Electronic Supporting Information

Wavelength Selective Separation of Metal Ions Using Electroactive Ligands

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Materials and instrumentation:

Unless otherwise specified, following reagents and substrates were used as received without further purification: 4-Nitrobenzaldehyde ($C_7H_5O_3N$, Aldrich, 98%); 2-Acetylpyridine (C_7H_7NO, Aldrich, ≥99%); sodium hydroxide (NaOH, Aldrich, 97%, beads, reagent grade); ethanol (EtOH, KOPTEC, 200 proof); pyridine (C_5H_5N, Aldrich, anhydrous, 99.8%); iodine (I, Aldrich, ≥99.8%, ACS reagent grade solid); ethyl ether ($C_4H_{10}O$, J. T Baker, anhydrous, ACS reagent grade); ammonium acetate ($C_2H_7NO_2$, Aldrich, reagent grade); Tin(II) Chloride dihydrate ($SnCl_2.2H_2O$, Alfa Aesar, reagent grade); hydrochloric acid (HCl, Aldrich, 37%, ACS reagent grade); Iron(II) Chloride ($FeCl_2$, Alfa Aesar, anhydrous, 99.5% metal basis); potassium hexafluorophosphate (KPF_6, Aldrich, 98%); silica gel (Sorbent Technologies, Inc., standard grade, 60 Å, 40-63 µm); acetonitrile (CH_3CN, Aldrich, ≥99.5%, ACS reagent grade); potassium nitrate (KNO_3, Alfa Aesar, 99%); deionized water; Ruthenium(III) Chloride ($RuCl_3$, TCI); sodium nitrite ($NaNO_2$, Aldrich, ≥97.0%, ACS reagent grade); NMR solvent acetonitrile-D3 (CD_3CN, D, 99.8%) was purchased from Cambridge Isotope Laboratories, Inc. The amine substituted ligand was synthesized according to previous reports.[1] The complexes Fe(tpy-Ph-NH_2)$_2$(PF_6)$_2$ (**Fe-N_2^+**) and Ru(tpy-Ph-NH_2)$_2$(PF_6)$_2$ (**Ru-N_2^+**)were synthesized following previous published procedures with minor variations.[2]

Nuclear Magnetic Resonance: All ^1H, ^{13}C, and ^{19}F NMR spectra were recorded using Bruker 400 MHz or 600 MHz spectrometers at room temperature. Chemical shifts for protons are reported in parts per million (ppm) relative to residual acetonitrile peak at 1.94 ppm. All NMR spectra were processed using MNOVA.

Absorption spectroscopy: The UV-visible spectra were recorded using an Agilent 8453 UV/Visible photo diode array spectrophotometer with 1 cm x 1 cm quartz cuvette.

Light Sources: Irradiation experiments with 455 nm and 617 nm light were performed using ThorLabs M455L3 (455 nm, M00339384, fwhm = 19.8 nm) and ThorLabs M617L3 (617 nm, M00436799, fwhm =

15.6 nm) LEDs. The LED was mounted and controlled by ThorLabs LEDD1B T-Cube series LED driver (M00401974). The light source for 700 nm was a Continuum Surelite EX Nd:YAG laser combined with a Continuum Horizon OPO (5−7 ns, operated at 10 Hz, beam diameter ∼0.5 cm, ~0.5 mJ/pulse). The light intensities were measured using an Ophir power meter (Vega 7Z01560) and sensor (3A-FS 7Z02628).

Kinetic measurements: All kinetic experiments were performed in dry deaerated acetonitrile at 4 ±1 ^{o}C with a screw capped 1 cm x 1 cm quartz 4 mL cuvette under nitrogen in dark. The reaction mixture was stirred with Starna Cells electronic cell stirrer (Model: SCS 1.11) equipped with a magnetic spin head (Catalog number: 9400). The experimental set-up is depicted in Figure S1. All kinetic data were processed using SPECFIT/32 software package.

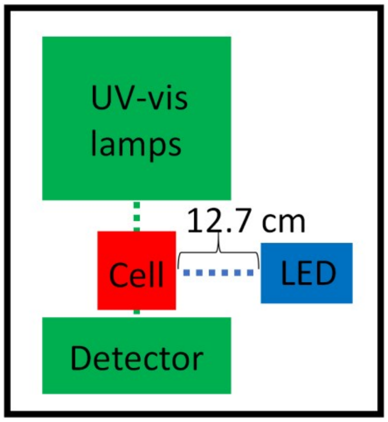
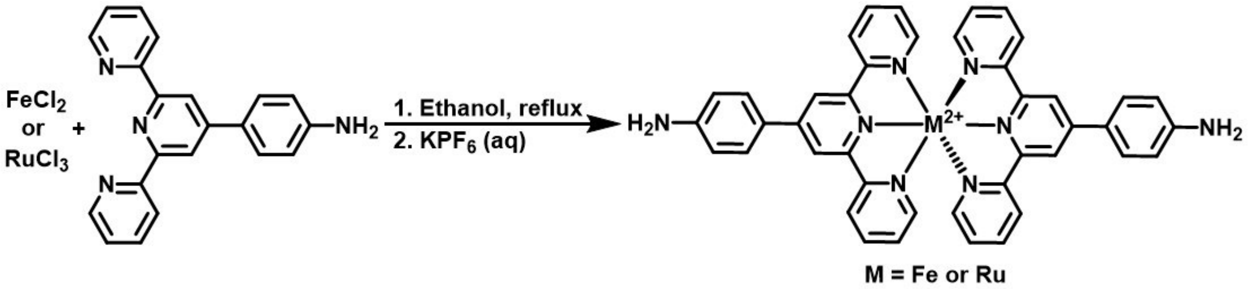


Figure S1. Experimental setup for kinetic measurements.

Attenuated total reflectance infrared spectra: ATR-IR spectra were recorded using a Bruker Alpha FTIR spectrometer (SiC Glowbar source, DTGS detector) with a Platinum ATR quickSnap sampling module (single reflection diamond crystal). Spectra were acquired from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. All ATR-IR spectra are reported in absorbance with a blank versus atmosphere.

Synthesis and characterization:



Scheme S1. Synthesis of $Fe(tpy\text{-}Ph\text{-}NH_2)_2(PF_6)_2$ and $Ru(tpy\text{-}Ph\text{-}NH_2)_2(PF_6)_2$.

$Fe(tpy\text{-}Ph\text{-}NH_2)_2(PF_6)_2$: A suspension of $FeCl_2$ (44.4 mg, 0.35 mmol, 1 eq.) in ethanol (10 mL) was slowly added to a stirring solution of amine substituted ligand (250 mg, 0.77 mmol, 2.2 eq.) in ethanol (40 mL). After the addition, the mixture was refluxed for 6 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and filtered to remove any remaining solids. Crude product was precipitated by adding water saturated KPF_6 (10 mL) and subsequently washed with water, small amount of ethanol, and diethyl ether. The crude was dissolved in minimum of acetonitrile and purified by flash chromatography with silica gel (eluent: CH_3CN/H_2O/sat. KNO_3(aq), 20:2:1). The fractions were combined and water saturated KPF_6 (2 mL) was added. The mixture was concentrated to remove acetonitrile and the solid suspended in water was filtered, washed with water and diethyl ether to give $Fe(tpy\text{-}Ph\text{-}NH_2)_2(PF_6)_2$ as a purple solid (278.5 mg, 80%). ^1H NMR (600 MHz, CD_3CN) δ 9.08 (s, 4H, Ar-H), 8.57 (d, *J* = 7.9 Hz, 4H, Ar-H), 8.13 (d, *J* = 8.3 Hz, 4H, Ar-H), 7.88 (td, *J* = 7.9, 1.3 Hz, 4H, Ar-H), 7.19 (d, *J* = 5.6 Hz, 4H, Ar-H), 7.06 (t, *J* = 6.5 Hz, 4H, Ar-H), 7.00 (d, *J* = 8.4 Hz, 4H, Ar-H), 4.84 (s, 4H, -NH2); ^{13}C NMR (101 MHz, CD_3CN) δ 160.93, 159.37, 154.08, 152.17, 151.50, 139.50, 130.03, 128.06, 125.18, 124.46, 120.80, 115.85. ATR-IR (cm^{-1}): 3399 for $-NH_2$

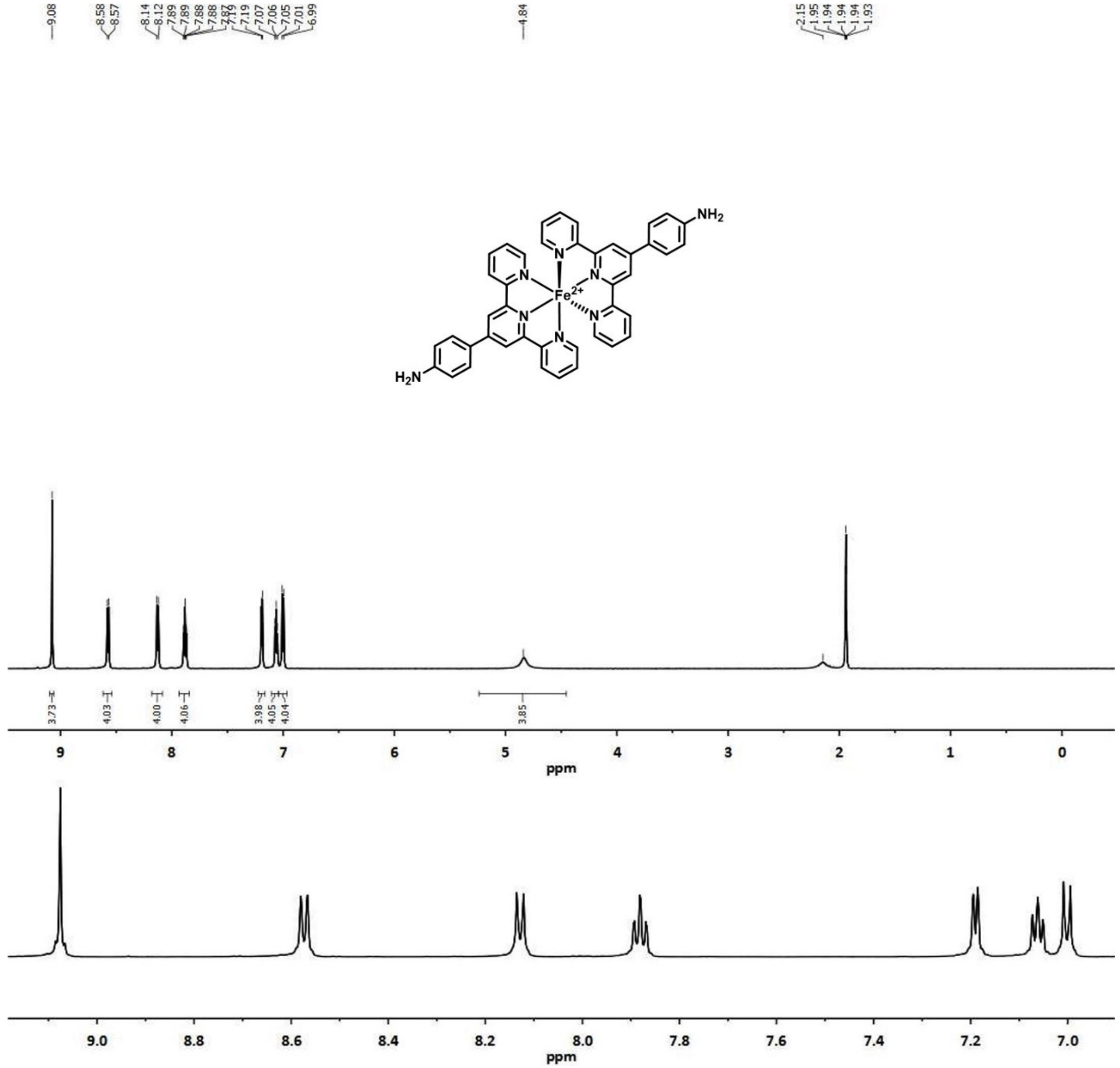


Figure S2. ^{1}H NMR (CD_3CN, 600 MHz) of Fe(tpy-Ph-NH_2)$_2$(PF_6)$_2$.

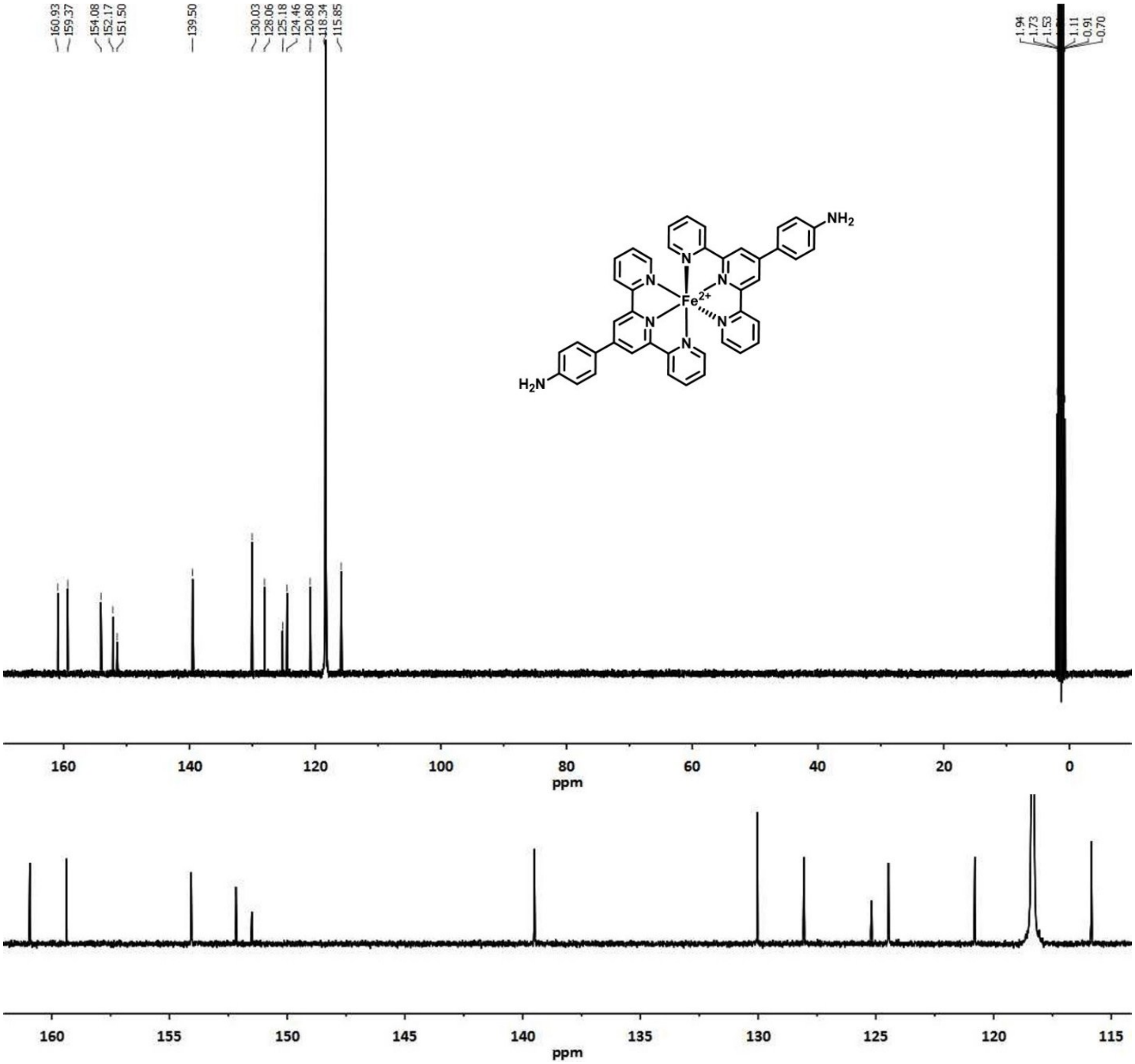


Figure S3. ^{13}C NMR (CD_3CN, 101 MHz) of $Fe(tpy\text{-}Ph\text{-}NH_2)_2(PF_6)_2$.

$Ru(tpy\text{-}Ph\text{-}NH_2)_2(PF_6)_2$: Amine substituted ligand (250 mg, 0.77 mmol, 2.2 eq), $RuCl_3$ (72.6 mg, 0.35 mmol, 1 eq) and ethanol (50 mL) was added to a flask and refluxed for 24 h under nitrogen atmosphere. The reaction work-up and purification procedure was same as for $Fe(tpy\text{-}Ph\text{-}NH_2)_2(PF_6)_2$. The complex obtained as a red solid (218.4 mg, 60%). ^{1}H NMR (400 MHz, CD_3CN) δ 8.90 (s, 4H, Ar-H), 8.61 (d, *J* = 8.0

Hz, 4H, Ar-H), 8.01 (d, *J* = 8.6 Hz, 4H, Ar-H), 7.92 (td, *J* = 7.9, 1.4 Hz, 4H, Ar-H), 7.42 (d, *J* = 4.8 Hz, 4H, Ar-H), 7.19 – 7.11 (m, 4H, Ar-H), 6.96 (d, *J* = 8.6 Hz, 4H, Ar-H), 4.77 (s, 4H, -NH2); ^{13}C NMR (101 MHz, CD_3CN) δ 159.56, 156.23, 153.39, 151.84, 149.46, 138.84, 129.87, 128.27, 125.46, 125.26, 120.84, 115.84. ATR-IR (cm^{-1}): 3392 for $-NH_2$

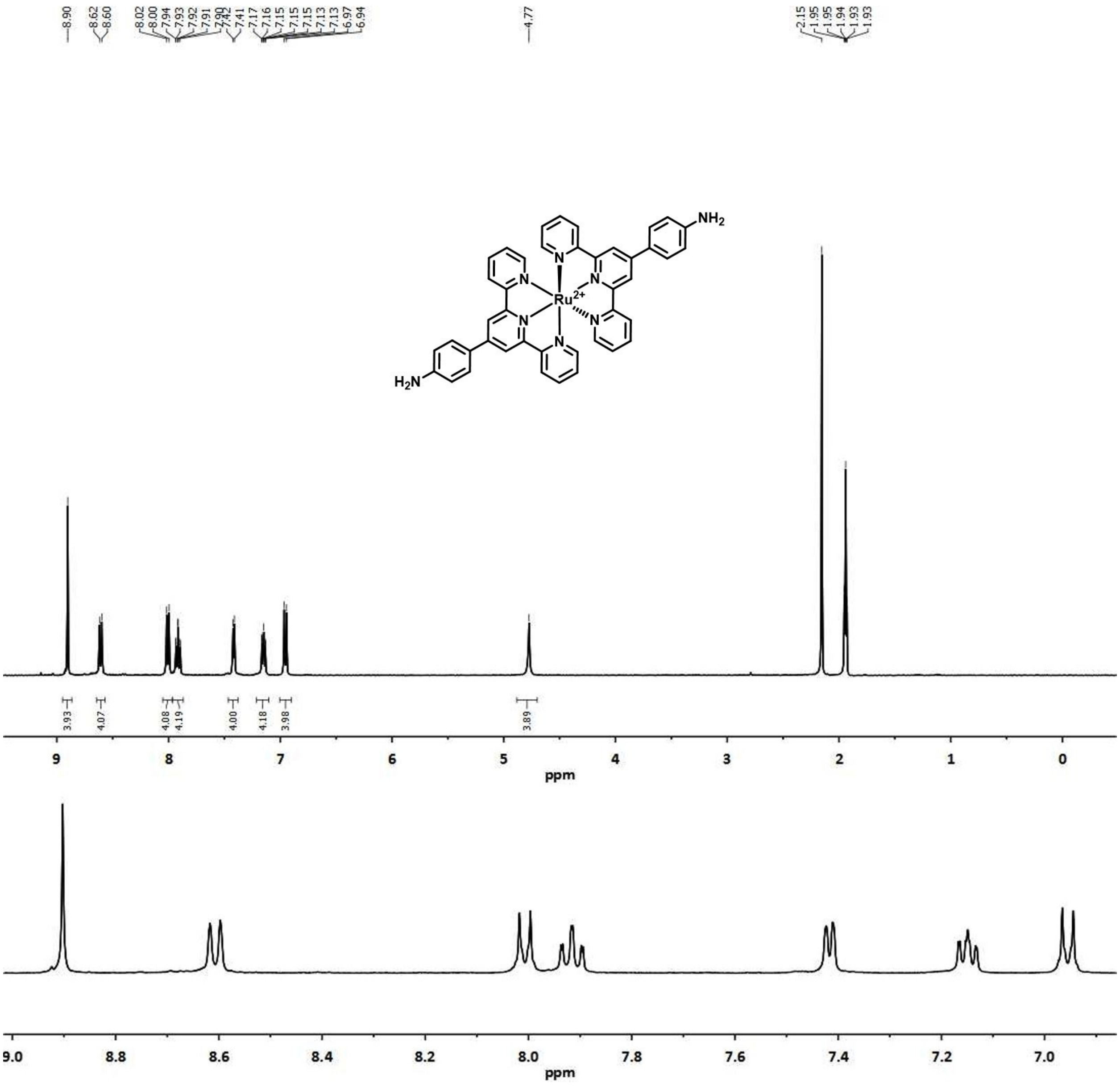


Figure S4. ^{1}H NMR (CD_3CN, 400 MHz) of $Ru(tpy\text{-}Ph\text{-}NH_2)_2(PF_6)_2$.

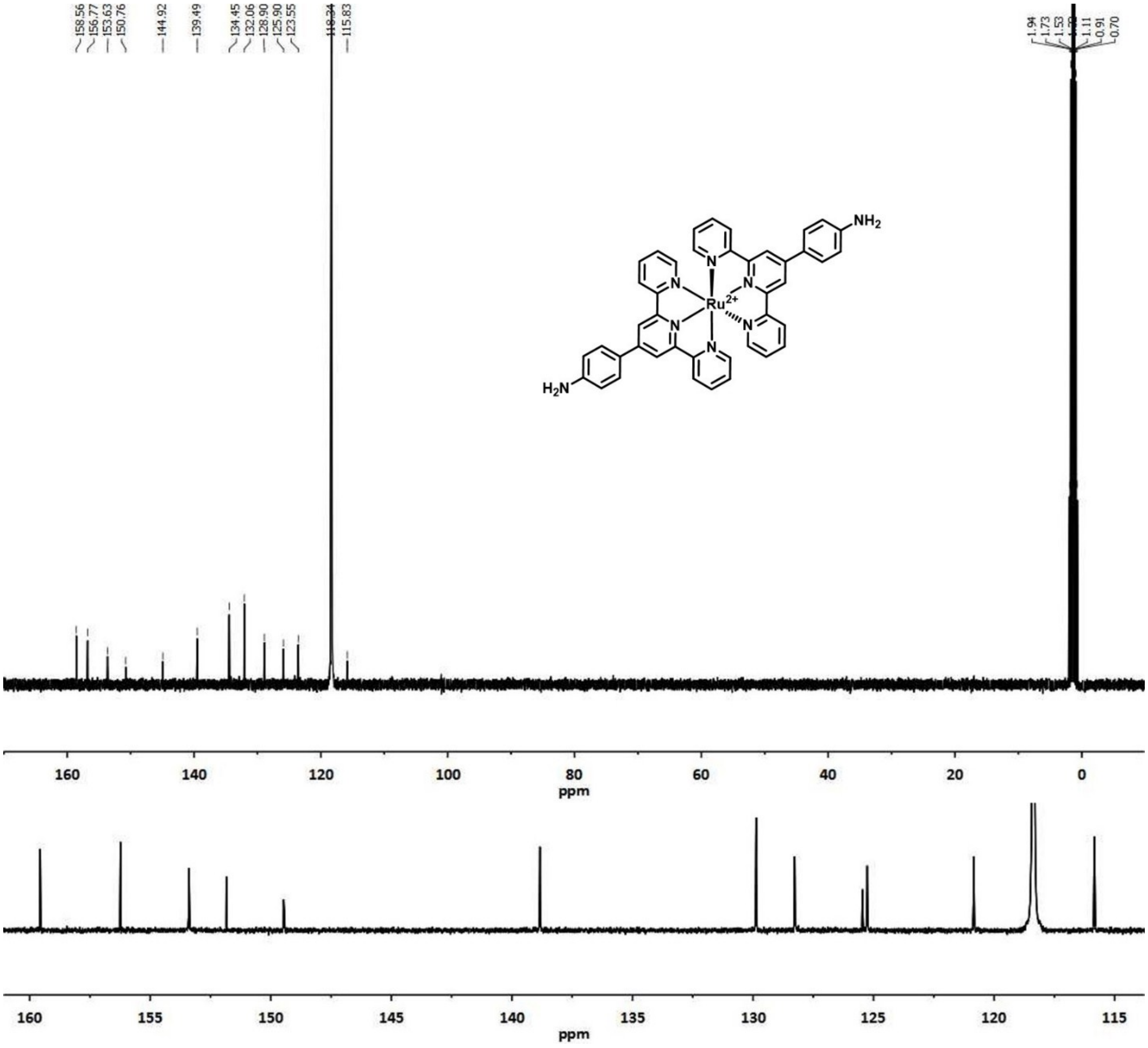
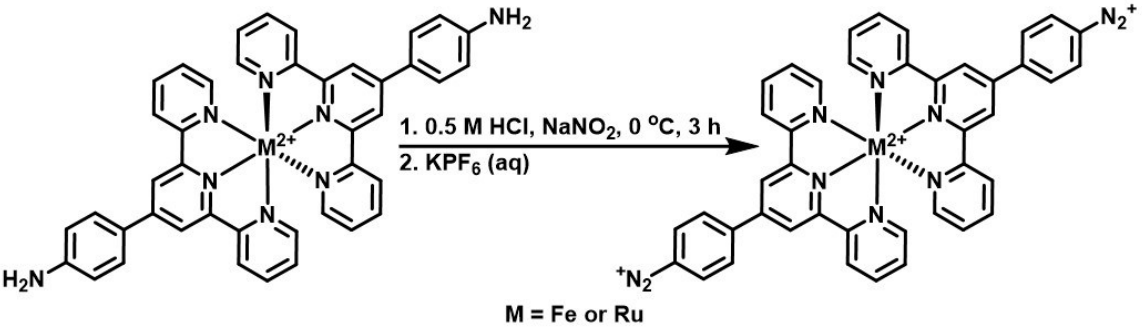


Figure S5. ^{13}C NMR (CD_3CN, 101 MHz) of Ru(tpy-Ph-NH_2)$_2$(PF_6)$_2$.



Scheme S2. Synthesis of **Fe-N_2^+** and **Ru-N_2^+**.

Fe-N_2^+ *and* ***Ru-N_2^+*:** A near saturated aqueous solution of $NaNO_2$ (4 eq) was added to a solution of Fe(tpy-Ph-NH_2)$_2$(PF_6)$_2$ or Ru(tpy-Ph-NH_2)$_2$(PF_6)$_2$ (1 eq.) dissolved in a minimum volume of 0.5 M HCl at 0 °C. The mixture was stirred for 3 h at this temperature. The diazotized complexes were precipitated by adding water saturated KPF_6. The precipitate was filtrated and washed with water, cold ethanol, and diethyl ether. The yield for diazotization was about 70% for both compounds. NMR for **Fe-N_2^+** wasn't amenable due its paramagnetic nature. However, the characteristic IR peak for diazonium moiety was observed at 2276 cm^{-1}.

***Characterization data for Ru-N_2^+*:** ^{1}H NMR (400 MHz, CD_3CN) δ 9.07 (s, 4H, Ar-H), 8.80 (d, *J* = 8.5 Hz, 4H, Ar-H), 8.66 (d, *J* = 7.4 Hz, 8H, Ar-H), 7.99 (t, *J* = 7.7 Hz, 4H, Ar-H), 7.44 (d, *J* = 5.4 Hz, 4H, Ar-H), 7.26 – 7.19 (m, 4H, Ar-H); ^{13}C NMR (101 MHz, CD_3CN) δ 158.56, 156.77, 153.63, 150.76, 144.92, 139.49, 134.45, 132.06, 128.90, 125.90, 123.55, 115.83. ATR-IR (cm^{-1}): 2270 for -N_2^+

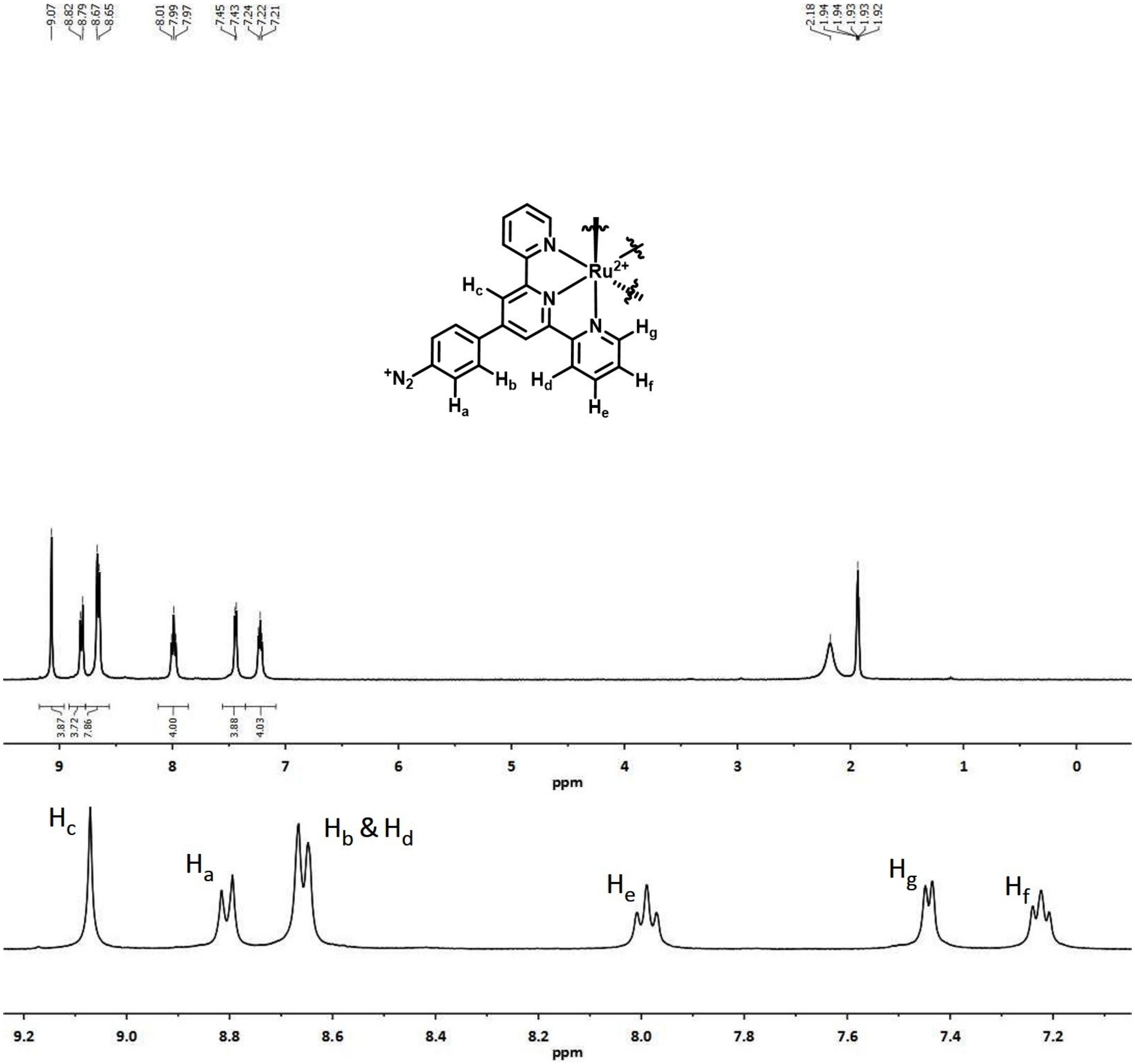


Figure S6. ^{1}H NMR (CD_3CN, 400 MHz) of **Ru-N_2^+**.

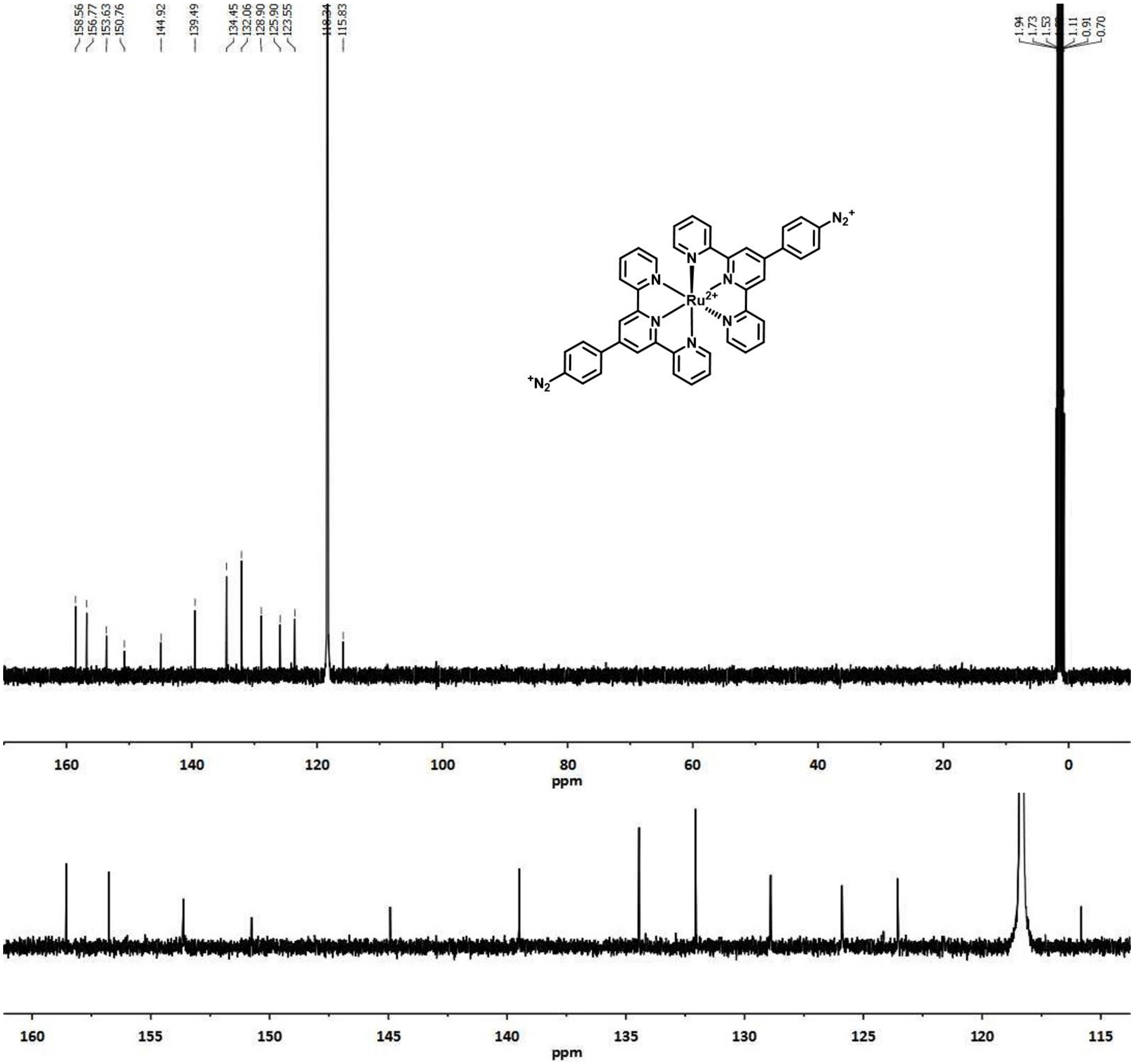


Figure S7. ^{13}C NMR (CD_3CN, 101 MHz) of **Ru-N_2^+**.

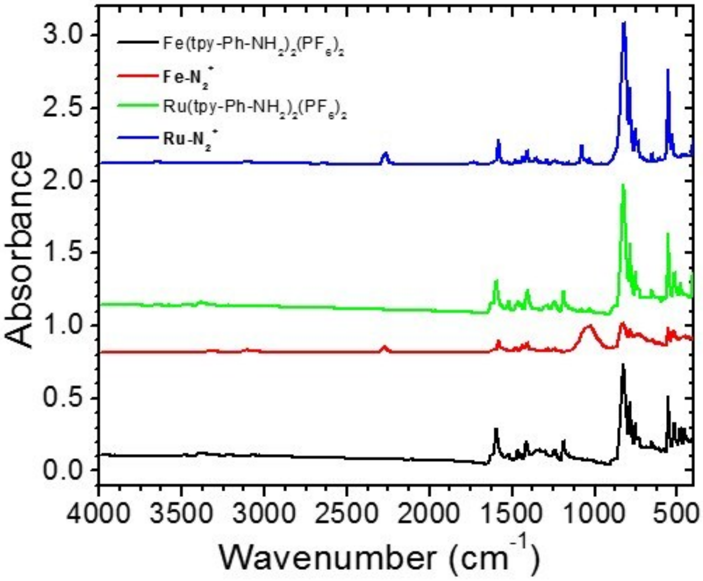


Figure S8. ATR-IR spectra for Fe(tpy-Ph-NH$_2$)$_2$(PF$_6$)$_2$, Ru(tpy-Ph-NH$_2$)$_2$(PF$_6$)$_2$, **Fe-N$_2^+$**, and **Ru-N$_2^+$**.

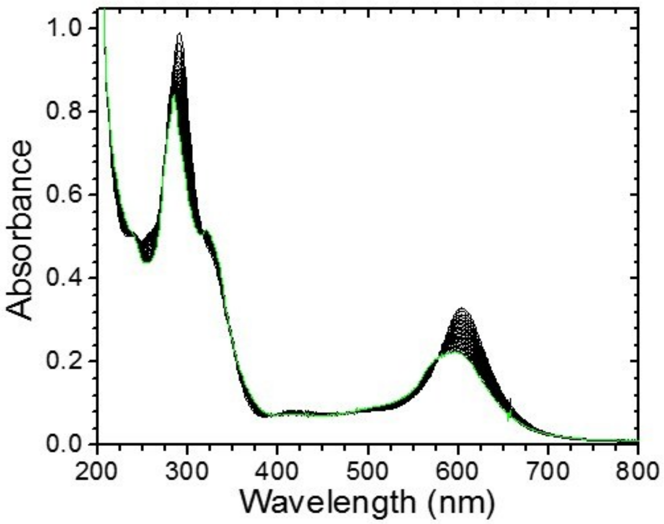


Figure S9. Changes in the absorption spectra for **Fe-N$_2^+$** in MeCN at 4 ±1 ^{o}C during irradiation with 617 nm light (700 mW) (0 hours (black) to 120 minutes (green) every 5 minutes).

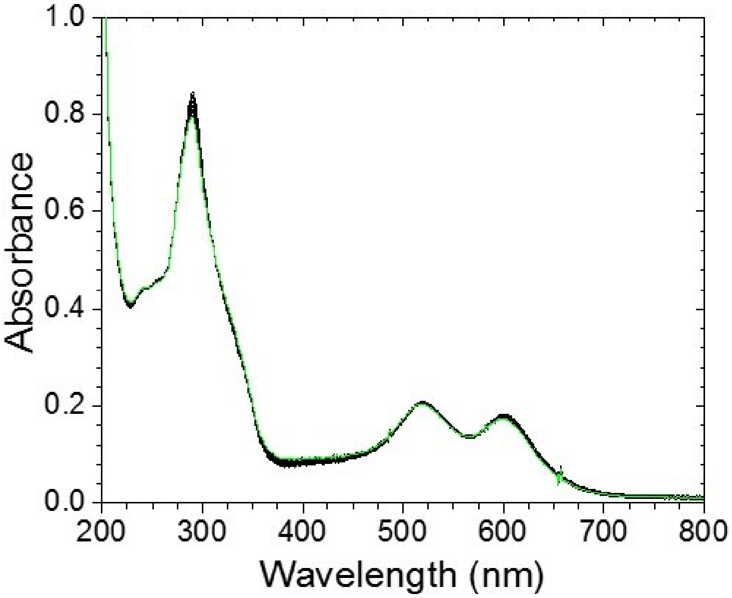


Figure S10. Changes in the absorption spectra for **Fe-N$_2^+$** : **Ru-N$_2^+$** 50:50 mixture in MeCN (6 μM) at 4 ±1 ^{o}C in dark (0 hours (black) to 120 minutes (green) every 5 minutes).

Photoreactions: Reaction conditions are summarized in table S1.

Table S1. Summary of reaction conditions.

Entry	Test sample (Conc.)	Temperature (°C)	Time (h)	Light source	Wavelength (intensity)
1	**Fe-N_2^+** (8 μM)	4 ±1	2	LED	617 nm (700 mW)
2	**Ru-N_2^+** (8 μM)	4 ±1	2	LED	455 nm (100 μW)
3	50:50 mix (6 μM)	4 ±1	2	LED	455 nm (100 μW)
4	50:50 mix (6 μM)	0	4	Nd:YAG laser	700 nm (5 mJ at 10 Hz)

Isolation and characterization of the photo product Ru-H: After the reaction, solvent was removed under reduced pressure and purified by flash chromatography with silica gel (eluent: CH_3CN/H_2O/sat. KNO_3(aq), 10:1:1). The fractions were combined and few milliliters of water saturated KPF_6 was added. The mixture was concentrated to remove acetonitrile and the solid suspended in water was filtered, washed with water and diethyl ether to give final photoproduct as a red solid. ^1H NMR (600 MHz, CD3CN) δ 9.03 (s, 4H), 8.67 (d, J = 8.0 Hz, 4H), 8.26 – 8.19 (m, 4H), 7.95 (td, J = 8.0, 1.4 Hz, 4H), 7.77 (t, J = 7.7 Hz, 4H), 7.69 (t, J = 7.4 Hz, 2H), 7.44 (d, J = 5.0 Hz, 4H), 7.18 (ddd, J = 7.2, 5.7, 1.2 Hz, 4H); ^{13}C NMR (101 MHz, CD_3CN) δ 159.23, 156.49, 153.45, 149.37, 139.07, 137.89, 131.42, 130.69, 128.82, 128.47, 125.57, 122.70. HRMS (ESI+): [C42H30N6Ru PF6]$^+$ Calculated: 865.1223 Found: 865.1238.

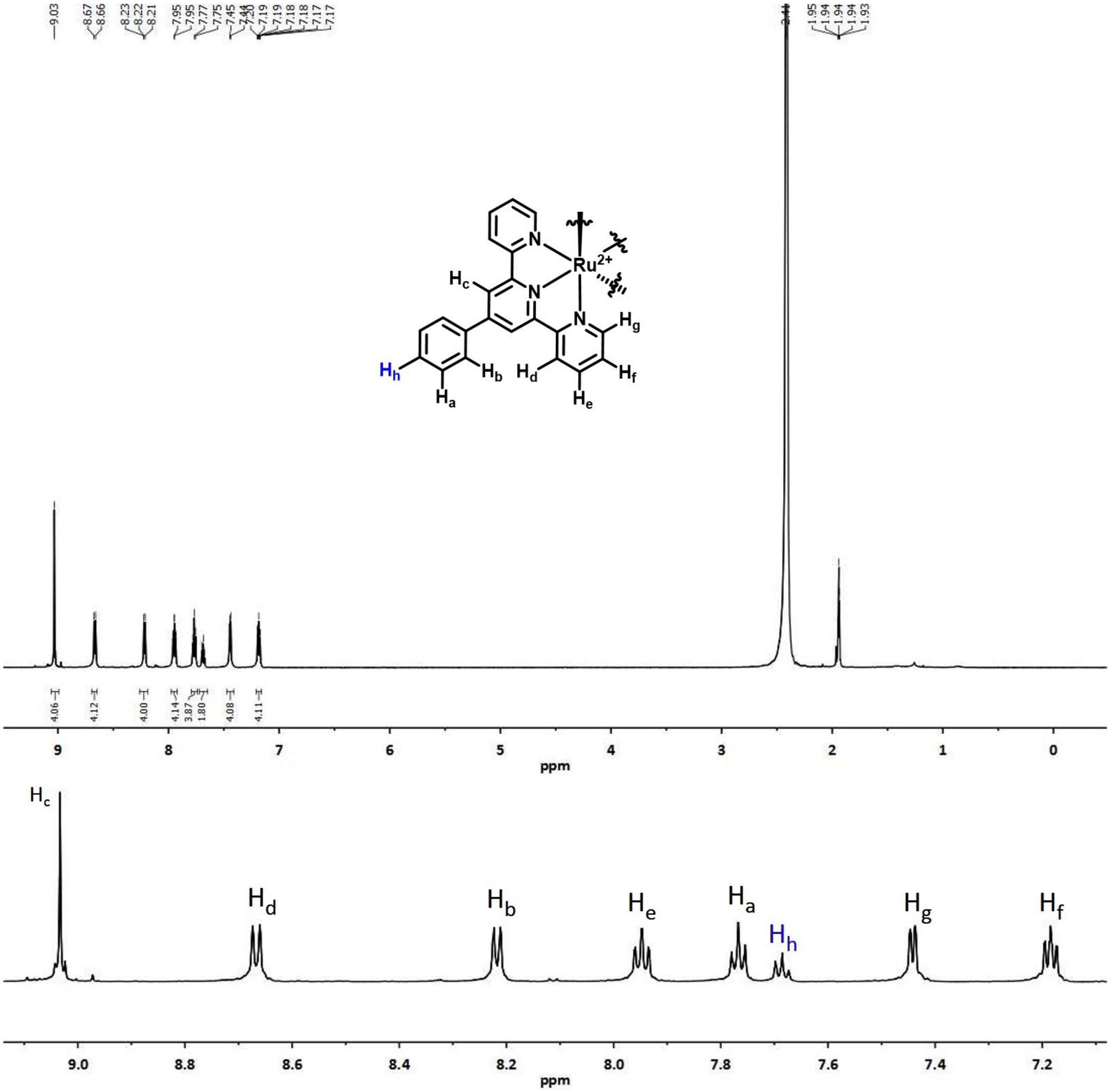


Figure S11. ^{1}H NMR (CD_3CN, 600 MHz) of the photoproduct.

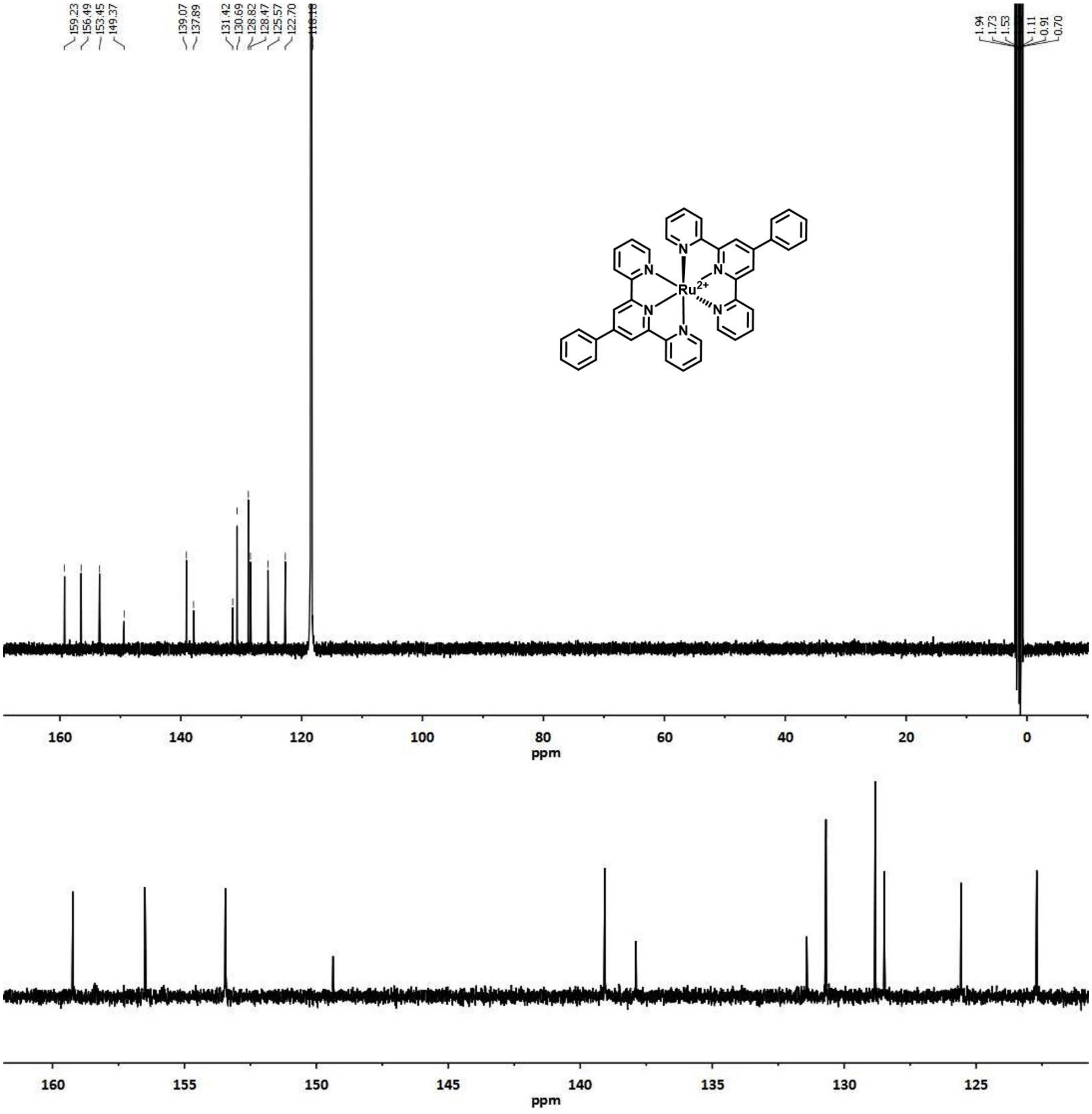


Figure S12. ^{13}C NMR (CD_3CN, 101 MHz) of the photoproduct mixture.

References:

1. M. Trigo-López, A. Muñoz, S. Ibeas, F. Serna, F. C. García, J. M. García, Sensors and Actuators B: Chemical **2016**, *226*, 118-126.
2. (a) G. D. Storrier, S. B. Colbran, D. C. Craig, Journal of the Chemical Society, Dalton Transactions **1997**, 3011-3028; (b) W. Y. Ng, X. Gong, W. K. Chan, Chemistry of Materials **1999**, *11*, 1165-1170. (c) R. Bangle, R. N. Sampaio, L. Troian-Gautier, G. J. Meyer, ACS Applied Materials & Interfaces **2018**, *10*, 3121-3132.