Supporting Information

Ligand Triplet Fueled Long-lived Charge-separation in Ru(II) Complexes with Bithienyl-functionalized Ligands

Marek B. Majewski,[§] Norma R. de Tacconi,[±] Frederick M. MacDonnell,[*±] Michael O. Wolf[*§]

[§]Department of Chemistry, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada and [±]Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX, 76019-0065 , United States

Experimental Details

All solvents and reagents including those for NMR analysis (Cambridge Isotope Laboratories) were obtained from commercial sources and used as received except where noted. ^{1}H NMR spectra were recorded on either a Bruker AV300 (300 MHz) or Bruker AV400-Indirect (400 MHz) spectrometer, and ^{13}C NMR spectra were collected on a Bruker AV600 (600 MHz) spectrometer. All chemical shifts are referenced to residual solvent signals which were previously referenced to tetramethylsilane. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet). EI-MS (Kratos MS-50), ESI-MS (Bruker Esquire), MALDI-TOF MS (Bruker Biflex IV), and elemental analysis were acquired at the UBC Microanalysis facility.

UV/Vis absorption spectra were obtained with a Varian Cary 5000 using Fisher (HPLC Grade) solvents. Fluorescence data was collected on a Photon Technology International fluorimeter using a 75 W arc lamp as the source.

Fluorescence lifetime measurements were carried out using a Horiba Jobin Yvon TBX Picosecond Photon Detection Module (Nanoled λ_{ex} = 453 nm). Transient absorbance spectra were collected using a Princeton Instruments Spectra Pro 2300i Imaging Triple Grating Monochromator/Spectrograph with a Hamamatsu Dynamic

Range Streak Camera (excitation source: EKSPLA Nd:YAG laser, λ_{ex} = 355 nm, fwhm = 35 ps).

Synthesis of Ligands and Metal Complexes

5-amino-1,10-phenanthroline,[1] $Ru(DMSO)_4Cl_2$,[2] $[Ru(phen)_3][PF_6]_2$,[3] and $Ru(phen)_2Cl_2$[4] were prepared by literature procedure. 2-thiophenecarboxylic acid and 5-(2,2´-bithiophene)carboxylic acid were prepared using a modified literature procedure,[5] where one equivalent of *n*-BuLi was used to drive the carboxylation of only the 2- or 5-position respectively. Homoleptic metal complexes **3** and **4** were prepared by reacting **1** or **2** with $Ru(DMSO)_4Cl_2$ and complex **5** was prepared through reaction of **2** with $Ru(phen)_2Cl_2$.

The asymmetrical substitution of the phen ligands **1** and **2** can result in several possible stereoisomers of **3** and **4**; however ^{1}H NMR spectroscopy of the homoleptic complexes showed no appreciable signal broadening, suggesting either only one isomer is formed or any isomers present are not sufficiently different to result in chemical shift differences.

N-(1,10-phenanthrolin-5-yl)-thiophene-2-carboxamide (**1**)

2-thiophenecarboxylic acid (2.00 mmol, 256 mg) was dissolved in 5 ml of CH_2Cl_2. $SOCl_2$ (5 mmol, 0.5 ml) and DMF (2 drops) were added to the suspension. The reaction mixture was heated to reflux for 1 h. The mixture was then cooled to room temperature and the solvent was removed under reduced pressure to yield a yellow oily residue. This residue, the acyl chloride of 2-thiophenecarboxylic acid was used without purification in the next step. The flask containing the acyl chloride was cooled to 0^o C and placed under N_2. To this residue a solution of 5-amino-1,10-phenanthroline (0.800 mmol, 156 mg) and TEA (0.1 ml) in 15 ml of $CHCl_3$ was added dropwise. A significant amount of gas evolved and was released. After addition, the reaction mixture was left to warm to room temperature, and then heated to reflux for 19 h under N_2. The crude product precipitated as a yellowish-orange fine solid at the end of the heating period, was isolated by filtration and recrystallized from EtOH-H_2O. Yield: 0.08 g (33%). ^{1}H NMR (400 MHz, MeOD) δ ppm 7.32 (dd, *J* = 5.03, 3.81 Hz, 1 H) 7.88 (dd, *J* = 5.18, 1.22 Hz, 1 H) 8.14 (dd, *J* = 3.81,

1.07 Hz, 1 H) 8.18 (dd, *J* = 8.53, 4.87 Hz, 1 H) 8.24 (dd, *J* = 8.22, 5.18 Hz, 1 H) 8.48 (s, 1 H) 8.99 (dd, *J* = 8.53, 1.52 Hz, 1 H) 9.09 (dd, *J* = 8.22, 1.22 Hz, 1 H) 9.25 (dd, *J* = 5.18, 1.52 Hz, 1 H) 9.32 (dd, *J* = 4.72, 1.37 Hz, 1 H). ^{13}C NMR (150.92 MHz, DMSO-d_6) δ ppm 123.08 (2xCH), 123.66, 125.76, 127.93, 128.30, 129.74, 131.57, 132.23, 132.37, 136.07, 139.18, 144.34, 145.86, 149.84, 150.04, 161.14. HR-EI MS *m/z* 305.06228 ($C_{17}H_{11}N_3OS$)

N-(1,10-phenanthrolin-5-yl)-2,2´-bithiophene-5-carboxamide (**2**)

Compound **2** was prepared using the same method as described for **1**. $CHCl_3$ was used in the preparation of the acyl chloride, and was thoroughly purged with N_2 prior to the addition of 5-(2,2´-bithiophene)carboxylic acid. The final product was used without purification. Yield: 0.162 g (84%). ^{1}H NMR (300 MHz, MeOD) δ ppm 7.13 (dd, *J* = 5.12, 3.58 Hz, 1 H) 7.40 (d, *J* = 4.10 Hz, 1 H) 7.44 (d, *J* = 3.84 Hz, 1 H) 7.50 (d, *J* = 5.12 Hz, 1 H) 8.05 (d, *J* = 4.10 Hz, 2 H) 8.22 (ddd, *J* = 18.11, 8.38, 4.99 Hz, 2 H) 8.49 (s, 1 H) 9.01 (dd, *J* = 8.58, 1.41 Hz, 1 H) 9.10 (dd, *J* = 8.19, 1.28 Hz, 1 H) 9.24 (dd, *J* = 5.12, 1.28 Hz, 1 H) 9.32 (dd, *J* = 4.74, 1.41 Hz, 1 H). ^{13}C NMR (150.92 MHz, MeOD) δ ppm 122.02 (2×CH), 124.72, 125.07, 125.50, 125.86, 126.46, 127.26, 128.74, 129.22, 131.63, 133.13, 135.58, 136.69, 136.81, 141.89, 142.39, 145.80, 146.65, 149.03, 160.86. HR-EI MS m/z 388.0578 ($C_{21}H_{14}N_3OS_2$)

*Ru(**1**)$_2$Cl$_2$*

Compound **1** (100 mg, 0.327 mmol, 2 eq) was dissolved in 10 ml of EtOH:H_2O (4:1). A large excess of LiCl was added (6 mmol). The mixture was warmed to dissolve **1** and purged with N_2 for 15 minutes prior to the addition of $Ru(DMSO)_2Cl_2$ (79.4 mg, 0.164 mmol). The reaction mixture was heated to reflux overnight, and then concentrated under reduced pressure until a brown solid precipitated. This crude product was isolated by filtration, washed with an excess of EtOH and acetone, and dried under vacuum. Due to poor solubility, this product was used in the next step without purification. Yield: 0.125 g (97%). MALDI-TOF MS *m/z* 749.8 $[M]^+$

*Ru(**2**)$_2$Cl$_2$*

Ru(**2**)$_2$Cl$_2$ was prepared using the same method as Ru(**1**)$_2$Cl$_2$. After heating to reflux, a very dark purple solid was suspended in the reaction mixture. This solid was isolated by filtration, washed with EtOH and acetone, dried under vacuum and used in the next step without further purification. Yield: 0.177 g (68%). MALDI-TOF MS *m/z* 911.2 $[M]^+$

*[Ru(**1**)$_3$][PF$_6$]$_2$* (**3**)

Ru(**1**)$_2$Cl$_2$ (80 mg, 0.10 mmol) and **1** (46 mg, 0.15 mmol) were combined in 10 ml of a EtOH:H_2O (4:1) mixture that had been purged with N_2 for 15 minutes. The reaction mixture was heated to reflux overnight, cooled to room temperature and the desired product was precipitated as an orange-brown solid through the addition of a saturated solution of NH_4PF_6. To purify the product, it was first dissolved in CH_3CN and then passed through a silica column using a CH_3CN:H_2O:$KNO_{3(aq)}$ (96:3:1) eluent. The major orange band was collected, concentrated under reduced pressure and converted to the hexafluorophosphate salt by addition of a saturated NH_4PF_6 solution. The resulting bright orange product was collected by vacuum filtration, washed with $NH_4PF_{6(aq)}$ and water, and then dried under vacuum to give pure **3**. Yield: 0.015 g (12 %). ^{1}H NMR (400 MHz, acetonitrile-d_3) δ ppm 7.28 - 7.33 (m, 5 H) 7.67 (dddd, *J* = 10.85, 8.19, 5.48, 2.59 Hz, 10 H) 7.82 (d, *J* = 4.87 Hz, 4 H) 8.03 (d, *J* = 3.96 Hz, 7 H) 8.04 - 8.07 (m, 3 H) 8.10 - 8.15 (m, 5 H) 8.51 (d, *J* = 1.83 Hz, 5 H) 8.60 (d, *J* = 8.22 Hz, 5 H) 8.72 (d, *J* = 8.53 Hz, 5 H) 9.31 (s, 5 H). ^{13}C NMR (150.92 MHz, acetonitrile-d_3) δ ppm 121.71 (2xCH), 124.86, 125.65, 127.34, 127.92, 129.45, 130.09, 132.04, 132.87, 133.24, 136.00, 145.92, 147.82, 152.11, 152.88, 161.01. HR-ESI MS m/z 1159.0570 [Ru(**1**)$_3$][PF$_6$]$^+$ ($C_{51}H_{33}N_9O_3F_6PS_3Ru$).

*[Ru(**2**)$_3$][PF$_6$]$_2$* (**4**)

Complex **4** was prepared and purified using the same method as for **3**. Yield: 0.030 g (18 %). ^{1}H NMR (400 MHz, acetonitrile-d_3) δ ppm 7.14 (dd, *J* = 5.03, 3.81 Hz, 1 H) 7.39 (d, *J* = 3.96 Hz, 1 H) 7.44 (d, *J* = 3.65 Hz, 1 H) 7.48 (d, *J* = 5.18 Hz, 1 H) 7.66 (dddd, *J* = 13.52, 8.26, 5.33, 2.74 Hz, 2 H) 7.93 (d, *J* = 3.96 Hz, 1 H) 8.00 - 8.06 (m, 1 H) 8.09 - 8.15 (m, 1 H) 8.50 (d, *J* = 2.44 Hz, 1 H) 8.58 (d, *J* = 8.53 Hz, 1 H) 8.72 (d, *J* = 8.53

Hz, 1 H) 9.31 (s, 1 H). ^{13}C NMR (150.92 MHz, acetonitrile-d_3) δ ppm 121.76, 124.05, 124.91, 125.32, 125.67, 126.47, 127.32, 128.11, 130.06, 130.41, 132.89, 133.19, 135.40, 136.00, 136.17, 142.95, 145.89, 147.82, 152.04, 152.87, 160.76. ESI MS *m/z* 1408.2 $[Ru(\mathbf{2})_3][PF_6]^+$. Anal. Calcd. for $C_{63}H_{41}F_{12}N_9O_4P_2RuS_6$ ($[Ru(\mathbf{2})_3][PF_6]_2$ + H_2O): C, 48.15; H, 2.63; N, 8.02. Found: C, 48.11; H, 2.80; N, 7.82.

*[Ru(**2**)(phen)$_2$][PF$_6$]$_2$* (**5**)

$Ru(phen)_2Cl_2$ (69 mg, 0.13 mmol) and **2** (50 mg, 0.13 mmol) were suspended in a mixture of 4:1 EtOH:H_2O that had been purged with N_2 for 15 minutes. The reaction mixture was left to reflux under N_2 overnight, then cooled to room temperature and filtered through glass wool to remove any insoluble impurities. The filtrate was added to a stirring saturated aqueous solution of NH_4PF_6 and the resulting orange-red precipitate was collected. The product was purified using column chromatography as in the synthesis of **3**. Yield: 0.040 g (27%). ^{1}H NMR (600 MHz, acetonitrile-d_3) δ ppm 7.13 (dd, *J*=5.12, 3.58 Hz, 1 H) 7.38 (d, *J*=4.10 Hz, 1 H) 7.44 (d, *J*=3.58 Hz, 1 H) 7.48 (dd, *J*=5.12, 1.02 Hz, 1 H) 7.58 - 7.68 (m, 4 H) 7.93 (d, *J*=4.10 Hz, 1 H) 7.97 - 7.99 (m, 1 H) 8.00 - 8.03 (m, 1 H) 8.05 - 8.09 (m, 2 H) 8.25 (s, 2 H) 8.48 (s, 1 H) 8.56 (d, *J*=7.68 Hz, 1 H) 8.60 (t, *J*=8.70 Hz, 2 H) 8.69 (d, *J*=7.68 Hz, 1 H) 9.35 (s, 1 H). ^{13}C NMR (150.92 MHz, acetonitrile-d_3) δ ppm 123.46, 125.85, 126.58, 127.11, 127.22, 127.36, 128.27, 129.06, 129.36, 129.39, 129.90, 131.83, 132.12, 132.33, 132.36, 134.56, 134.95, 137.70, 138.11, 138.15, 144.74, 147.70, 149.22, 149.27, 149.65, 153.80, 154.25, 154.28, 154.36, 154.39, 154.60, 162.50. ESI MS *m/z* 994.2 $[Ru(\mathbf{2})(phen)_2][PF_6]^+$. Anal. Calcd. for $C_{45}H_{31}F_{12}N_7O_2P_2RuS_2$ ($[Ru(\mathbf{2})(phen)_2][PF_6]_2$ + H_2O): C, 46.72; H, 2.70; N, 8.47. Found: C, 46.78; H, 2.83; N, 8.42.

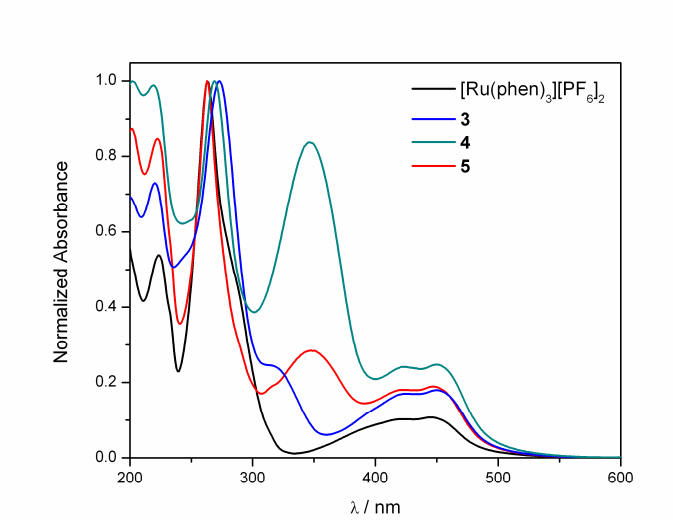

Figure S1. Normalized absorbance spectra of $[Ru(phen)_3][PF_6]_2$ (black), **3** (blue), **4** (teal), **5** (red).

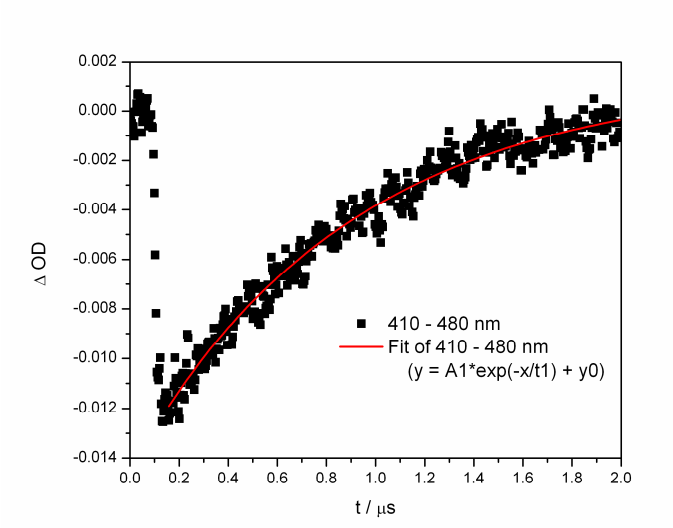

Figure S2. Time resolved transient absorption decay curve of complex **3** (410 – 480 nm) with monoexponential fit shown in red.

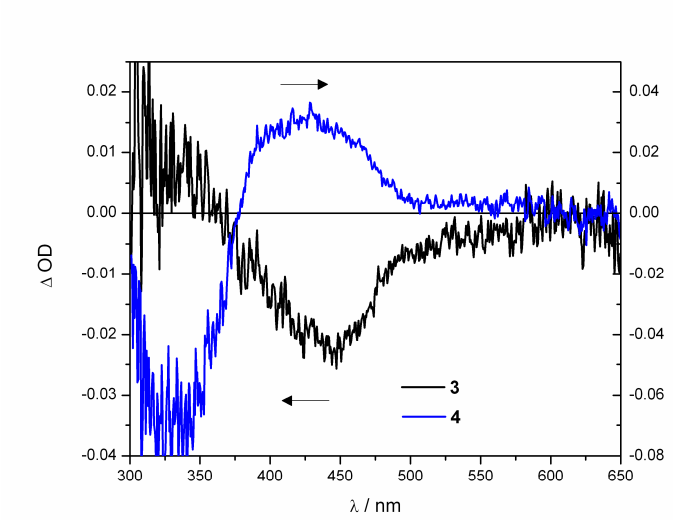

Figure S3. Differential absorption spectra of complexes **3** (black) and **4** (blue) 6 ns after excitation (λ_{ex} = 355 nm)

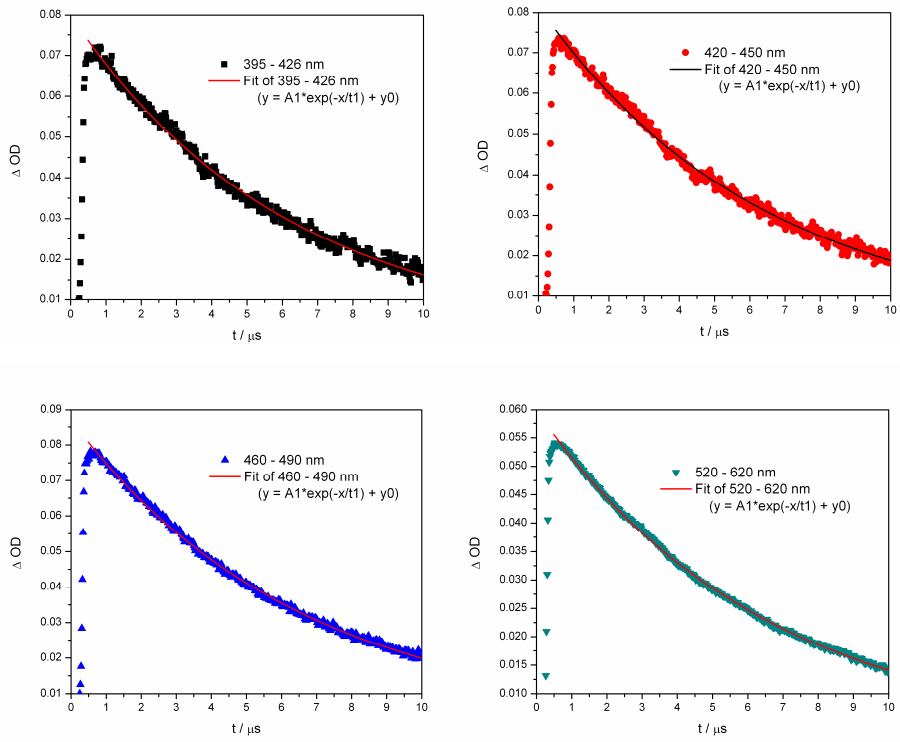

Figure S4. Time resolved transient absorption decay curves of complex **4** at various wavelengths with monoexponential fits shown in black and red.

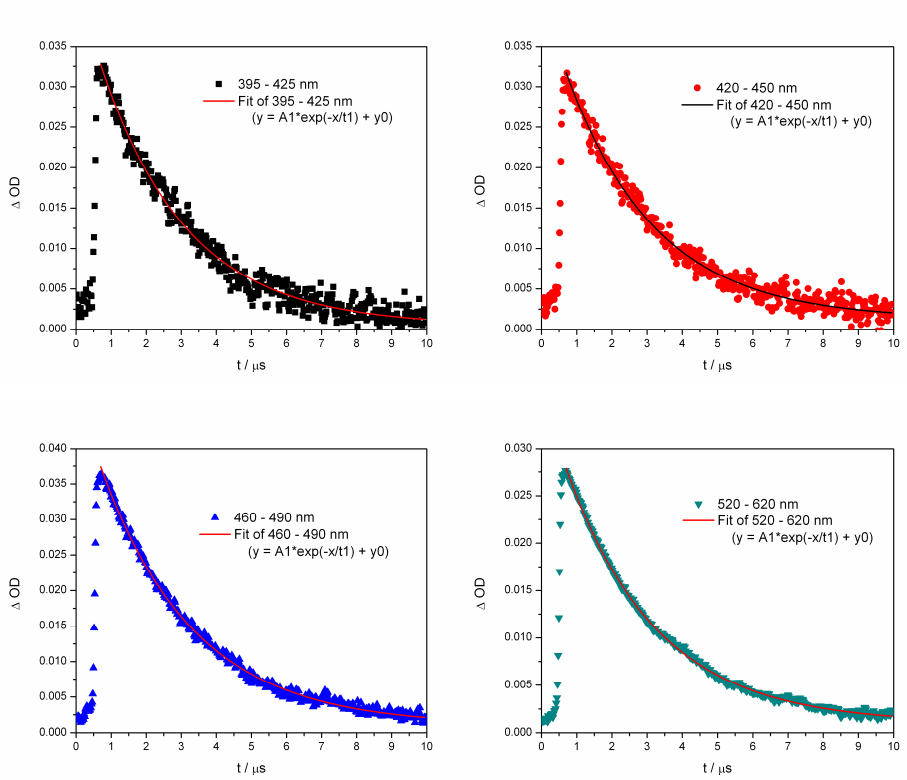

Figure S5. Time resolved transient absorption decay curves of complex **5** at various wavelengths with monoexponential fits shown in black and red.

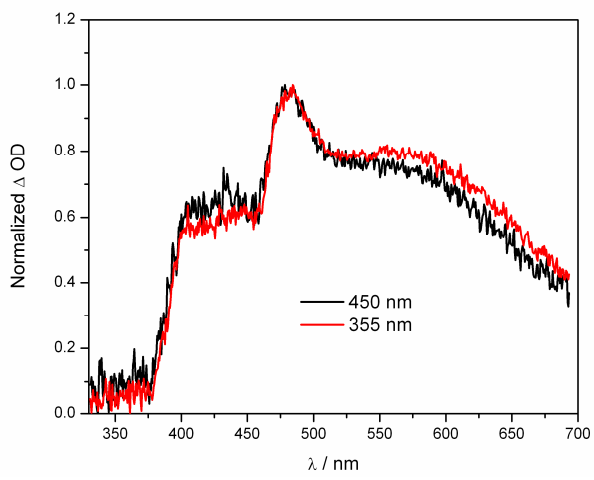

Figure S6. Differential transient absorption spectrum of complex **4** 200 ns after excitation at 450 nm (black) and 355 nm (red).

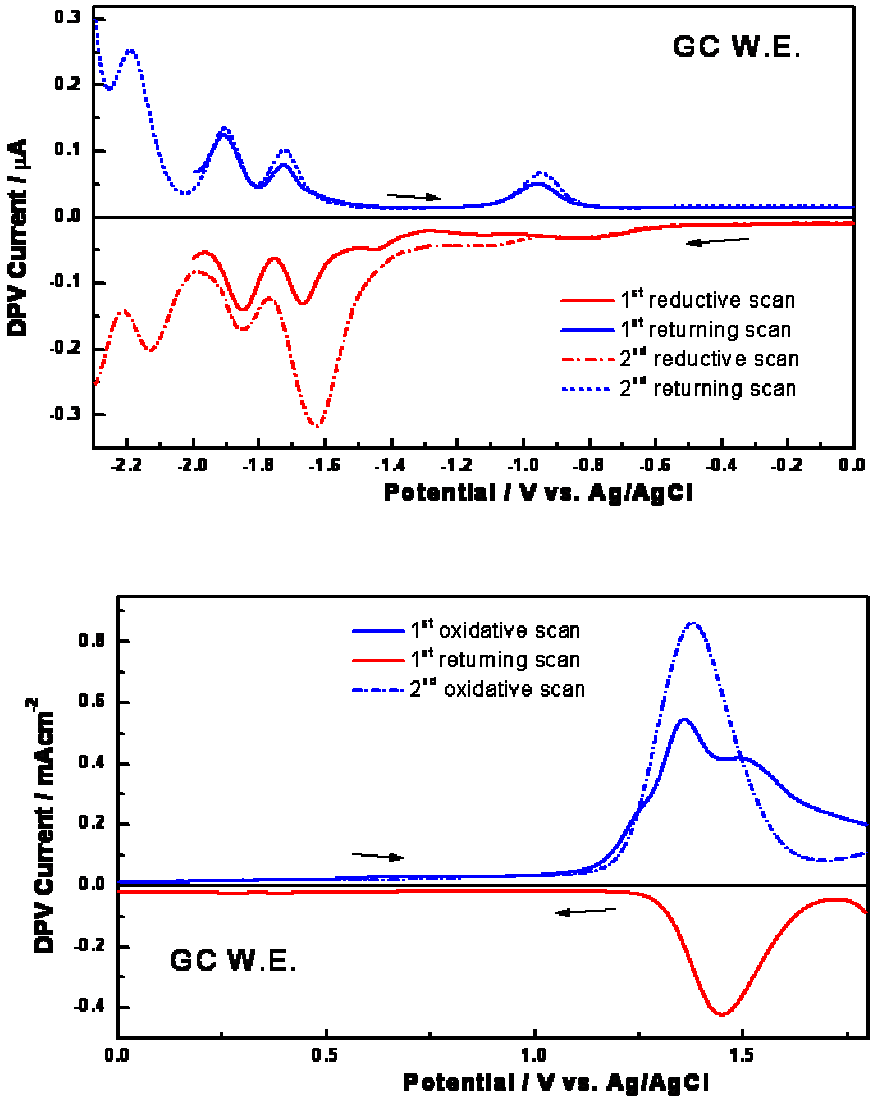

Figure S7. DPV - Reduction (top) and oxidation (bottom) of 200 μM **4** in CH_3CN containing *n*-$[Bu_4N]PF_6$ (0.1 M) using a GC disk electrode (1 mm diameter). Voltammograms were obtained with two different negative potential limits. DPV parameters: Potential pulse amplitude = 0.05 V, step size = 0.004 V, pulse duration = 0.05 s, pulse period = 0.2 V.

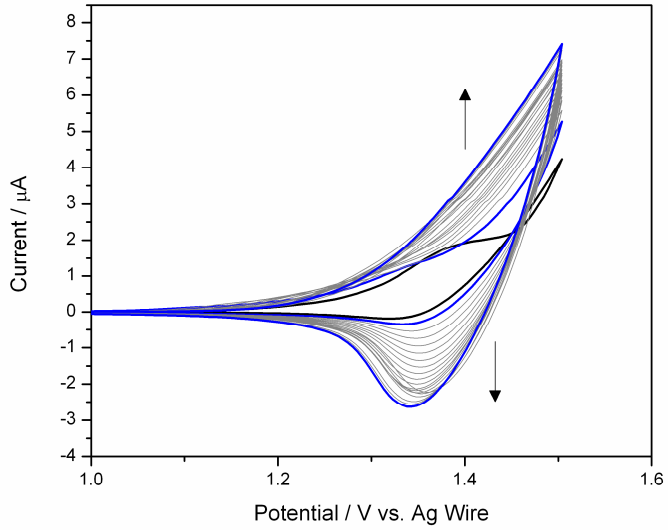

Figure S8. Cyclic voltammetry showing electropolymerization of complex **4** (ITO working electrode, Pt mesh counter electrode, 100 mV/s, CH_3CN, 0.1 M *n*-$[Bu_4N]PF_6$)

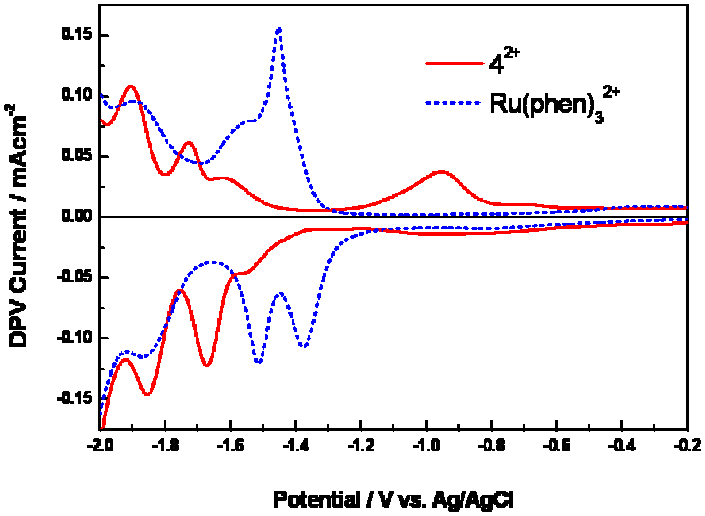

Figure S9. Comparison of DPV for the electroreduction of $\mathbf{4}^{2+}$ (red line) and $Ru(phen)_3^{2+}$ (dashed blue line) in MeCN containing *n*-$[Bu_4N]PF_6$ (0.1 M) using a Pt disk electrode (105 mm diameter). DPV parameters: Potential pulse amplitude = 0.05 V, step size = 0.004 V, pulse duration = 0.05 s, pulse period = 0.2 V.

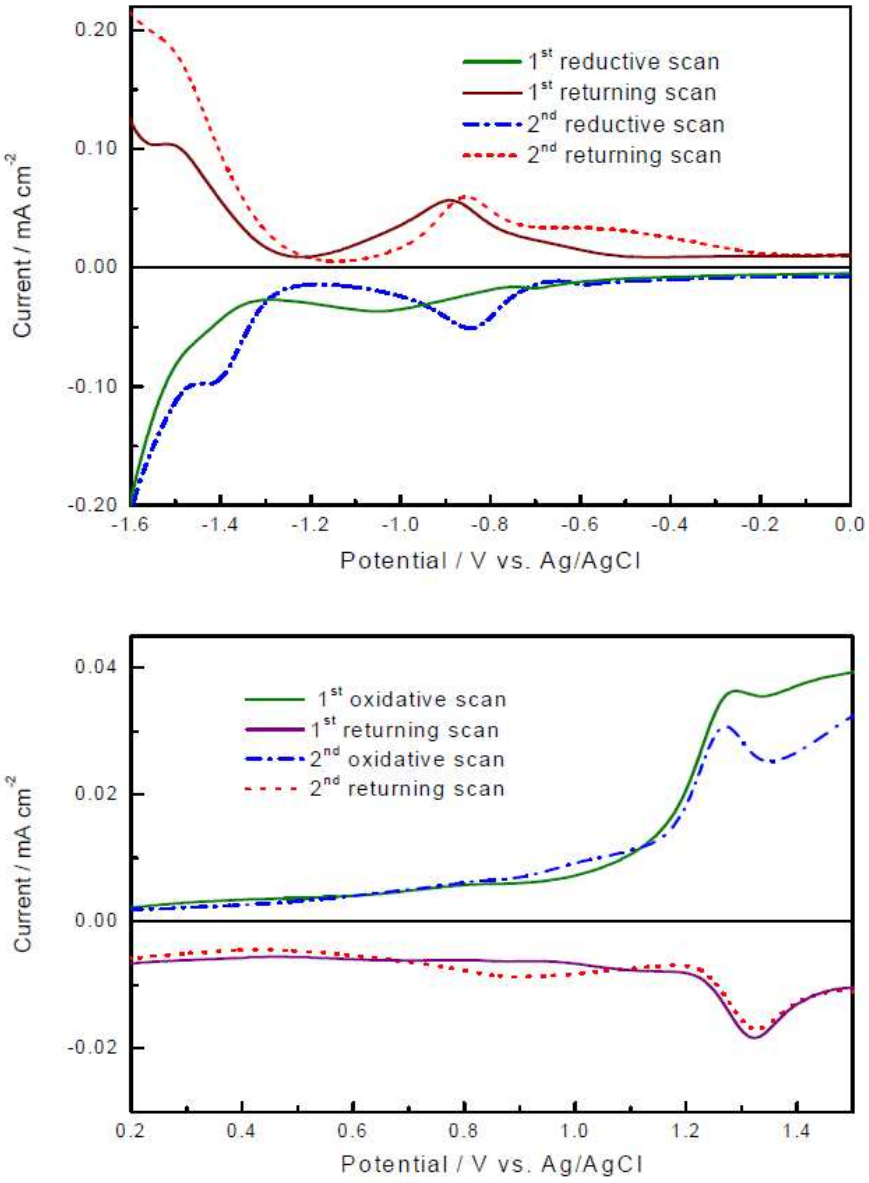

Figure S10. DPV - electroreduction (top) and electrooxidation (bottom) of complex **3** (50 μM) in CH_3CN containing 0.1 M *n*-$[Bu_4N]PF_6$ as supporting electrolyte and using a Pt disk electrode (1 mm diameter). DPV parameters: Potential pulse amplitude = 0.05 V. step size = 0.004 V, pulse duration = 0.05 s, pulse period = 0.2 V.

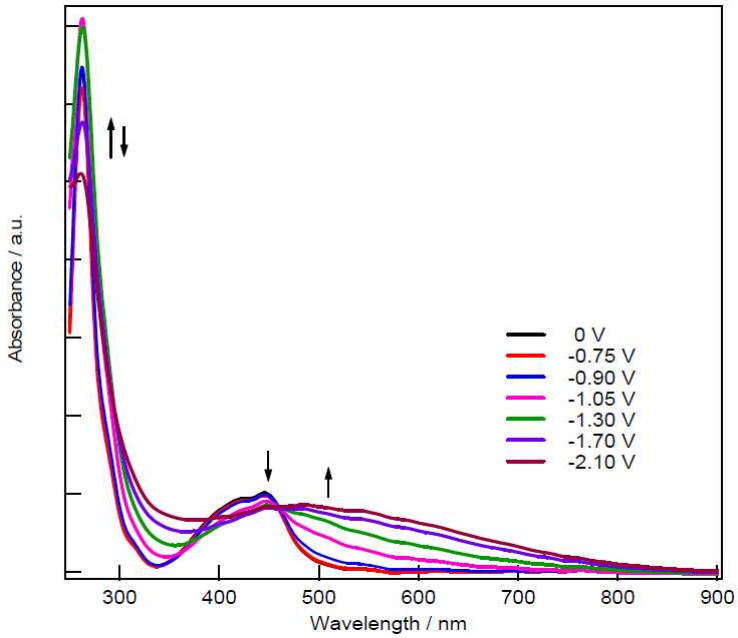

Figure S11. Absorption spectra recorded at selected potentials during the electroreduction of $Ru(phen)_3^{2+}$ (100 μM) in 0.1 M *n*-$[Bu_4N]PF_6/CH_3CN$ using progressively negative potentials from 0.0 V to -2.1 V. Working electrode: Pt mesh in capillary cell.

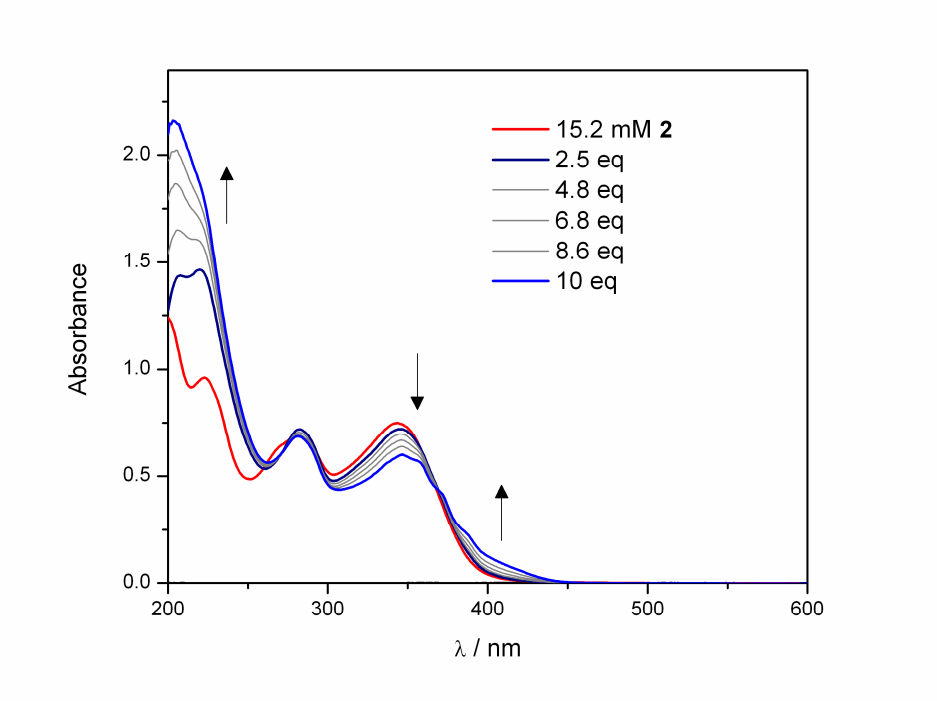

Figure S12. Oxidation of **2** with increasing amounts of $NOPF_6$ in CH_3CN.

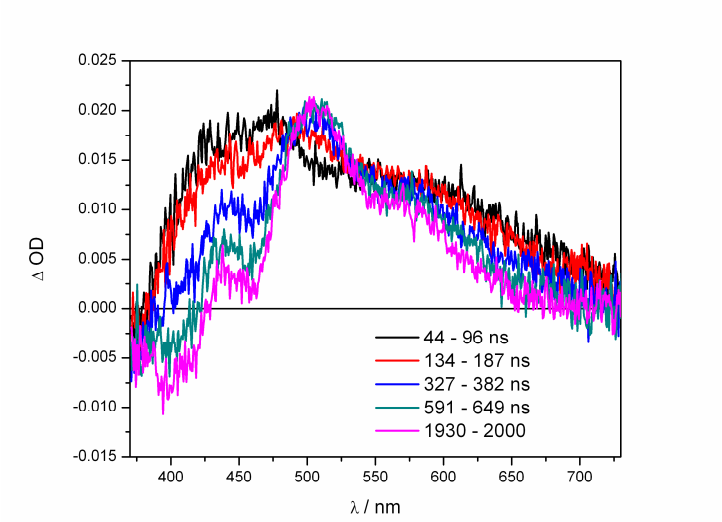

Figure S13. Differential absorption spectra of complex **4** in the presence of TTF, illustrating decreases in absorption in the 400-450 nm region up to 2 μs after excitation (λ_{ex} = 355 nm). Addition of a sacrificial electron donor, tetrathiafulvalene (TTF), to **4** during the TA experiment results in bleaching of the high energy bands of **4**, concomitant with the growth of bands corresponding to TTF^{+}. TTF donates an electron to the oxidized bithienyl moiety formed via reductive quenching of the photoexcited Ru(III).

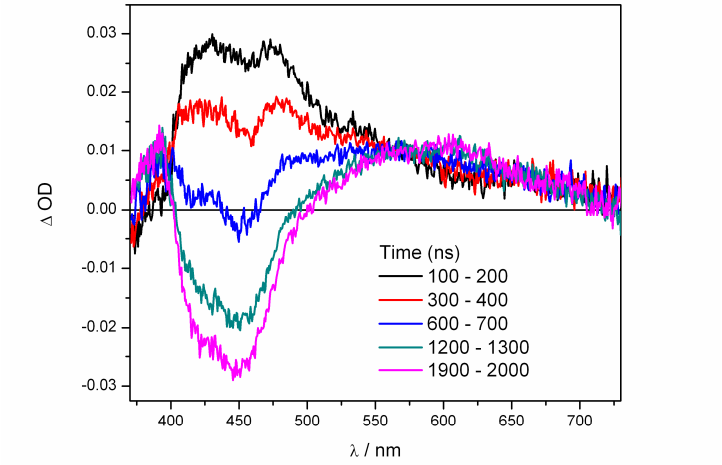

Figure S14. Differential absorption spectra of **4** in the presence of MV^{2+}, up to 2 μs after excitation. Pictured is the bleaching of the bands corresponding to the excited state **4** species concomitant with growth of bands corresponding to the formation of $MV^{\cdot+}$ at 400 nm and ~600 nm. (λ_{ex} = 355 nm). Addition of an electron acceptor, methyl viologen (MV^{2+}), yields reversible electron transfer from photoexcited **4** to form $MV^{\cdot+}$ as evidenced by growth of these bands. Importantly, bleaching in the 400–500 nm region also occurs, indicating the spectral features of both the oxidized and reduced species in

the ILCT state overlap to a significant extent. These data together with the TTF experiments support the formation of the charge separated ILCT species in **4**.

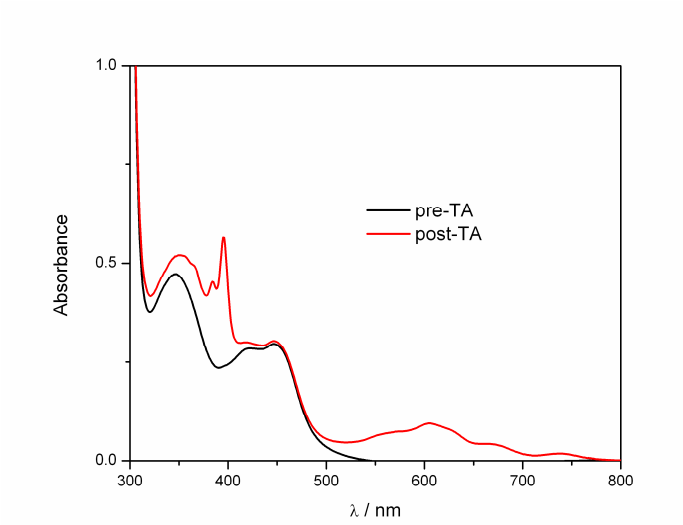

Figure S15. Ground state absorption spectrum of complex **4** (CH_3CN) in the presence of an excess of MV^{2+} before laser irradiation at 355 nm (black), and after irradiation (red). Bands at 400 nm, and ~600 nm correspond to the reduced $MV^{\cdot+}$ species.

References

(1) García-Fresnadillo, D.; Orellana, G. *Helv. Chim. Acta* **2001**, *84*, 2708.
(2) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.
(3) Elliott, C. M.; Hershenhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7519.
(4) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(5) Kagan, J.; Arora, S. K.; Ustunol, A. *J. Org. Chem.* **1983**, *48*, 4076.