

Supporting Information

Exploiting Conformational Dynamics to Facilitate Formation and Trapping of Electron Transfer Photoproducts in Metal Complexes

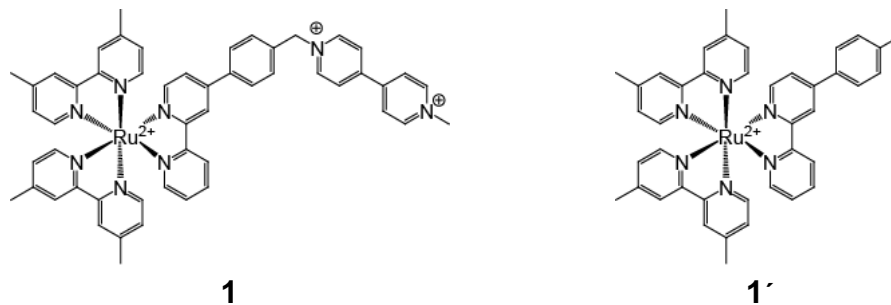
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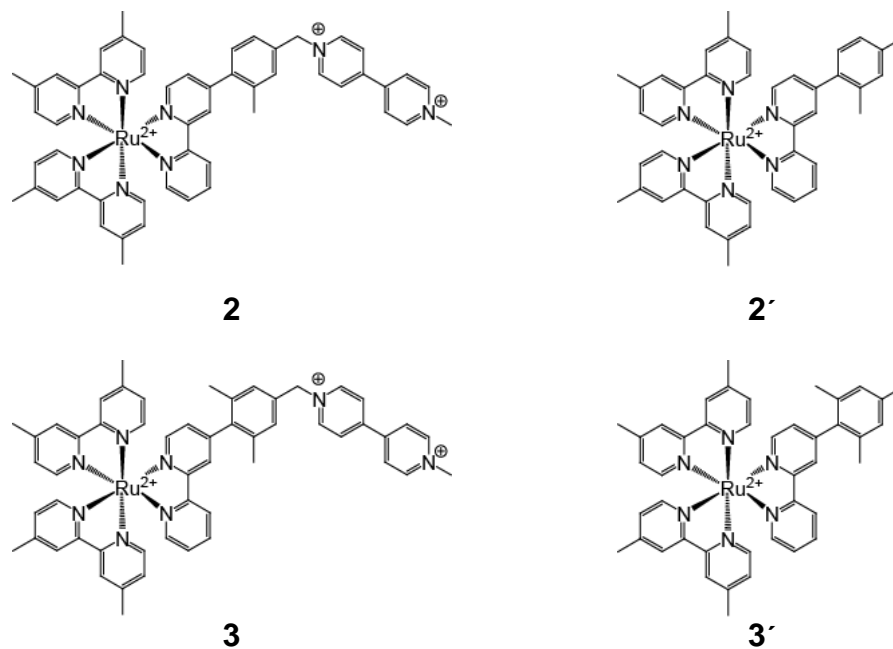
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Reference 16 in the manuscript (also reference 12 in this Supporting Information document) is as follows:

- (16) Gaussian 09, Revision A.1 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc.: Wallingford CT, 2009.

Supporting Figures & Tables:





Scheme S1. Donor and D-A complexes discussed herein (isolated as PF_6^- salts).

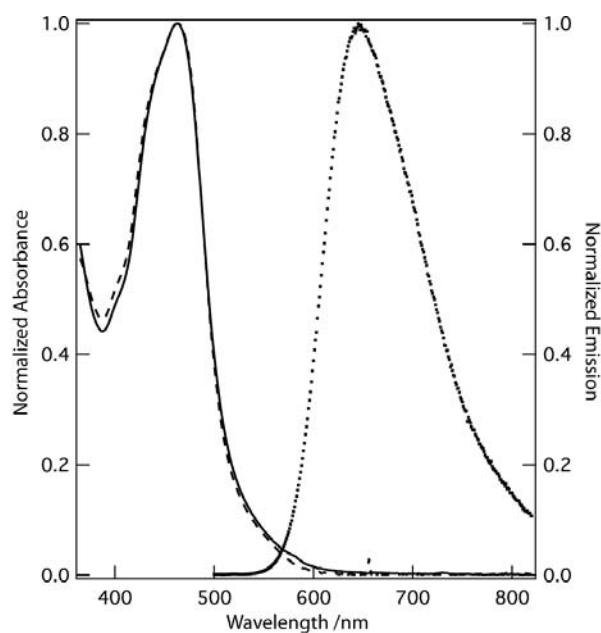


Figure S1. Normalized UV-visible absorption spectrum for **1'** (solid) and **1** (dashed) in 298 K CH_3CN . The corrected emission spectrum of **1'** collected in deoxygenated CH_3CN at 298 K is also shown (dotted).

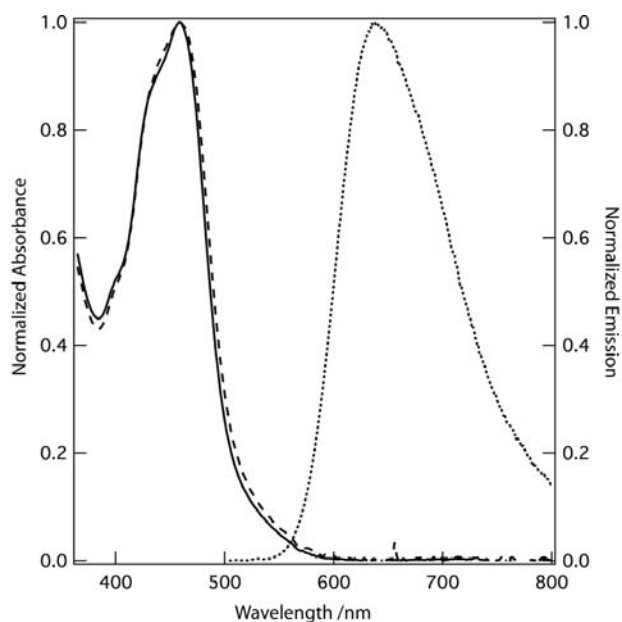


Figure S2. Normalized UV-visible absorption spectrum for **2'** (solid) and **2** (dashed) in 298 K CH_3CN . The corrected emission spectrum of **2'** collected in deoxygenated CH_3CN at 298 K is also shown (dotted).

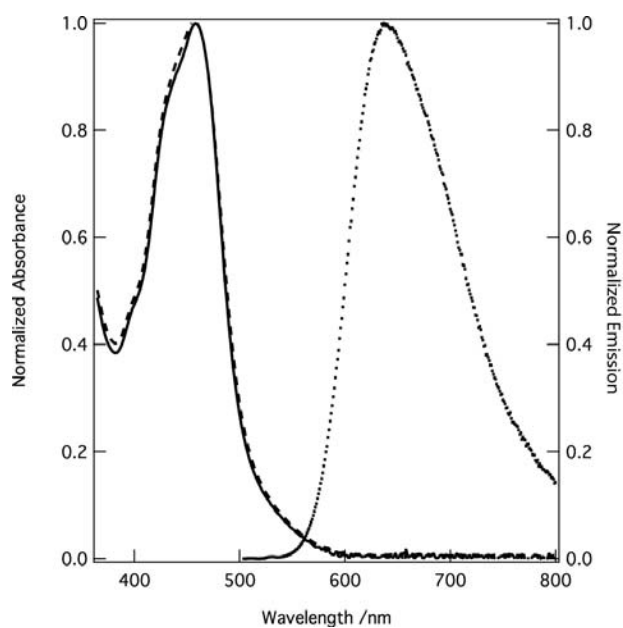


Figure S3. Normalized UV-visible absorption spectrum for **3'** (solid) and **3** (dashed) in 298 K CH_3CN . The corrected emission spectrum of **3'** collected in deoxygenated CH_3CN at 298 K is also shown (dotted).

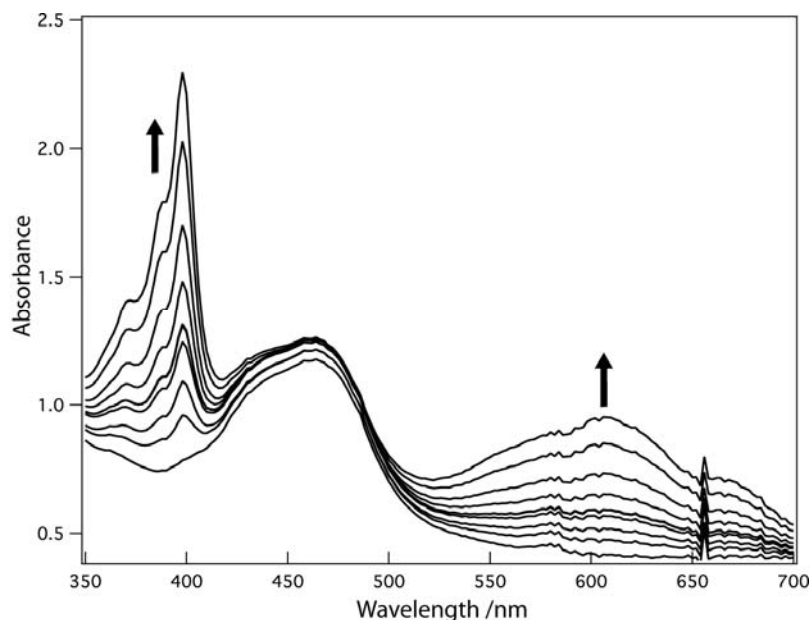


Figure S4. Spectroelectrochemical data for **1** recorded over a 45 min. period of bulk electrolysis with voltage held at -800 mV versus Ag/AgNO₃. The growth of features at ~ 400 nm and ~ 610 nm indicate production of reduced methyl viologen. Features including discontinuities at ~ 580 nm and 657 nm are an artifact of the blanking procedure.

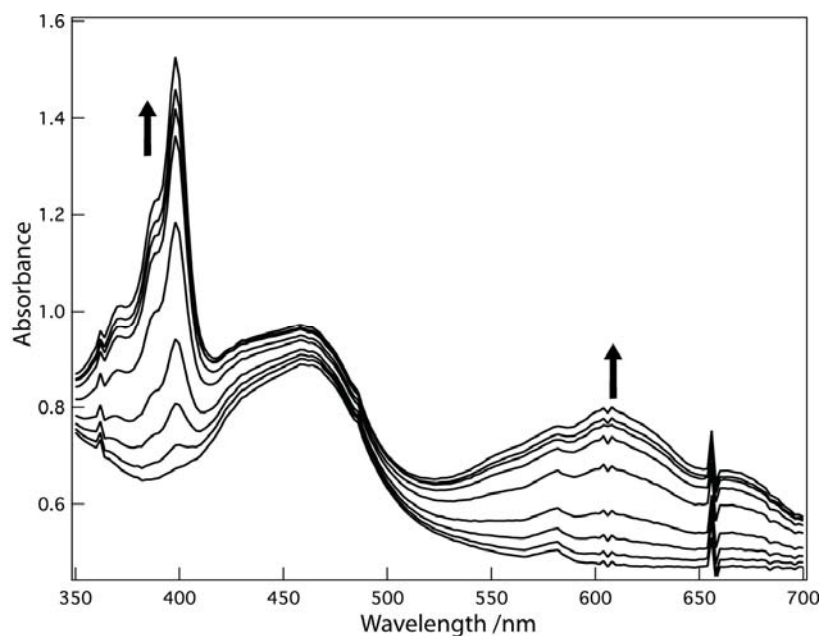


Figure S5 Spectroelectrochemical data for **2** recorded over a 30 min. period of bulk electrolysis with voltage held at -800 mV versus Ag/AgNO₃. The growth of features at ~ 400 nm and ~ 610 nm indicate production of reduced methyl viologen. Features including discontinuities at ~ 580 nm and 657 nm are an artifact of the blanking procedure.

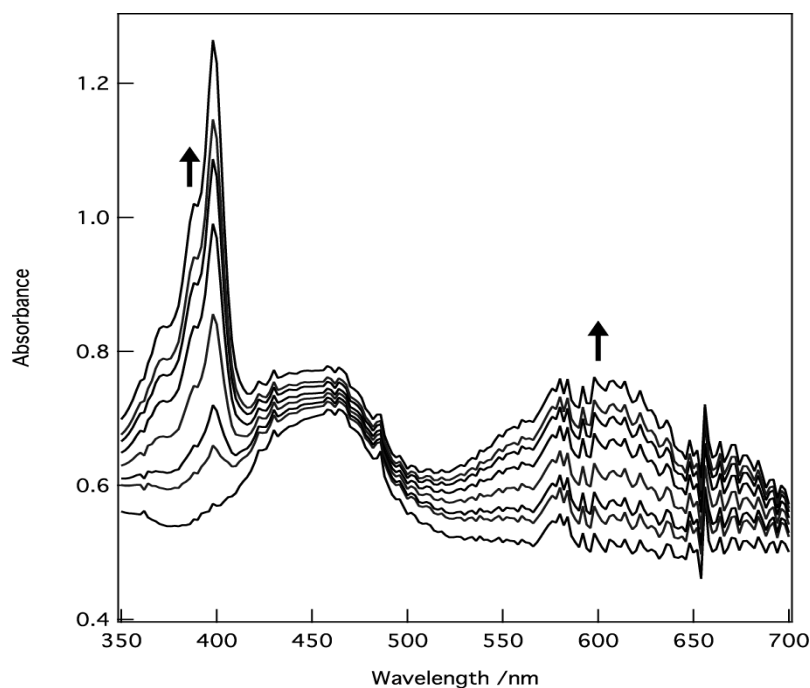


Figure S6 Spectroelectrochemical data for **3** recorded over a 23 min. period of bulk electrolysis with voltage held at -1000 mV versus Ag/AgNO₃. The growth of features at ~400 nm and ~610 nm indicate production of reduced methyl viologen. Features including discontinuities at ~580 nm and 657 nm and sharp noise peaks throughout the spectra are an artifact of the blanking procedure and the low concentration of this sample.

Table S1. Electrochemical Data in Room Temperature CH₃CN vs. SCE

Complex	(Ru ^{III/II}) /V	MV ^{2+/1+} /V	MV ^{1+/0} /V	1 st Ligand Red. /V	2 nd Ligand Red. /V	$\Delta E_{(\text{redox})}$ /V	ΔG_{MLCT} /eV
	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$		
[Ru(dmb) ₃](PF ₆) ₂	1.14 (3 ^{+/2+})	--	--	-1.44 (2 ^{+/1+})	-1.61 (1 ^{+/0})	2.56	2.16
1 '	1.16 (3 ^{+/2+})	--	--	-1.42 (2 ^{+/1+})	-1.59 (1 ^{+/0})	2.58	2.11
2 '	1.17 (3 ^{+/2+})	--	--	-1.42 (2 ^{+/1+})	-1.60 (1 ^{+/0})	2.59	2.13
3 '	1.20 (3 ^{+/2+})	--	--	-1.41 (2 ^{+/1+})	-1.62 (1 ^{+/0})	2.61	2.14
1	1.16 (5 ^{+/4+})	-0.40 (4 ^{+/3+})	-0.79 (3 ^{+/2+})	-1.42 (2 ^{+/1+})	-1.60 (1 ^{+/0})	--	--
2	1.18 (5 ^{+/4+})	-0.40 (4 ^{+/3+})	-0.81 (3 ^{+/2+})	-1.42 (2 ^{+/1+})	-1.61 (1 ^{+/0})	--	--
3	1.18 (5 ^{+/4+})	-0.40 (4 ^{+/3+})	-0.80 (3 ^{+/2+})	-1.42 (2 ^{+/1+})	-1.61 (1 ^{+/0})	--	--

All measurements were made using a freshly prepared solution of 0.1 M NH₄PF₆ in anhydrous CH₃CN.

Synthetic Details:

General. All reagents and materials from commercial sources were used as received. Solvents were purchased from Sigma-Aldrich or Mallinckrodt Chemicals. All deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. The 4,4'-dimethyl-2,2'-bipyridine (dmb) was purchased from Sigma-Aldrich. The various aryl boronic acids needed for the Suzuki couplings were obtained either from Combi-Blocks or Cuschem, Inc. The 4-bromo-2,2'-bipyridine (brbpy) was obtained from Shanghai Elittes Organics Co, Ltd. The ligands 4-(1-(1'-methyl-4,4'-bipyridinediium-1-yl)-methylphenyl)-2,2'-bipyridine¹ (bpy- ϕ -MV²⁺), 4-*p*-tolyl-2,2'-bipyridine² (*p*-tol-bpy) and the acceptor synthon (1-methyl-4,4'-bipyridinium)PF₆³ were prepared according to previously published procedures. [Ru(dmb)₃](PF₆)₂ was prepared according to previously reported procedures using Ru(DMSO)₄Cl₂ and the dmb ligand.⁴ ¹H and 2D-NMR spectra were recorded on a Varian Inova 500 MHz, Varian Inova 400 MHz or a Bruker Avance-III 300 MHz spectrometer. Accurate mass measurements were obtained in house from the University of Colorado's Central Analytical Laboratory.

General Procedure for Suzuki Coupling Reactions. 1 eq. of brbpy and 1.4 eq. of arylboronic acid were reacted with 3 eq. of Na₂CO₃ and 2.5 mol % of Pd(PPh₃)₄ in a degassed solution of 1:1 H₂O:CH₃CN at reflux under argon for 72 - 96 hours (progress monitored by TLC). The solvent was removed and the residual oil extracted in H₂O/CH₂Cl₂. The organic layer was again dried down and the residue was purified on a silica column using 20% ethyl acetate in hexanes unless otherwise noted.

4-(2,4-dimethylphenyl)-2,2'-bipyridine. Yield: 35% ¹H NMR (CDCl₃) δ : 2.33 (s, 3H), 2.40 (s, 3H), 7.13 (m, 3H), 7.23 (m, 1H), 7.40 (m, 1H), 7.79 (t, 1H, J = 1.8 Hz, 5.8 Hz), 8.27 (d, 1H, J = 0.8 Hz), 8.31 (d, 1H, J = 8.0 Hz), 8.62 (ddd, 1H, J = 0.9 Hz, 1.8 Hz, 4.8 Hz), 8.67 (dd, 1H, J = 0.7 Hz, 5.0 Hz). ESI-MS: 283.1 [L—Na⁺], 261.1 [L—H⁺].

4-(4-formyl-2-methylphenyl)-2,2'-bipyridine. This complex was purified on a silica column run with 10% MeOH in CHCl₃. Yield: 28% ¹H NMR (CDCl₃) δ: 2.40 (s, 3H), 7.30 (m, 1H), 7.35 (ddt, 1H, J = 1.8 Hz, 1.8 Hz, 3.6 Hz, 7.2 Hz), 7.48 (m, 1H), 7.84 (m, 3H), 8.42 (m, 1H), 8.48 (m, 1H), 8.69 (tdd, 1H, J = 0.9 Hz, 2.1 Hz, 2.7 Hz, 2.7 Hz), 8.77 (dd, 1H, J = 0.8 Hz, 5.0 Hz), 10.02 (s, 1H). ESI-MS: 275.1 [L—H⁺].

4-mesityl-2,2'-bipyridine. Yield: 15% ¹H NMR (CD₃CN) δ: 2.16 (s, 6H), 2.31 (s, 3H), 6.99 (s, 2H), 7.18 (dd, 1H, J = 1.7 Hz, 4.9 Hz), 7.38 (ddd, 1H, J = 1.2 Hz, 4.8 Hz, 7.5 Hz), 7.90 (td, 1H, J = 1.8 Hz, 7.8 Hz, 7.9 Hz), 8.19 (s, 1H), 8.47 (d, 1H, J = 8.0 Hz), 8.62 (m, 1H), 8.70 (d, 1H, J = 4.9 Hz).

4-(4-formyl-2,6-dimethylphenyl)-2,2'-bipyridine. This complex was purified on a silica column run with 10% MeOH in CHCl₃. Yield: 34% ¹H NMR (CDCl₃) δ: 2.13 (s, 6H), 7.13 (dd, 1H, J = 1.7 Hz, 4.9 Hz), 7.29 (ddd, 1H, J = 1.2 Hz, 4.8 Hz, 7.5 Hz), 7.62 (s, 2H), 7.81 (m, 1H), 8.24 (dd, 1H, J = 0.9 Hz, 1.6 Hz), 8.45 (m, 1H), 8.64 (ddd, 1H, J = 0.9 Hz, 1.8 Hz, 4.8 Hz), 8.77 (dd, 1H, J = 0.9 Hz, 4.9 Hz), 9.99 (s, 1H).

Details of Ligand Synthesis. 4-(4-hydroxymethyl-2-methylphenyl)-2,2'-bipyridine. 0.41 mmol of 4-(4-formyl-2-methylphenyl)-2,2'-bipyridine was dissolved in MeOH and an excess of NaBH₄ was slowly added at room temperature. The reaction was stirred at room temperature for 12 hours. The reaction was then quenched with saturated NH₄Cl and the solvent removed. The residue was extracted in H₂O/CH₂Cl₂ and the organic layer dried down. The residue was purified on a silica column using a solution of 10% MeOH in CH₂Cl₂ yielding 0.36 mmol of the desired product. Yield: 90% ¹H NMR (CDCl₃) δ: 2.35 (s, 3H), 4.49 (s, 2H), 7.03 (m, 1H), 7.22 (s, 1H), 7.36 (d, 1H, J = 5.6 Hz), 7.44 (d, 1H, J = 8.2 Hz), 7.52 (s, 1H), 7.88 (t, 1H, J = 7.7 Hz, 7.7 Hz), 8.36 (d, 1H, J = 8.0 Hz), 8.48 (d, 1H, J = 4.9 Hz), 8.56 (s, 1H), 8.65 (s, 1H).

4-(4-hydroxymethyl-2,6-dimethylphenyl)-2,2'-bipyridine. 0.57 mmol of 4-(4-formyl-2,6-dimethylphenyl)-2,2'-bipyridine was dissolved in MeOH and an excess of NaBH₄ was slowly

added at room temperature. The reaction was stirred at room temperature for 12 hours. The reaction was then quenched with saturated NH_4Cl and the solvent removed. The residue was extracted in $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ and the organic layer dried down. The residue was purified on a silica column using a solution of 10% MeOH in CH_2Cl_2 yielding 0.51 mmol of the desired product. Yield: 91% ^1H NMR (CDCl_3) δ : 2.03 (s, 6H), 4.65 (s, 2H), 7.11 (m, 3H), 7.30 (m, 1H), 7.82 (m, 1H), 8.23 (dd, 1H, $J = 0.9$ Hz, 1.6 Hz), 8.43 (dt, 1H, $J = 1.1$ Hz, 1.1 Hz, 8.0 Hz), 8.64 (ddd, 1H, $J = 0.9$ Hz, 1.8 Hz, 4.8 Hz), 8.72 (dd, 1H, $J = 0.8$ Hz, 4.9 Hz).

4-(4-chloromethyl-2-methylphenyl)-2,2'-bipyridine. 0.36 mmol of 4-(4-hydroxymethyl-2-methylphenyl)-2,2'-bipyridine was dissolved in 3 mL of chloroform and chilled in an ice bath. To this mixture a dilute mixture of SOCl_2 was added (1:3 SOCl_2 to CHCl_3) and the mixture was stirred in the ice bath for 10 minutes. The reaction was then removed from the ice bath and stirred at room temperature for an additional 30 minutes. At the end of this time the product was extracted with 5 ml of water. The organic layer was dried down and an NMR immediately taken to ensure the product was present. The product was then taken on crude to the next step due to the high reactivity of the primary chloride. ^1H NMR (CDCl_3) δ : 2.35 (s, 3H), 4.59 (s, 2H), 7.13 (ddd, 1H, $J = 0.5$ Hz, 2.3 Hz, 8.2 Hz), 7.32 (t, 1H, $J = 4.9$ Hz, 4.9 Hz), 7.50 (t, 1H, $J = 8.0$ Hz, 8.0 Hz), 7.81 (dd, 3H, $J = 1.7$ Hz, 4.5 Hz), 8.25 (d, 1H, $J = 6.8$ Hz), 8.40 (dd, 1H, $J = 6.9$ Hz, 11.8 Hz), 8.71 (d, 1H, $J = 6.7$ Hz), 8.81 (dd, 1H, $J = 1.7$ Hz, 4.5 Hz)

4-(4-chloromethyl-2,6-dimethylphenyl)-2,2'-bipyridine. 0.50 mmol of 4-(4-hydroxymethyl-2,6-dimethylphenyl)-2,2'-bipyridine was dissolved in 3 mL of chloroform and chilled in an ice bath. To this mixture a dilute mixture of SOCl_2 was added (1:3 SOCl_2 to CHCl_3) and the mixture was stirred in the ice bath for 10 minutes. The reaction was then removed from the ice bath and stirred at room temperature for an additional 30 minutes. At the end of this time the product was extracted with 5 ml of water. The organic layer was dried down and an NMR immediately taken to ensure the product was present. The product was then taken on crude to the

next step due to the high reactivity of the primary chloride. ¹H NMR (CDCl₃) δ: 2.05 (s, 6H), 4.52 (s, 2H), 7.16 (s, 2H), 7.38 (m, 1H), 7.49 (dd, 1H, J = 1.4 Hz, 7.3 Hz), 8.19 (t, 1H, J = 7.5 Hz, 7.5 Hz), 8.63 (s, 1H), 8.84 (d, 1H, J = 4.5 Hz), 8.98 (m, 2H).

4-(1-(1'-methyl-4,4'-bipyridinediium-1-yl)-methyl)-2-methylphenyl)-2,2'-bipyridine (bpy-*o*-tolyl-MV²⁺). 0.35 mmol of 4-(4-chloromethyl-2-methylphenyl)-2,2'-bipyridine and 0.5 mmol of [1-methyl-4,4'-bipyridinium]PF₆ were refluxed in 18 ml of CH₃CN under N₂ for 6 days. The CH₃CN was then removed by rotary evaporation. The solid was dissolved in H₂O and filtered through a medium frit. A 5-fold excess of NH₄PF₆ was added to the filtrate, and the resulting precipitate was filtered through a medium frit and rinsed with water. Yield: 60 mg (40%). ¹H NMR (CD₃CN) δ: 2.39 (s, 3H), 4.41 (s, 3H), 5.75 (s, 2H), 7.26 (m, 2H), 7.40 (s, 1H), 7.62 (d, 1H, J = 6.5 Hz), 7.65 (d, 1H, J = 8.3 Hz), 7.66 (d, 1H, J = 8.3 Hz), 7.83 (m, 1H), 7.91 (m, 1H), 8.22 (m, 1H), 8.32 (dd, 4H, J = 7.3 Hz, 13.2 Hz), 8.47 (d, 1H, J = 8.1 Hz), 8.81 (d, 2H, J = 6.8 Hz), 8.90 (d, 2H, J = 7.0 Hz)

4-(1-(1'-methyl-4,4'-bipyridinediium-1-yl)-methyl)-2,6-dimethylphenyl)-2,2'-bipyridine (bpy-dimethyl-*φ*-MV²⁺). 1.2 mmol of 4-(4-chloromethyl-2,6-dimethylphenyl)-2,2'-bipyridine and 2.0 mmol of [1-methyl-4,4'-bipyridinium]PF₆ were refluxed in 18 ml of CH₃CN under N₂ for 14 days. The CH₃CN was then removed by rotary evaporation. The solid was dissolved in H₂O and filtered through a medium frit. A 5-fold excess of NH₄PF₆ was added to the filtrate, and the resulting precipitate was filtered using a medium frit and rinsed with water. Yield: 168 mg (32%). ¹H NMR (CD₃CN) δ: 2.08 (s, 6H), 4.41 (s, 3H), 5.81 (s, 2H), 7.28 (dd, 1H, J = 1.6 Hz, 5.0 Hz), 7.31 (s, 2H), 7.46 (dd, 1H, J = 5.4 Hz, 7.0 Hz), 7.97 (td, 1H, J = 1.7 Hz, 7.8 Hz, 7.9 Hz), 8.19 (s, 1H), 8.40 (d, 2H, J = 6.8 Hz), 8.42 (d, 2H, J = 7.0 Hz), 8.46 (d, 1H, J = 8.0 Hz), 8.65 (d, 1H, J = 4.9 Hz), 8.76 (d, 1H, J = 5.0 Hz), 8.85 (d, 2H, J = 6.7 Hz), 9.00 (d, 2H, J = 7.0 Hz).

General Procedure for Donor Complex Synthesis. The bis-heteroleptic ruthenium donor complexes were prepared from a [Ru(dmb)₂Cl₂]Cl • 2H₂O precursor synthesized using a

ruthenium blue starting material and the dmb ligand as previously reported.⁵ This intermediate was then used directly by refluxing with 1.5 eq. of donor ligand (either *p*-tol-bpy, 4-(2,4-dimethylphenyl)-2,2'-bipyridine, or 4-mesityl-2,2'-bipyridine) in EtOH for 8 hours under N₂. Following reflux the EtOH was removed by rotary evaporation. The residue was purified by column chromatography on silica with 5:4:1 CH₃CN/H₂O/sat. KNO₃ yielding the Ru complex as the nitrate salt. The solution was concentrated and a 10-fold excess of NH₄PF₆ was then added; the precipitate was collected in a medium frit, and washed with water.

[Ru(dmb)₂(*p*-tol-bpy)](PF₆)₂ (1'**). Yield: 30 mg (76%) ¹H NMR (CD₃CN) δ: 2.45 (s, 3H), 2.54 (m, 12H), 7.25 (dd, 4H, J = 5.9 Hz, 11.8 Hz), 7.39 (t, 3H, J = 7.4 Hz, 7.4 Hz), 7.55 (m, 3H), 7.60 (m, 2H), 7.71 (d, 1H, J = 6.0 Hz), 7.77 (d, 1H, J = 5.1 Hz), 7.79 (d, 2H, J = 8.3 Hz), 8.10 (td, 1 H, J = 1.5 Hz, 7.9 Hz, 8.1 Hz), 8.36 (m, 4H), 8.67 (d, 1H, J = 8.3 Hz), 8.72 (d, 1H, J = 1.8 Hz). Acc. Mass: found 861.1832 [M²⁺ + PF₆⁻]; calcd. 861.1838.**

[Ru(dmb)₂(4-(2,4-dimethylphenyl)-2,2'-bipyridine)](PF₆)₂ (2'**). Yield: 60 mg (60%) ¹H NMR (CD₃CN) δ: 2.33 (s, 3H), 2.38 (s, 3H), 2.53 (m, 12H), 7.14 (m, 1H), 7.24 (m, 4H), 7.38 (m, 1H), 7.54 (m, 4H), 7.56 (dd, 1H, J = 5.6 Hz, 9.4 Hz), 7.60 (d, 1H, J = 5.8 Hz), 7.69 (d, 1H, J = 5.8 Hz), 7.74 (d, 1H, J = 4.9 Hz), 8.32 (dd, 6H, J = 11.5 Hz, 15.6 Hz), 8.45 (d, 1H, J = 1.7 Hz), 8.52 (d, 1H, J = 8.2 Hz). Acc. Mass: found 874.8403 [M²⁺ + PF₆⁻]; calcd. 874.8408.**

[Ru(dmb)₂(4-mesityl-2,2'-bipyridine)](PF₆)₂ (3'**). Yield: 36 mg (48%) ¹H NMR (CD₃CN) δ: 1.96 (s, 6H), 2.31 (s, 3H), 2.53 (s, 12H), 7.02 (d, 2H, J = 7.0 Hz), 7.19 (dd, 1H, J = 1.8 Hz, 5.8 Hz), 7.24 (m, 4H), 7.37 (m, 1H), 7.55 (m, 4H), 7.73 (m, 2H), 7.99 (m, 1H), 8.32 (d, 1H, J = 1.2 Hz), 8.35 (s, 4H), 8.44 (d, 1H, J = 7.9 Hz). Acc. Mass: found 888.8669 [M²⁺ + PF₆⁻]; calcd. 888.8674.**

General Procedure for D-A Complex Synthesis. The bis-heteroleptic ruthenium complexes containing an electroactive ligand were prepared using a modified procedure to that described above. The [Ru(dmb)₂Cl₂]Cl was first converted to [Ru(dmb)₂CO₃] as previously

described.⁶ This complex was then reacted with 1.5 eq. of the electroactive ligand (either bpy- ϕ -MV, bpy-*o*-tolyl-MV, bpy-dimethyl- ϕ -MV) in 50:50 H₂O/EtOH saturated with KNO₃. This mixture was stirred at room temperature for five to seven days in the dark. After this time, the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica with 5:4:1 CH₃CN/H₂O/sat. KNO₃ yielding the Ru complex as the nitrate salt. The solution was concentrated and a 10-fold excess of NH₄PF₆ was then added; the precipitate was collected in a medium frit, and washed with water.

[Ru(dmb)₂(bpy- ϕ -MV)](PF₆)₄ (1). Yield: 35 mg (65 %) ¹H NMR (CD₃CN) δ : 2.57 (d, 12H, J = 9.8 Hz), 4.44 (s, 3H), 6.00 (s, 2H), 7.25 (dd, 4H, J = 5.7 Hz, 13.3 Hz), 7.40 (m, 1H), 7.55 (m, 4H), 7.60 (d, 1H, J = 5.8 Hz), 7.66 (dd, 1H, J = 2.0 Hz, 6.0 Hz), 7.73 (m, 4H), 7.99 (d, 1H, J = 8.4 Hz), 8.05 (td, 1H, J = 1.4 Hz, 7.9 Hz, 8.0 Hz), 8.41 (m, 4H), 8.51 (d, 2H, J = 6.8 Hz), 8.56 (d, 2H, J = 7.0 Hz), 8.73 (d, 1H, J = 8.2 Hz), 8.79 (d, 1H, J = 1.8 Hz), 9.00 (d, 2H, J = 6.8 Hz), 9.21 (d, 2H, J = 7.0 Hz). Acc. Mass: found 588.1182 [M⁴⁺ + 2(PF₆)]; calcd. 588.1166.

[Ru(dmb)₂(bpy-*o*-tolyl-MV)](PF₆)₄ (2). Yield: 17 mg (35%) ¹H NMR (CD₃CN) δ : 2.38 (s, 3H), 2.56 (d, 12H, J = 3.1 Hz), 4.43 (s, 3H), 5.93 (s, 2H), 7.26 (m, 4H), 7.42 (d, 2H, J = 5.9 Hz), 7.49 (d, 1H, J = 7.9 Hz), 7.57 (m, 5H), 7.63 (d, 1H, J = 5.7 Hz), 7.75 (d, 2H, J = 5.8 Hz), 8.06 (td, 1H, J = 1.5 Hz, 7.8 Hz, 8.0 Hz), 8.42 (d, 4H, J = 6.8 Hz), 8.50 (dd, 5H, J = 6.3 Hz, 12.8 Hz), 8.59 (d, 1H, J = 8.1 Hz), 8.89 (d, 2H, J = 6.7 Hz), 9.10 (d, 2H, J = 6.7 Hz). Acc. Mass: found 595.1231 [M⁴⁺ + 2(PF₆)]; calcd. 595.1245.

[Ru(dmb)₂(bpy-dimethyl- ϕ -MV)](PF₆)₄ (3). Yield: 8 mg (14%) ¹H NMR (CD₃CN) δ : 2.38 (s, 6H), 2.53 (d, 12H, J = 4.7 Hz), 4.4 (s, 3H), 5.79 (s, 2H), 7.17 (dd, 1H, J = 5.8, 1.8 Hz), 7.24 (m, 4H), 7.28 (s, 1H), 7.33 (s, 1H), 7.38 (m, 1H), 7.35 (m, 4H), 7.75 (dd, 2H, J = 11.4, 5.4 Hz), 7.99 (dd, 1H, J = 11.3, 4.6 Hz), 8.29 (d, 1H, J = 1.3 Hz), 8.37 (m, 6H), 8.44 (m, 3H), 8.85 (d, 2H, J = 6.7 Hz), 9.00 (d, 2H, J = 7.1 Hz). Acc. Mass: found 602.1327 [M⁴⁺ + 2(PF₆)]; calcd. 602.1323.

Physical Experimental Methods:

Absorption Spectra. For all spectroscopic measurements the acetonitrile used is Burdick & Jackson UV-grade that has been further purified using an in house distillation system based on the Grubbs Apparatus.^{7,8} Absorption spectra were measured with a Hewlett-Packard HP8452A diode array UV-Vis spectrophotometer.

Cyclic Voltammetry. Electrochemical measurements were carried out with a CH Instruments 601C electrochemical analyzer. Solutions of the compound were dissolved in anhydrous CH₃CN containing 0.1 M NH₄PF₆ as the supporting electrolyte. A standard three-electrode setup was used with a working Pt electrode, Pt wire counter electrode, and a Ag/AgNO₃ reference electrode. All measurements were made after an argon purge.

Spectro-Electrochemistry. Measurements were taken using the CH Instruments 601C electrochemical analyzer. Spectra were recorded with a Hewlett-Packard HP8452A diode array UV-Vis spectrophotometer. These experiments were carried out in a home built OTTLE cell as previously reported with the Pt mesh held at constant voltage (see captions of *Figures S4, S5, and S6* for these values).¹

Picosecond Transient Absorption Kinetics. Transient absorption kinetics of **1** were taken using a previously described Ti:Sapphire amplified laser system and spectrometer.² Transient absorption kinetics of **2** and **3** were acquired using the same methods but a second spectrometer based on a broadband laser pulse train derived from a commercially available chirped-pulse amplified (CPA) Ti:Sapphire laser system coupled to a home-built non-collinear optical parametric amplifier (NOPA). The oscillator is a Clark NJA-1000 pumped by a Coherent Verdi V-8 which operates at 100 MHz and produces pulses centered at ~800 nm with a temporal FWHM of ~200 fs and pulse energies of ~ 3 nJ. The pulse train is then coupled to a Clark CPA-1000 regenerative amplifier pumped by a nanosecond YLF (Quantronix; Darwin) resulting in a 1KHz pulse train centered at ~800 nm with ~250 fs temporal FWHM pulses with approximately

~400 mJ per pulse. The output beam was then split with ~320 mW of the power going to pump a home-built NOPA^{9,10} to produce 500 ± 10 nm pulses. The NOPA pulses are then compressed via a prism compressor to a time resolution of ~100 fs/pulse as determined by cross-correlation of the pump beam with a white light beam in an optical cell containing a 4:1 mixture of acetonitrile and 1-methylnaphthalene.¹¹ The 500 nm pulse train was passed through an optical chopper (ThorLabs MC1000A) synchronized at $\omega/2$ (500 Hz) with respect to the 1 KHz laser system, directed onto computer controlled translation stages (Newport MM3000 .049 fs/step time resolution, 14 inches of travel; Velmex 169 fs/step time resolution, 48 inches of travel) and gently focused (using a 300mm focal length lens) into a 2 mm path length optical cell containing the sample dissolved in acetonitrile with an optical density of ~0.5 ($\sim 1.6 \times 10^{-4}$ M) at 480 nm. The pump polarization was set horizontal at the sample and ~2 μ J/pulse were used for excitation. The sample (~1 mL) was continuously stirred using a small stir bar driven by a rotating magnet mounted at the face of the sample. Sample degradation was not observed in the comparison between visible absorption spectra collected before and after the transient absorption measurements were made. Probe pulses with a horizontal polarization were derived from white-light continuum generated by focusing ~3 μ J of the amplified pulse train into a 1 mm disk of sapphire. An off-axis parabolic mirror was used to collimate the white light after its generation and a spherical concave mirror with a focal length of 250 mm was used to focus it into the sample at an acute angle ($< 5^\circ$) with respect to the pump. After the sample, the broadband probe was passed through a collimating lens and analyzed for single wavelength or spectral measurements. The broadband probe was coupled into a 220 mm scanning monochromator (Spex; 220M) set to the appropriate wavelength. A 1200 grooves/mm grating was used with 0.5 mm entrance and exit slits providing spectral resolution of 1.55 nm. An amplified Si photodiode (Thor labs; PDA-55) joined to the exit slit of the monochromator was used to collect the signal. This was then sent to a digital lock-in amplifier (Stanford Research; SR830 DSP) synchronized to the chopper frequency. The lock-in reports a change in transmittance as excited state absorption or bleach transitions are produced by the

pump pulse. Kinetics traces were collected by monitoring this signal as a function of the position of the motorized translation stage and the data are reported as a normalized change in transmittance ($-\Delta T$). The kinetics traces reported herein represent an average of 6 scans of positions in the forward direction of the translation stage. The data collection software was written in house (National Instruments, Labview 8.5). For fitting of these data to the kinetics model discussed herein, we used the commercially available data analysis software Igor Pro 6.0 (WaveMetrics).

Fitting of Spectral Data. Errors reported in the manuscript are based on fitting of three separate data sets collected for each of the D–A molecule **1–3**. The fitting of any single wavelength kinetics trace was done using a biexponential function based on a three state model which has been described elsewhere.¹ Only data two picoseconds and greater after the arrival of the pump pulse in the sample were fit with the biexponential model due to the existence of faster components that have not yet been characterized. The values of τ_{ET} and τ_{BET} were recovered using the following methodology: (1) τ_{BET} was found by fitting three separate portions of the decay (between $\frac{3}{4}$ and $\frac{1}{4}$ of the maximum signal) to a single exponential. The three values of τ_{BET} were then averaged. (2) The entire data set was then fit with the biexponential function with the caveat that τ_{BET} is kept as a fixed parameter locked to the average value determined as described above. This fitting routine was found to be superior to free fitting of all the variables as it results in less ambiguity in the τ_{ET} value as judged by the uncertainty in the fit value and visualization of the residuals. It is noted, however, that the values of both τ_{ET} and τ_{BET} obtained with this protocol are in close agreement to those obtained using a fitting protocol in which all parameters including τ_{BET} are allowed to freely vary. In fact the values of τ_{ET} and τ_{BET} obtained this way are well within the 2σ error bars we have reported in the manuscript.

Computational Details:

Density Functional Theory (DFT) electronic structure calculations were carried out using the Gaussian09 software package.¹² For all compounds the Hartree-Fock/density functional model (HF/DFT) B3LYP was used. B3LYP combines Becke's 3-parameter hybrid exchange (B3) with the non-local correlation functional of Lee, Yang, and Parr (LYP).^{13,14} B3LYP was chosen as it is one of the most widely used functional models for transition metal complexes.¹⁵⁻¹⁸ For ruthenium atoms the LANL2DZ¹⁹ basis set was used along with the corresponding pseudo-potential for the metal atom while C, H, and N were treated with 6-31G.

Charge-separated states of donor-acceptor complexes were modeled with the lowest-energy triplet determined using unrestricted methods. For these, spin contamination was found to be negligible based on the expectation values of the total spin angular momentum operator S^2 . For these calculations the electronic structure was modeled with a self-consistent reaction field (SCRF) with the use of a polarizable continuum model (PCM) using the dielectric for acetonitrile.^{20,21}

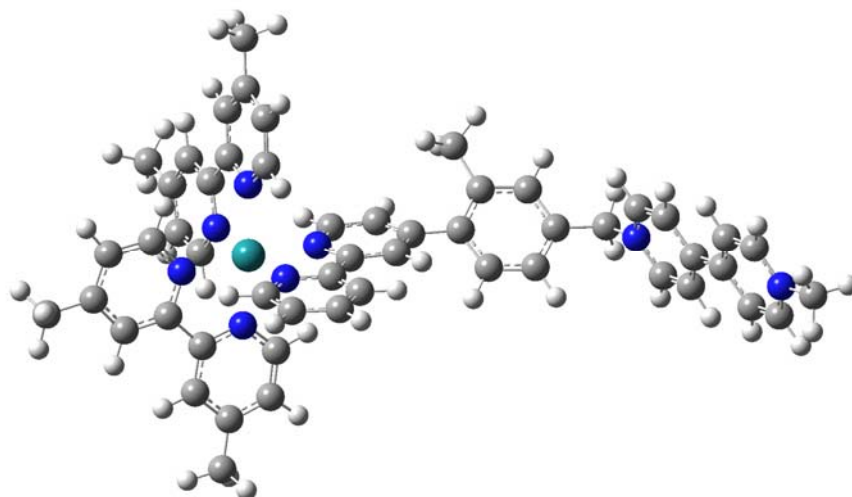
This research was supported in part by the National Science Foundation through TeraGrid resources provided by the National Center for Supercomputing Applications with all computations performed on the Cobalt computer cluster.²²

Complex 2

Lowest Energy Triplet optimized with PCM for CH₃CN

Total Energy = -2581.1839930 Hartrees

$\theta = 47^\circ$ average



Cartesian Coordinates for Complex 2:

C	-4.03499	-3.80613	-3.14058	C	-0.26911	-3.42773	2.301727
C	-2.89278	-2.99449	-3.19715	Ru	-1.63629	-3.62442	2.487434
C	-2.70588	-1.9992	-2.25179	C	-3.3874	-0.29003	0.226182
N	-3.59686	-1.76514	-1.26806	C	2.539654	1.591826	-1.25342
C	-4.7179	-2.53483	-1.18819	C	3.033339	2.911187	-1.13366
C	-4.94769	-3.55456	-2.11076	C	4.369113	3.147365	-1.4892
C	-5.12278	1.126699	-1.88206	C	5.208785	2.139571	-1.96762
C	-5.88829	2.152356	-2.41701	C	4.708173	0.835941	-2.07494
C	-6.0872	3.329277	-1.68507	C	3.394936	0.570361	-1.71088
C	-5.47786	3.411913	-0.42596	C	6.631435	2.468624	-2.37941
C	-4.71267	2.357476	0.064413	N	7.643445	1.652234	-1.67856
N	-4.54241	1.221078	-0.67132	C	8.423277	0.745955	-2.35019
C	-5.63174	-2.20578	-0.07932	C	9.36423	-0.0079	-1.7072
C	-4.04365	2.363531	1.377829	C	9.588339	0.1105	-0.29703
N	-5.22962	-1.18124	0.724882	C	8.751555	1.071665	0.360085
C	-6.019	-0.79842	1.748789	C	7.822535	1.800132	-0.32457
C	-7.22423	-1.42268	2.025965	C	10.5716	-0.66339	0.399686
C	-7.66244	-2.48469	1.221713	C	10.79749	-0.5431	1.808697
C	-6.83873	-2.86214	0.155822	C	11.74856	-1.28807	2.448515
C	-4.07331	3.440238	2.26252	N	12.52882	-2.19097	1.777032
C	-3.40836	3.37342	3.49174	C	12.34661	-2.34256	0.42713
C	-2.71487	2.189879	3.782826	C	11.40987	-1.62114	-0.25762
C	-2.71008	1.149927	2.867542	C	13.59293	-2.93271	2.465693
N	-3.3625	1.22546	1.690735	H	-2.14645	-3.13285	-3.97191
C	-2.5246	-2.73044	1.90154	H	-1.83282	-1.36005	-2.27851
C	-1.2473	1.519692	-1.0501	H	-5.84058	-4.1619	-2.03311
C	0.032757	1.942758	-1.37188	H	-4.95544	0.209364	-2.43161
C	1.144928	1.219416	-0.91192	H	-6.32516	2.026492	-3.40132
C	0.886023	0.079721	-0.13306	H	-5.60781	4.307934	0.168417
C	-0.42024	-0.3035	0.157754	H	-5.66142	0.020847	2.359208
N	-1.47783	0.419158	-0.30953	H	-7.81587	-1.07628	2.866332
C	-0.76984	-1.47616	0.980225	H	-7.15014	-3.67153	-0.49277
N	-2.10391	-1.68093	1.171297	H	-4.61399	4.341352	2.000814
C	0.166823	-2.34587	1.540529	H	-2.17621	2.073453	4.716907
				H	-2.18256	0.227211	3.07217

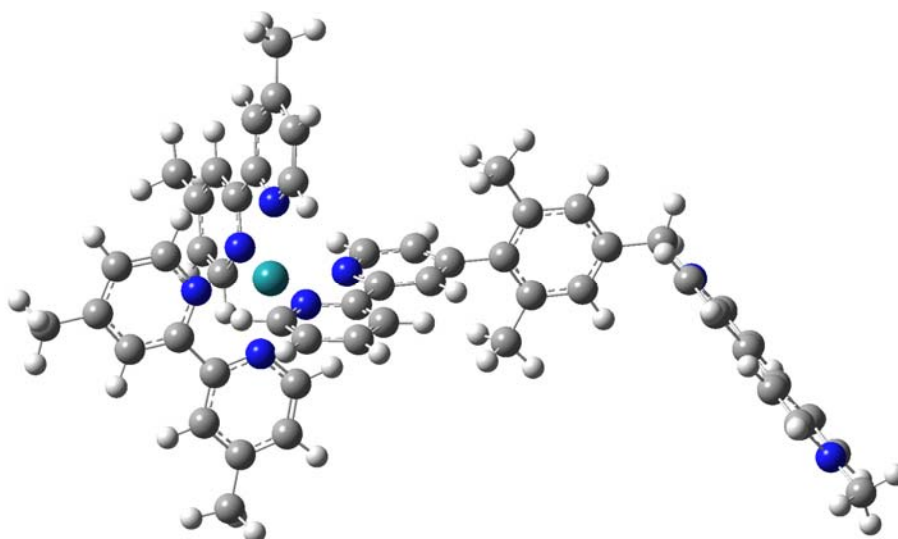
H	-3.59483	-2.84115	2.019749	C	-4.26032	-4.90322	-4.14264
H	-2.11741	2.05728	-1.40477	H	-3.48433	-5.67158	-4.04364
H	0.149532	2.817124	-1.99925	H	-5.23487	-5.37846	-4.00973
H	1.716701	-0.4927	0.259307	H	-4.19668	-4.51046	-5.16326
H	1.225966	-2.18546	1.386823	C	-8.95931	-3.19074	1.499863
H	0.452995	-4.10712	2.741311	H	-9.22115	-3.88302	0.696463
H	-2.01848	-4.45238	3.07263	H	-8.88497	-3.76041	2.434144
H	4.761064	4.15591	-1.382	H	-9.77387	-2.46975	1.625418
H	5.338303	0.030323	-2.44026	C	-6.9354	4.453241	-2.21004
H	3.00922	-0.43959	-1.81376	H	-7.92973	4.418313	-1.74715
H	6.849581	3.522821	-2.18589	H	-6.49671	5.42594	-1.96781
H	6.773438	2.297629	-3.44954	H	-7.06636	4.381058	-3.29244
H	9.936977	-0.69671	-2.31441	C	-3.44344	4.516132	4.466859
H	8.831548	1.255085	1.423723	H	-3.83601	5.426173	4.007282
H	7.182854	2.526659	0.160592	H	-4.08343	4.261206	5.320561
H	10.22063	0.141059	2.417257	H	-2.44327	4.720966	4.861964
H	11.92847	-1.20396	3.512861	C	2.213478	4.068012	-0.60524
H	12.98766	-3.06747	-0.059	H	1.662321	4.572957	-1.40858
H	11.32825	-1.80765	-1.3205	H	1.484601	3.754126	0.147379
H	13.38823	-2.93953	3.536317	H	2.867661	4.81662	-0.14897
H	14.56255	-2.45919	2.284366	H	8.251343	0.667869	-3.41639
H	13.61557	-3.96057	2.098876				

Complex 3

Lowest Energy Triplet optimized with PCM for CH₃CN

Total Energy = -2620.49806506 Hartrees

$\theta = 88^\circ$ average



Cartesian Coordinates for Complex 3:

C	-3.48063	4.47367	2.401516	C	-2.34215	2.4523	1.738122
C	-2.36348	3.628199	2.470052	N	-3.37188	2.074949	0.954741
				C	-4.47009	2.875492	0.865806

C	-4.53805	4.07149	1.578879	C	11.51469	1.212581	0.739052
C	-4.95714	-0.52179	2.340518	C	13.47488	3.718265	-1.21535
C	-5.69908	-1.35643	3.160353	H	-1.49214	1.783267	1.778749
C	-6.04328	-2.64265	2.719997	H	-5.41621	4.699657	1.497959
C	-5.60979	-3.01988	1.444311	H	-4.68154	0.475157	2.659287
C	-4.85948	-2.14565	0.659787	H	-5.86437	-4.00229	1.066201
N	-4.53465	-0.90481	1.119515	H	-5.96155	-0.26992	-1.93973
C	-5.53827	2.384281	-0.02291	H	-6.94	3.986994	0.274809
C	-4.37082	-2.46363	-0.69366	H	-5.14345	-4.46476	-0.83233
N	-5.28173	1.200389	-0.64735	H	-2.61384	-0.86821	-2.98871
C	-6.21259	0.670052	-1.46568	H	-3.75828	2.460758	-2.43996
C	-7.42553	1.294255	-1.70656	H	-2.04474	-1.75176	1.716267
C	-7.71949	2.514755	-1.08085	H	0.249522	-2.61444	2.091561
C	-6.74625	3.04833	-0.22929	H	1.621813	0.050265	-0.98745
C	-4.5838	-3.68436	-1.3324	H	1.065201	1.573597	-2.31159
C	-4.07985	-3.91604	-2.6166	H	0.204734	3.250194	-3.91543
C	-3.35516	-2.87676	-3.21824	H	-2.26982	3.709124	-3.99251
C	-3.16688	-1.68358	-2.54038	H	4.67558	-4.14378	-0.54863
N	-3.66798	-1.47069	-1.30733	H	5.352126	-1.22659	2.531507
C	-2.68897	2.293678	-2.43917	H	6.767478	-4.09523	0.48756
C	-1.2111	-1.37617	1.136828	H	6.802508	-3.55698	2.166603
C	0.077728	-1.85088	1.341549	H	10.12532	-0.53389	2.250356
C	1.132397	-1.34415	0.570944	H	8.565057	-0.37356	-1.81683
C	0.82776	-0.35823	-0.37542	H	6.932764	-2.0538	-1.15457
C	-0.48291	0.088194	-0.53614	H	9.876336	1.126798	-2.25833
N	-1.48969	-0.42907	0.222339	H	11.56613	2.814113	-2.73838
C	-0.88636	1.109837	-1.51833	H	13.18763	2.516667	1.086914
N	-2.22143	1.378643	-1.56983	H	11.57575	0.813582	1.743286
C	0.00396	1.780723	-2.35782	H	13.05104	4.446157	-1.90889
C	-0.48102	2.725468	-3.25921	H	14.32363	3.214751	-1.68831
C	-1.84961	2.984801	-3.30491	H	13.81439	4.236491	-0.31791
Ru	-3.42759	0.307569	-0.20047	C	-3.53292	5.757906	3.179992
C	2.535384	-1.83704	0.731802	H	-4.47393	6.289079	3.020089
C	2.991678	-2.8952	-0.07843	H	-3.42144	5.559427	4.251988
C	4.315145	-3.32795	0.072995	H	-2.70689	6.415729	2.886499
C	5.173344	-2.73732	1.00135	C	-9.02659	3.216756	-1.31883
C	4.696126	-1.69374	1.801031	H	-9.11683	4.118571	-0.70934
C	3.384069	-1.22836	1.682523	H	-9.11912	3.499714	-2.37388
C	6.59892	-3.23545	1.142591	H	-9.8665	2.552035	-1.08838
N	7.608288	-2.20358	0.81521	C	-6.83805	-3.57613	3.588698
C	8.512156	-1.76786	1.748612	H	-7.73187	-3.07643	3.976786
C	9.454636	-0.82357	1.45196	H	-7.14312	-4.47262	3.044177
C	9.547905	-0.23812	0.147748	H	-6.23974	-3.88625	4.453966
C	8.586214	-0.73004	-0.79507	C	-4.30157	-5.2212	-3.32791
C	7.663739	-1.67546	-0.45108	H	-4.85862	-5.92926	-2.71035
C	10.52168	0.756991	-0.18755	H	-4.85831	-5.05745	-4.25785
C	10.57936	1.38099	-1.47582	H	-3.34267	-5.67512	-3.60224
C	11.51429	2.333223	-1.76947	C	2.091291	-3.56223	-1.09403
N	12.44205	2.741692	-0.84747	H	1.211478	-4.01284	-0.61903
C	12.43065	2.167187	0.39595	H	1.722044	-2.84869	-1.84018

H	2.626327	-4.35393	-1.62537	H	-6.00704	-0.99884	4.136782
H	8.434043	-2.21543	2.731483	H	-1.50931	3.879669	3.089384
C	2.901589	-0.09597	2.561132	H	-8.13568	0.82545	-2.378996
H	2.566482	0.762899	1.96731				
H	2.055258	-0.40172	3.187818				
H	3.700974	0.246723	3.22348				
H	-2.93583	-2.9904	-4.21191				

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