Supporting Information

Experimental

NMR spectra were obtained on a General Electric QE-300 spectrometer at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. Chemical shifts were reported in parts per million relative to TMS. Luminescence measurements were done with a Perkin-Elmer LS50B luminescence spectrometer. UV-Vis spectra were recorded on a Lambda 3B spectrometer. All spectra were corrected for the background spectrum of the solvent. Cyclic voltammetric (CV) measurements were carried out by using a Bioanalysis BAS Epsilon Electroanalytical System. The CV experiments were performed in a one-compartment cell equipped with a glass carbon working electrode, a saturated calomel reference electrode (SCE), and a Pt wire as the auxiliary electrode. Infrared spectra were taken on a Thermo Nicolet AVATAR 370 RT-IR spectrometer. Mass spectra were obtained on a ABI Voyager DE-STR (MALDI-TOF) and a Thermo Finnigan LCQ DecaXP Plus with Surveyor LC-MS. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are not corrected. Elemental analyses were carried out by QTI, P.O. Box 470, Whitehouse, NJ 08888-0470.

2,9-Di-(2'-pyridyl)-1,10-phenanthroline (2): A mixture of 2,9-dichloro-1,10-phenanthroline (505 mg, 2.0 mmol), 2-(tri-*n*-butylstannyl)pyridine (3.00 g, 8 mmol), $Pd(PPh_3)_4$ (320 mg), and freshly distilled toluene (30 mL) was refluxed for 40 h under argon. The solvent was removed by distillation and the residue was treated with CH_2Cl_2 and water. The organic phase was dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product, dissolved in minimum amount of dichloromethane, was added dropwise to ether. The precipitate was collected and washed with ether to afford a white powder (302 mg, 0.90 mmol). From the filtrate, over 1.5 days, an additional 115 mg of a light yellow solid was recovered for a total yield of 417 mg (62%): mp 205-206 ^{o}C; ^{1}H NMR ($CDCl_3$): δ 9.12 (d, J = 8.1 Hz, 2H), 8.91 (d, J = 8.4 Hz, 2H), 8.79 (dd, J = 4.5, 1.8 Hz, 2H), 8.43 (d, J = 8.7 Hz, 2H), 8.03 (dt, J = 8.1, 1.8 Hz, 2H), 7.88 (s, 2H), 7.44 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 156.2, 155.9, 149.1, 145.7, 137.1, 137.0, 129.1, 126.7, 124.2,

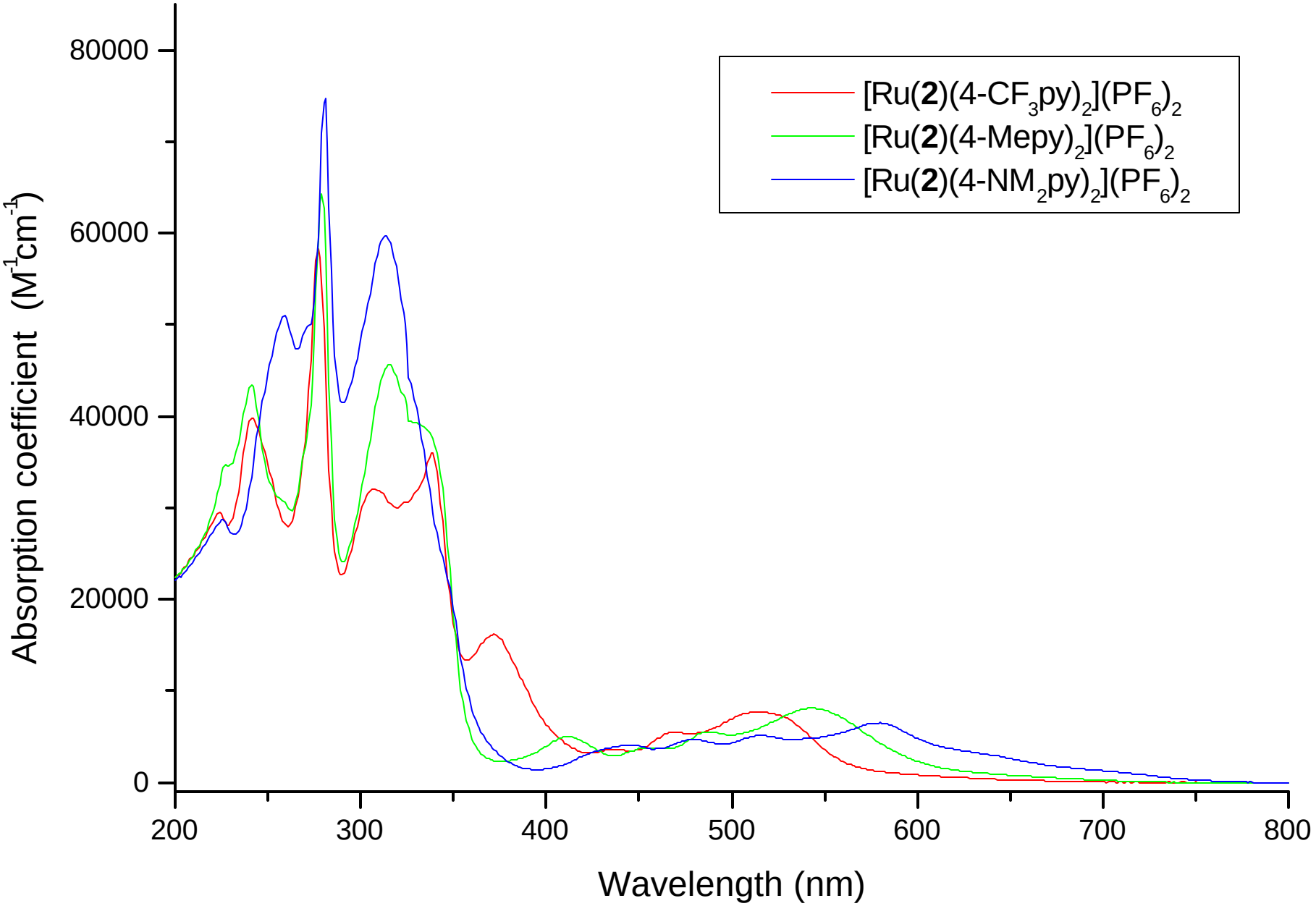
122.2, 120.6; IR (ATR, cm^{-1}): 1591(s), 1496 (m), 1464 (s), 1436 (w), 1416 (w), 1364 (vw), 1111 (m), 862 (s), 817 (m), 782 (s), 775 (s), 746 (s0, 737 (vs).

[Ru(2)(4-MePy)$_2$](PF$_6$)$_2$: A mixture of **2** (50 mg, 0.15 mmol), $RuCl_3 \cdot 3H_2O$ (40 mg, 0.15 mmol), and absolute ethanol (24 mL) was refluxed for 1.5 h. To the reaction mixture was then added water (10 mL), 4-picoline (0.5 mL, 5.1 mmol), triethylamine (0.3 mL), and LiCl (10 mg). The mixture was refluxed overnight and a red solution was obtained to which NH_4PF_6 (260 mg, 1.59 mmol) was introduced. The solvents were removed by distillation. The brown residue was treated with water, filtered, washed with water and dried in the air. Chromatography on alumina eluting with acetone followed by re-crystallization from acetone-water gave a purple-brown solid (69 mg, 50%): ^{1}H NMR (acetone-d_6): δ 10.29 (d, *J* = 5.1 Hz, 2H), 8.89 (d, *J* = 9.0 Hz, 2H), 8.81 (d, *J* = 9.0 Hz, 2H), 8.69 (d, *J* = 7.2 Hz, 2H), 8.60 (s, 2H), 8.38 (m, 2H), 8.16 (m, 2H), 7.95 (d, *J* = 6.8 Hz, 4H), 6.89 (d, *J* = 6.8 Hz, 4H), 2.81 (s, 6H); IR (ATR, cm^{-1}): 1621 (vw), 1603 (vw), 1504 (vw), 1450 (vw), 1361 (vw), 838 (vs), 807 (sh), 774 (w), 733 (w). Anal. Calcd for $C_{34}H_{28}N_6F_{12}P_2Ru \cdot 1/2C_2H_6O$: C, 44.98; H, 3.34; N, 8.99. Found: C, 45.10; H 3.10; N, 8.77. **[Ru(2)$_2$](PF$_6$)$_2$** was recovered as brown-red solid from the last fraction of the column (8 mg, 5 %): ^{1}H NMR (300 MHz, acetone-d_6): δ 9.15 (d, *J* = 9.3 Hz, 2H), 8.94 (d, *J* = 8.7 Hz, 2H), 8.82 (m, 4H), 8.50 (dd, *J* = 3.6,1.5 Hz, 4H), 8.00 (dt, *J* = 8.1,1.8 Hz, 2H), 7.69 (d, *J* = 4.5 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.11 (m, 4H), 6.87 (m, 4H), 6.36 (d, *J* = 7.2 Hz, 2H); MS (MALDI-TOF, no matrix): *m/z* = 915.3 $[M\text{-}PF_6]^+$, 769.3 $[M\text{-}2PF_6]^+$.

[Ru(2)(4-NMe$_2$Py)$_2$](PF$_6$)$_2$: The same procedure as described for [Ru(**2**)(4-MePy)$_2$](PF$_6$)$_2$ was followed. A mixture of **2** (42.9 mg, 0.127 mmol) and $RuCl_3 \cdot 3H_2O$ (38.3 mg, 0.146 mmol) in absolute ethanol (20 mL) was refluxed for 2 h. Water (10 mL), 4-dimethylaminopyridine (0.5 mL), triethylamine (0.3 mL), and LiCl (10 mg) were introduced. The mixture was further refluxed overnight, generating a purple solution. NH_4PF_6 (170 mg) was added, and the solution was concentrated to give dark precipitate which was separated from the red solution. After chromatography on alumina eluting with acetone, a brown powder (118 mg, 95%) was obtained from the purple fraction: ^{1}H

NMR (acetone-d_6): δ 10.25 (d, *J* = 4.5 Hz, 2H), 8.89 (d, *J* = 8.7 Hz, 2H), 8.73 (d, *J* = 8.1 Hz, 4H), 8.56 (s, 2H), 8.40 (dt, *J* = 8.4, 1.2 Hz, 2H), 8.15 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 4H), 6.14 (d, *J* = 7.2 Hz, 4H), 2.76 (s, 12H); IR (ATR, cm^{-1}): 1623 (w), 1541 (w), 1448 (vw), 1395 (vw), 1361 (vw), 1234 (w), 1024 (w), 846 (vs), 839 (vs), 827 (vs), 803 (w), 772 (w), 730 (w). Anal. Calcd for $C_{36}H_{34}N_8F_{12}P_2Ru$: C, 44.58; H, 3.51; N, 11.56. Found: C, 44.19; H 3.34; N, 11.32.

[Ru(2)(4-CF_3py)$_2$](PF_6)$_2$: The same procedure as described for [Ru(**2**)(4-MePy)$_2$](PF_6)$_2$ was followed, using **2** (35.7 mg, 0.107 mmol), $RuCl_3 \cdot 3H_2O$ (28.2 mg, 0.106 mmol), ethanol (20 + 5 mL), water (10 mL), 4-trifluoromethylpyridine (0.2 mL, 1.727 mmol), triethylamine (0.3 mL), and NH_4PF_6 (163 mg, 1 mmol). Chromatography on alumina eluting with acetone gave a red-purple solution, which was further purified by chromatography on silica gel eluting with ethyl acetate. The first fraction was evaporated and yielded a red powder (5 mg, 5 %): ^{1}H NMR (300 MHz, acetone-d_6): δ 10.28 (d, *J* = 4.5 Hz, 2H), 8.88 (m, 4H), 8.66 (d, *J* = 7.8 Hz, 2H), 8.63 (s, 2H), 8.55 (d, *J* = 6.6 Hz, 4H), 8.38 (dt, *J* = 1.5, 7.8 Hz, 2H), 8.13 (m, 2H), 7.36 (d, *J* = 6.3 Hz, 4H); IR (ATR, cm^{-1}): 1601 (vw), 1421 (vw), 1326 (m), 1182 (vw), 1135 (w), 1089 (w), 1056 (vw), 836 (vs), 774 (w), 731 (w), 678 (w). Further elution of the column provided [Ru(**2**)(4-CF_3py)Cl](PF_6) as brown solid (42 mg, 52%): ^{1}H NMR (acetone-d_6): δ 10.07 (d, *J* = 4.2, 1.5 Hz, 2H), 8.82 (d, *J* = 8.4 Hz, 2H), 8.71 (d, *J* = 7.8 Hz, 2H), 8.60 (d, *J* = 8.7 Hz, 2H), 8.49 (d, *J* = 6.9 Hz, 2H), 8.43 (s, 2H), 8.34 (dt, *J* = 7.8, 1.5 Hz, 2H), 8.05 (m, 2H), 7.27 (d, *J* = 7.2 Hz, 2H); IR (ATR, cm^{-1}): 1603 (vw), 1419 (vw), 1332 (m), 1179 (w), 1142 (w), 1092 (w), 1056 (vw), 838 (vs), 773 (m), 730 (m), 680 (vw); MS (LC-MS, acetone): *m/z* = 617.9 $[M\text{-}PF_6]^+$, 763.7 $[M]^+$.


80000
60000
40000
20000
0
Absorption coefficient (M-1cm-1)
200
300
400
500
600
700
800
Wavelength (nm)
[Ru(2)(4-CF3py)2](PF6)2
[Ru(2)(4-Mepy)2](PF6)2
[Ru(2)(4-NM2py)2](PF6)2

[Ru(**2**)(4-NMe$_2$py)$_2$](PF$_6$)$_2$