono exponential decay (Formula S12).

\[ I(t) = A \times \exp(-t/\tau) \]

S12

Figure S13. Luminescence decay of K₃[{(SO₃Ph₂phen)₂Ru(dpp)}₂RhCl₂] (red) and [{(Ph₂phen)₂Ru(dpp)}₂RhCl₂]Cl₅ (blue) in deoxygenated aqueous solutions. SO₃Ph₂phen = 4,7-diphenyl-1,10-phenanthroline 4',4''-disulfonate, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine.
**Photoreduction.** Photochemical reduction was carried out in screw-top 0.4 cm quartz cuvettes (Starnes Cell Inc.) in ultrapure water. A stock solution (130 µM) of the photocatalyst was combined with pH 4 ascorbate buffer (2.2 M) in a 1:1 ratio to obtain a final concentration of 65 µM photocatalyst and 1.1 M ascorbate buffer. The resulting solutions were then purged with argon for 20 minutes prior to analysis. Samples were irradiated with light from a 470 nm LED source having a light flux of $6.27 \times 10^{19}$ photons/min. Electronic absorption was measured using a Hewlett Packard 8453 diode array spectrophotometer.

![Diagram](image)

**Figure S14.** Photoreduction of $\left[\left\{(\text{SO}_3\text{Ph})(\text{phen})\text{Ru(dpp)}\right\}\text{RhCl}_2\right]^{3-}$ to $\left[\left\{(\text{SO}_3\text{Ph})(\text{phen})\text{Ru(dpp)}\right\}\text{Rh}\right]^{3-}$. SO$_3$Phphen = 4,7-diphenyl-1,10-phenanthroline 4',4''-disulfonate, dpp = 2,3-bis(2-pyridyl)pyrazine.

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*9*
Hydrogen Production. Hydrogen production experiments were carried out as previously reported. A stock solution (130 µM) of the photocatalyst was combined with pH 4 ascorbate buffer (2.2 M) in a 1:1 ratio and purged with argon for 20 min. Samples tested under air saturated conditions were prepared as above and purged with breathing air for 20 min. The samples were irradiated with 470 nm light having a flux of $2.36 \times 10^{19}$ photons/min. Hydrogen production was monitored in real-time using HY-OPTIMA™ 700 in-process analyzers and verified by injecting a 100 µL headspace sample into a Shimadzu GC-2014 having a 5 Å molecular sieves PLOT column using high purity argon as the carrier gas. A calibration curve was generated by injecting known amounts of hydrogen gas and integrating signal intensities. Reported hydrogen production values are the average of three experiments. Turnovers were calculated by taking the ratio of the moles of H$_2$ produced to the moles of catalyst (Formula S15).

\[
TON = \frac{\text{moles of } H_2 \text{ produced}}{\text{moles of catalyst}}
\]

S15
References