

Exploring the Emergent Redox Chemistry of Pd(II) Nodes with Pendant Ferrocenes: from Precursors, through Building Blocks, to Self-Assemblies

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Supporting Information

Spectroscopic, electrochemical, and spectroelectrochemical characterization

Figure S1: UV-Vis spectra of Fc-containing compounds	S2
Figure S2: ¹ H-NMR spectrum of Pd(dppf)Cl₂ in D ₂ -DCM.....	S3
Figure S3: ¹ H-NMR spectrum of [Pd(dppf)(ACN) ₂](PF ₆) ₂ in D ₂ -DCM	S4
Figure S4: ¹ H-NMR spectra of Pd(dppf)bpy and Pd(dppf)TPT in D ₂ -DCM	S5
Figure S5: ¹ H-DOSY-NMR spectrum of Pd(dppf)TPT in D ₂ -DCM.....	S6
Figure S6: Full ESI-FT-ICR MS of Pd(dppf)bpy	S7
Figure S7: Full ESI-FT-ICR MS of Pd(dppf)TPT	S7
Figure S8: Cyclic voltammograms of Pd(dppf)Cl₂ Fc-centered oxidation.....	S8
Figure S9: Full cyclic voltammograms of Pd(dppf)Cl₂	S8
Figure S10: Cyclic voltammograms of Pd(dppf)bpy Fc-centered oxidation	S9
Figure S11: Full cyclic voltammograms of Pd(dppf)bpy	S9
Figure S12: Cyclic voltammograms of Pd(dppf)bpy reduction events	S10
Figure S13: Full cyclic voltammograms of Pd(dppf)TPT	S10
Figure S14: Cyclic voltammograms of Pd(dppf)TPT Fc-centered oxidation at 250 mV/s.....	S11
Figure S15: Cyclic voltammograms of Pd(dppf)TPT Fc-centered oxidation at 100 mV/s.....	S11
Figure S16: Cyclic voltammograms of Pd(dppf)TPT Fc-centered oxidation at 80 mV/s.....	S12
Figure S17: Cyclic voltammograms of Pd(dppf)TPT Fc-centered oxidation at 60 mV/s.....	S12
Figure S18: Cyclic voltammograms of Pd(dppf)TPT Fc-centered oxidation at 40 mV/s.....	S13
Figure S19: Cyclic voltammograms of Pd(dppf)TPT Fc-centered oxidation at 20 mV/s.....	S13
Figure S20: Cyclic voltammograms of Pd(dppf)TPT Fc-centered oxidation at 10 mV/s.....	S14
Figure S21: Plots of peak current vs. square root of scan rate with linear fits for Pd(dppf)TPT	S14
Figure S22: Spectroelectrochemical UV-Vis spectra of oxidized Fc-containing compounds	S15
Figure S23: Images of FTO film working electrodes used in diffuse reflectance spectroelectrochemistry	S16

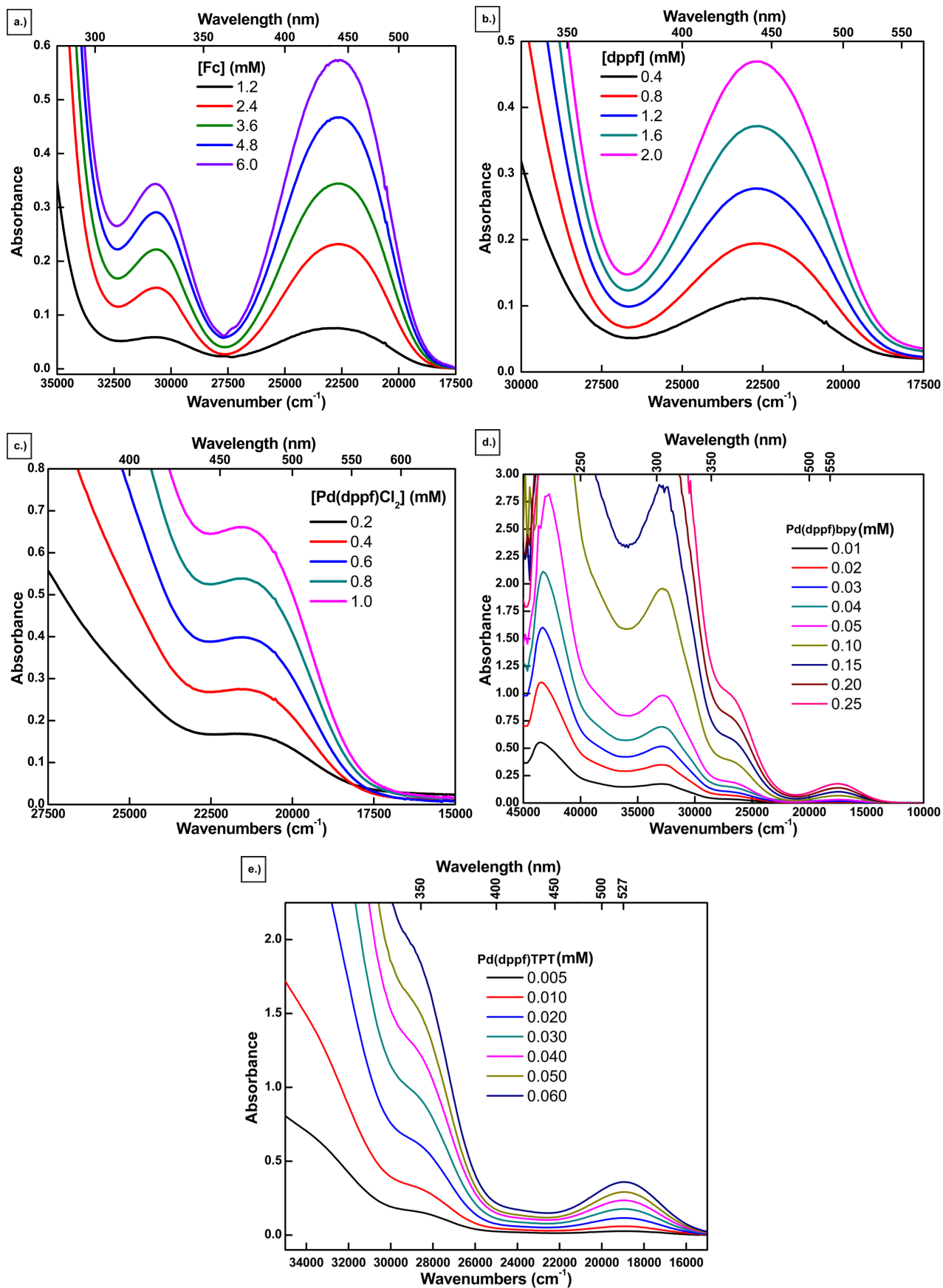


Figure S1: UV-Vis absorbance spectra of a.) **Fc**, b.) **dppf**, c.) **Pd(dppf)Cl₂**, d.) **Pd(dppf)bpy**, e.) **Pd(dppf)TPT**. All spectra were acquired at the specified sample concentration in dry DCM.

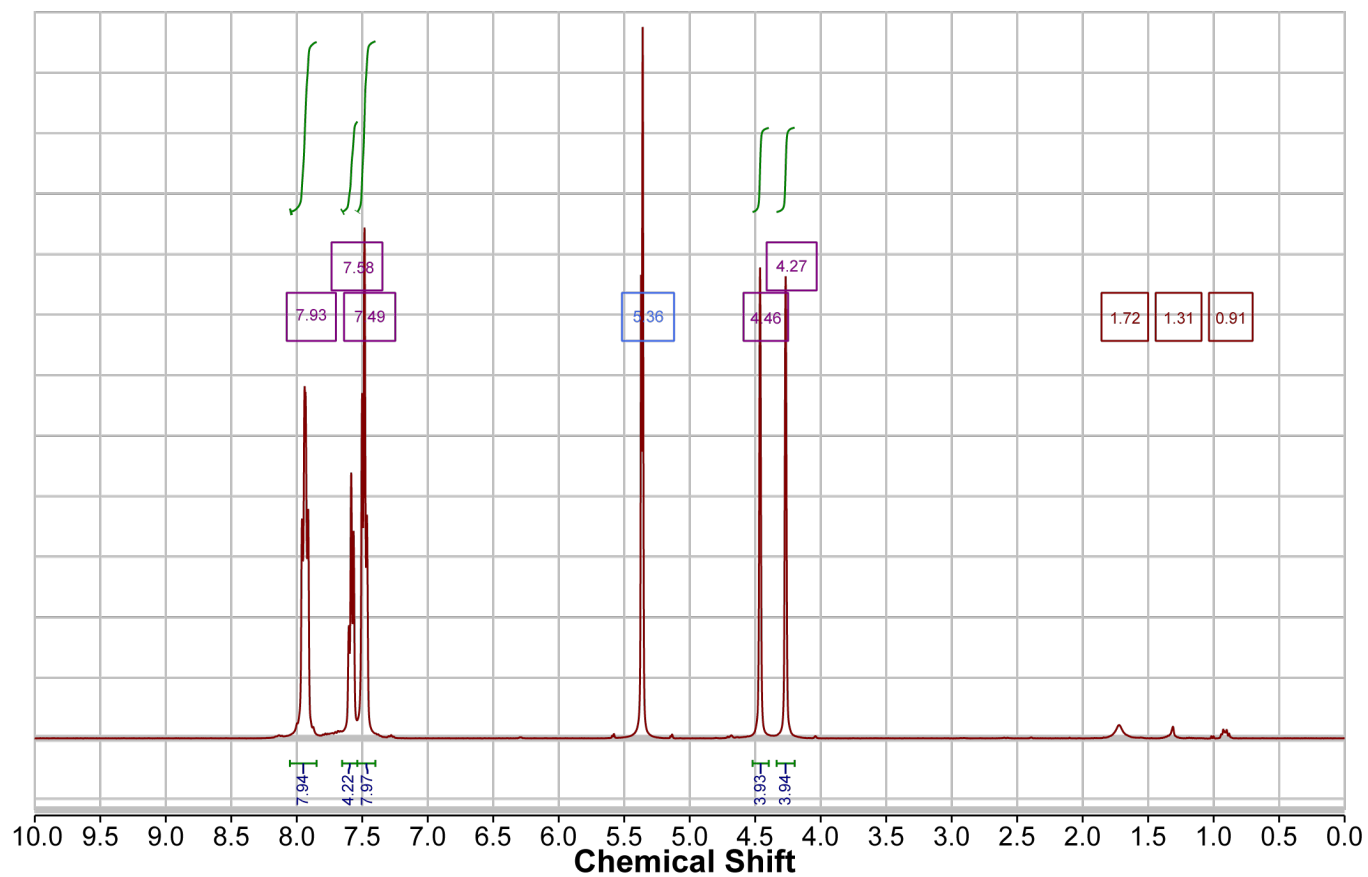


Figure S2: ^1H -NMR spectrum of $\text{Pd}(\text{dppf})\text{Cl}_2$ acquired in $\text{D}_2\text{-DCM}$.

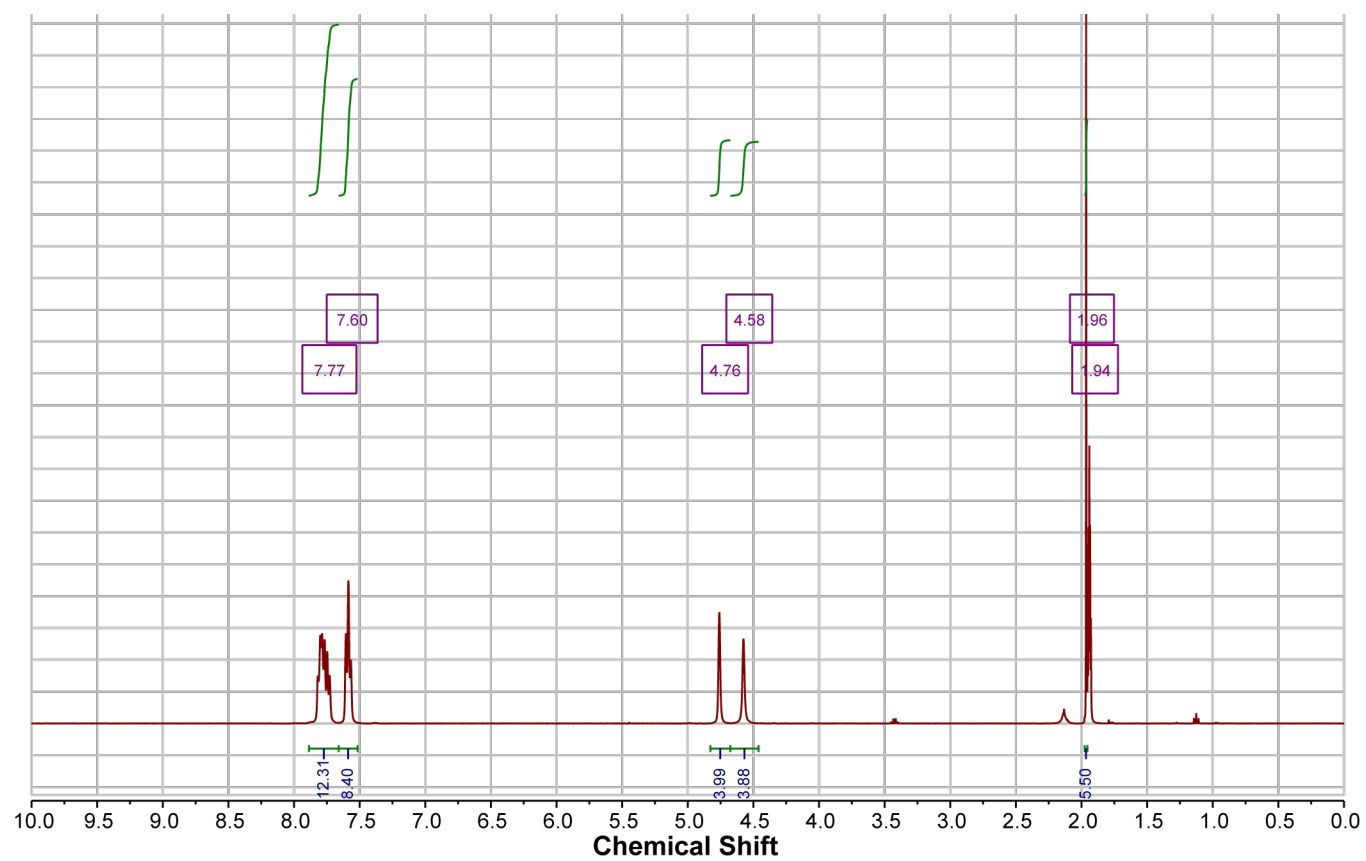


Figure S3: ^1H -NMR spectrum of $[\text{Pd}(\text{dppf})(\text{ACN})_2](\text{PF}_6)_2$ acquired in $\text{D}_2\text{-DCM}$.

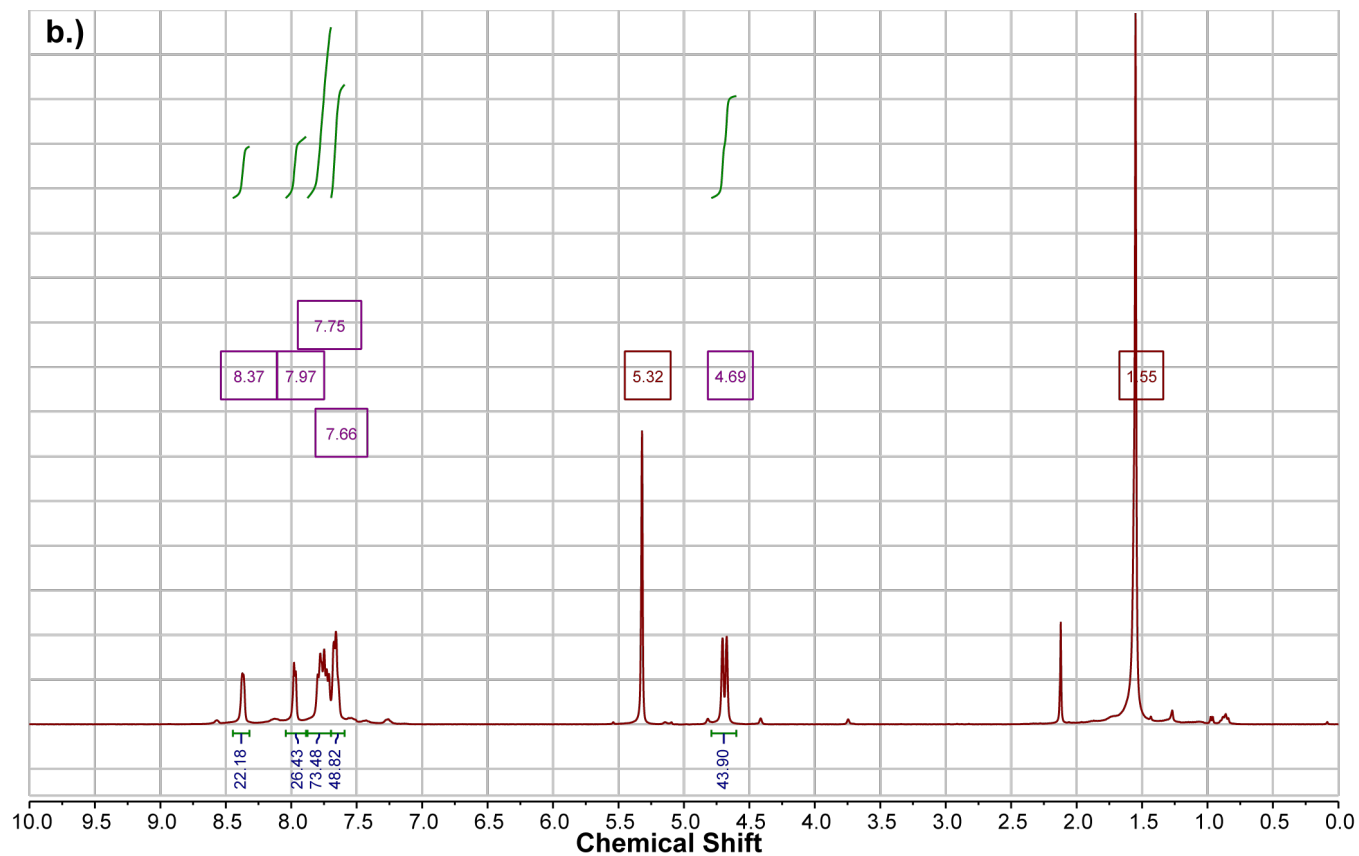
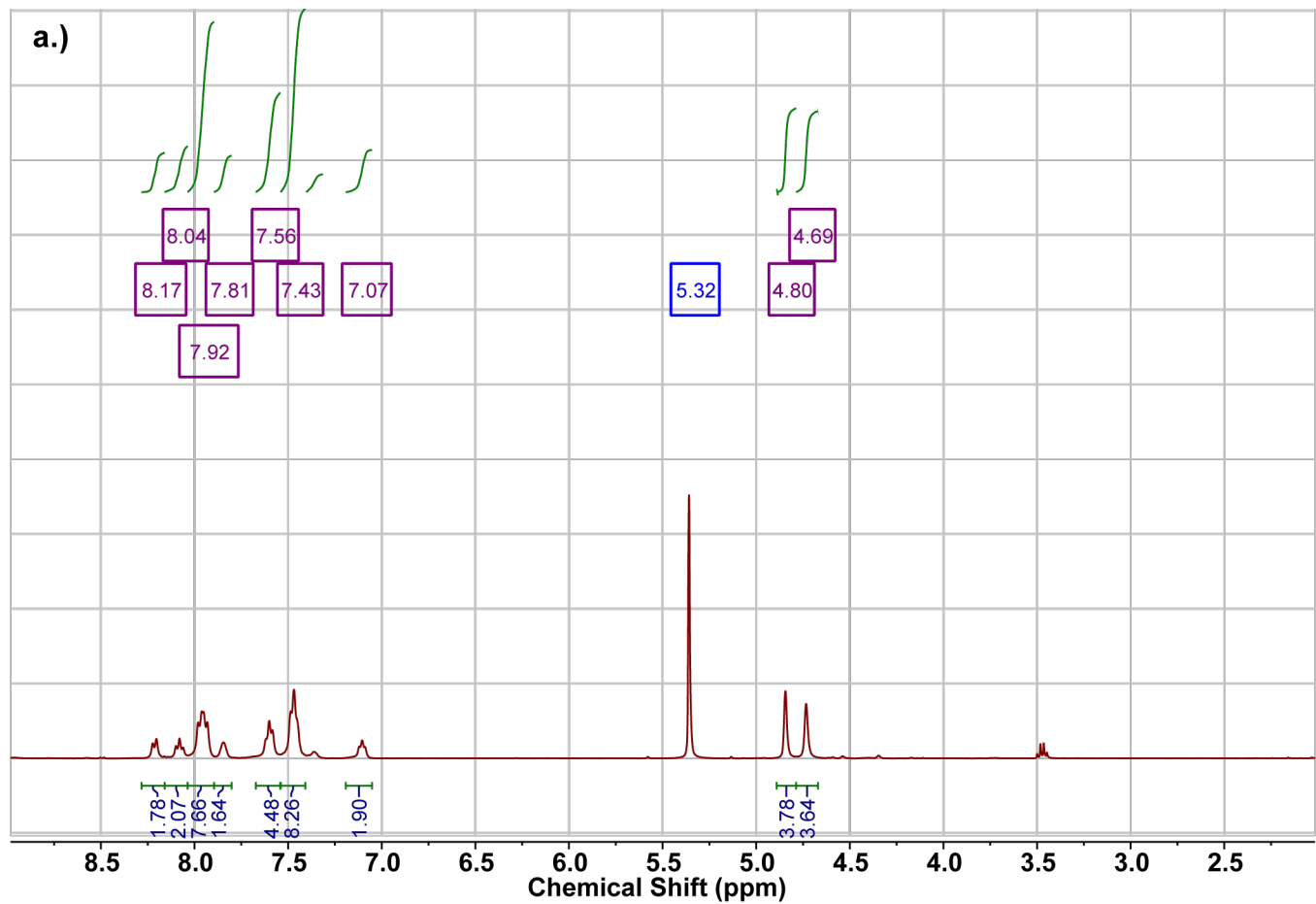


Figure S4: ^1H -NMR spectra of a.) $\text{Pd}(\text{dppf})\text{bpy}$ and b.) $\text{Pd}(\text{dppf})\text{TPT}$ acquired in $\text{D}_2\text{-DCM}$.

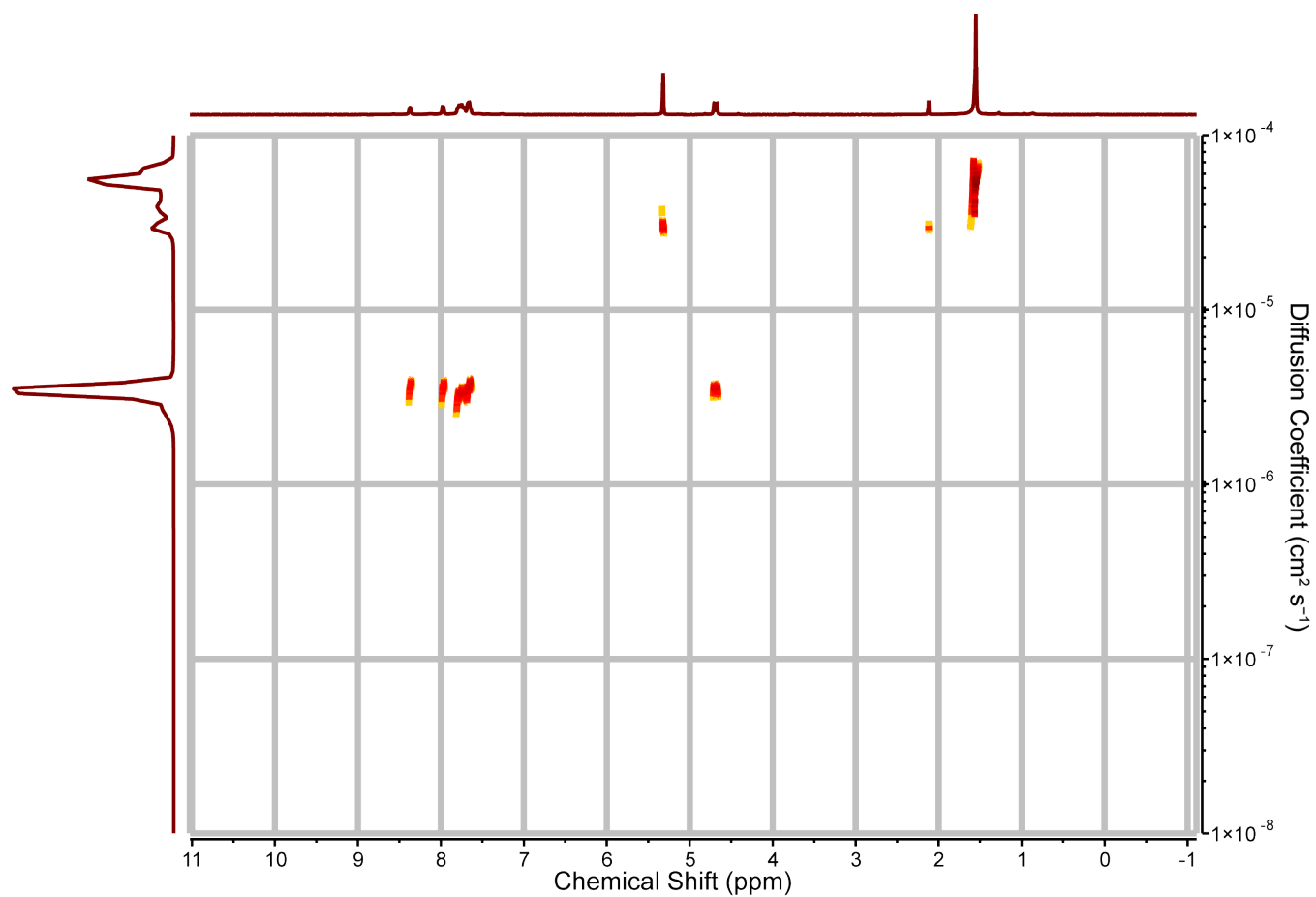


Figure S5: ^1H -DOSY NMR spectrum of **Pd(dppf)TPT** acquired in D_2 -DCM.

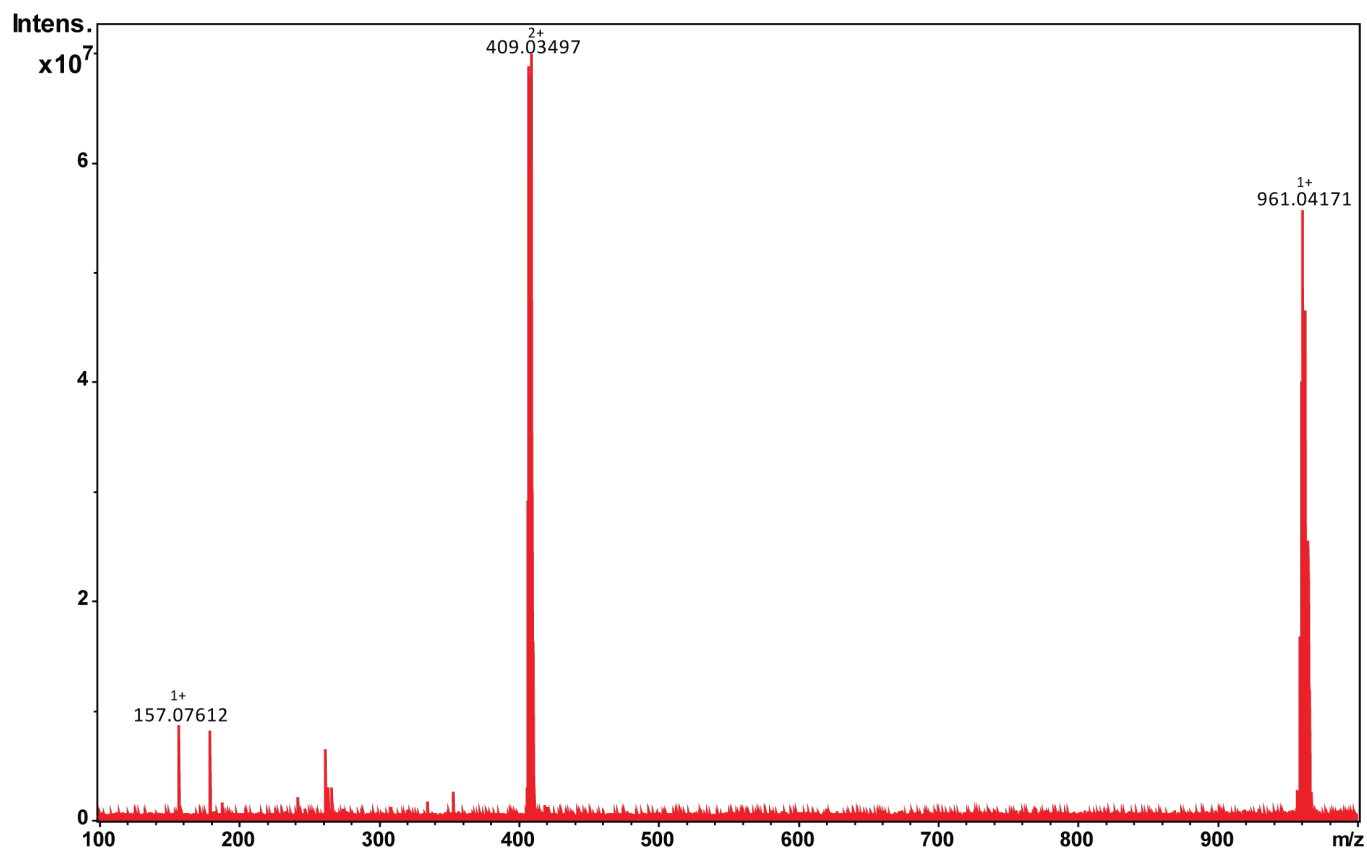


Figure S6: Full ESI-FT-ICR MS of $\text{Pd}(\text{dppf})\text{bpy}$ acquired from a solution in DCM.

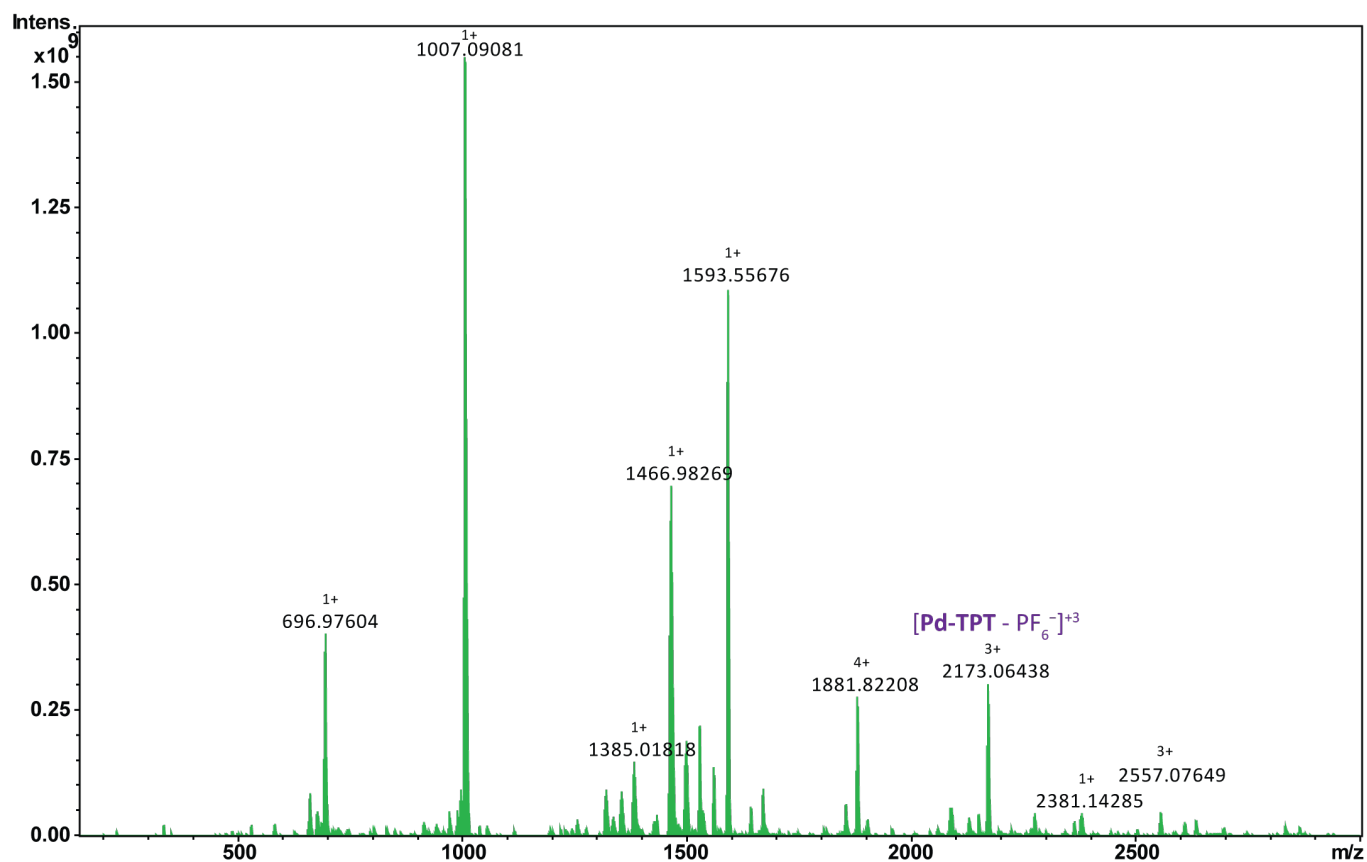


Figure S7: Full ESI-FT-ICR MS of $\text{Pd}(\text{dppf})\text{TPT}$ acquired from a solution in DCM.

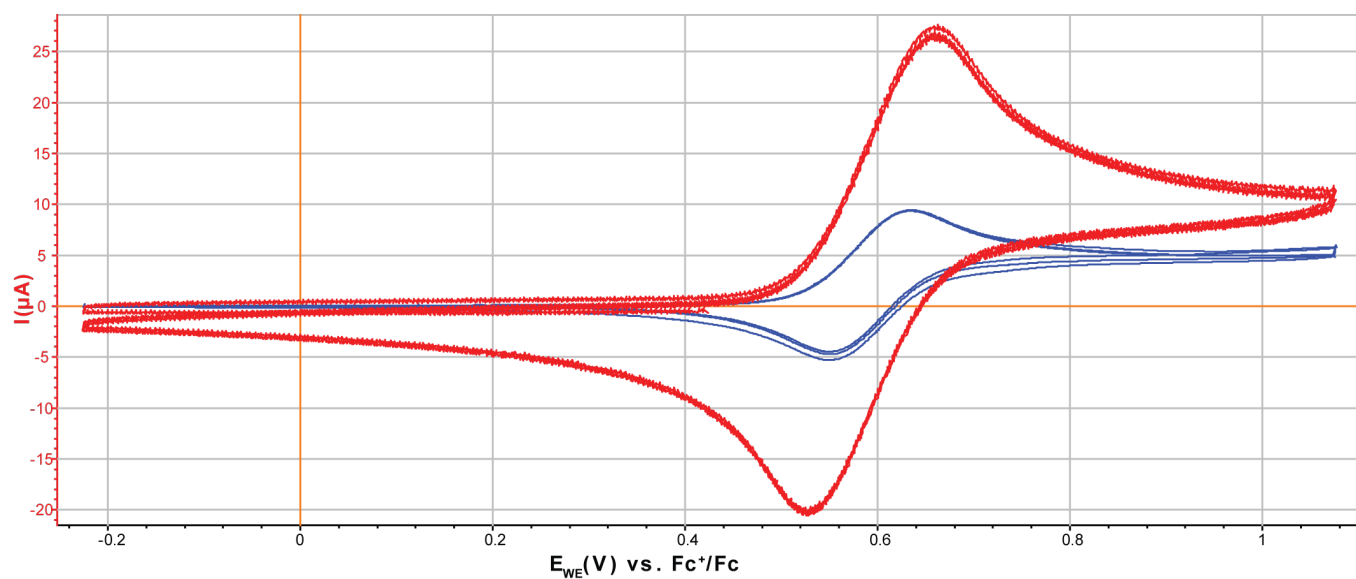


Figure S8: Cyclic voltammograms of Pd(dppf)Cl₂ (1.00 mM). Fc-centered oxidation event at scan rates of 100 mV s⁻¹ (red) and 10 mV s⁻¹ (blue). Shown are 3 cycles starting from E_{oc} in DCM (100 mM TBAPF₆).

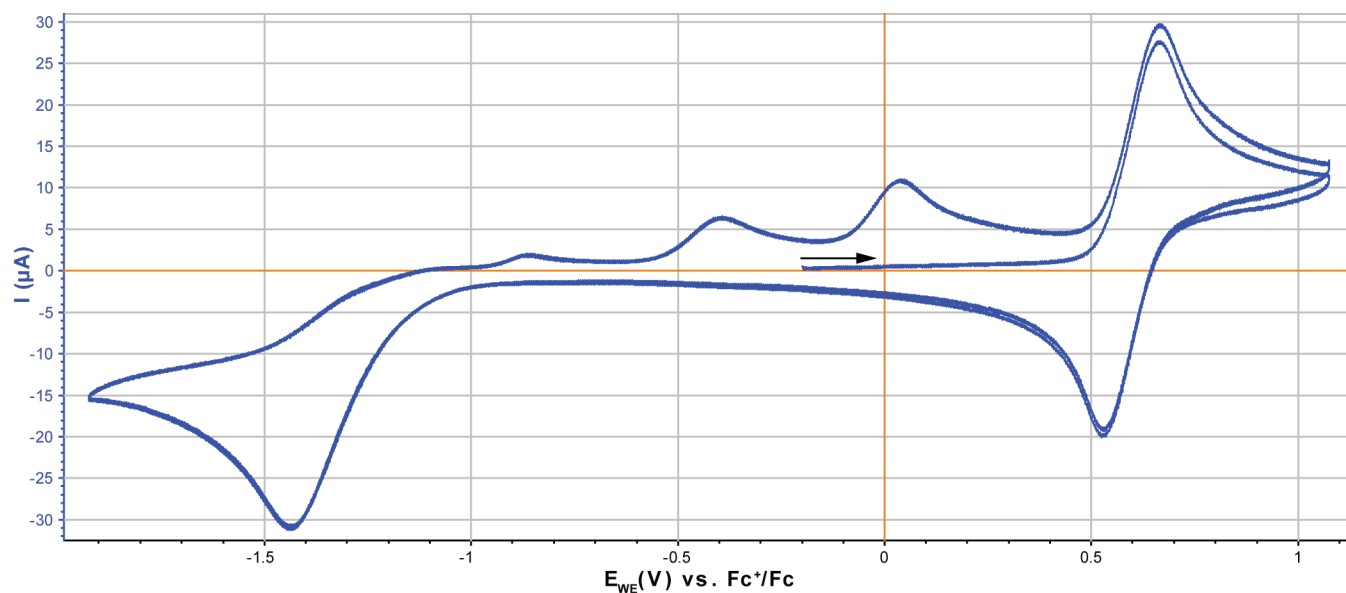


Figure S9: Cyclic voltammograms of Pd(dppf)Cl₂ (1.00 mM). Shown are 3 cycles starting from E_{oc} at 100 mV/s in DCM (100 mM TBAPF₆).

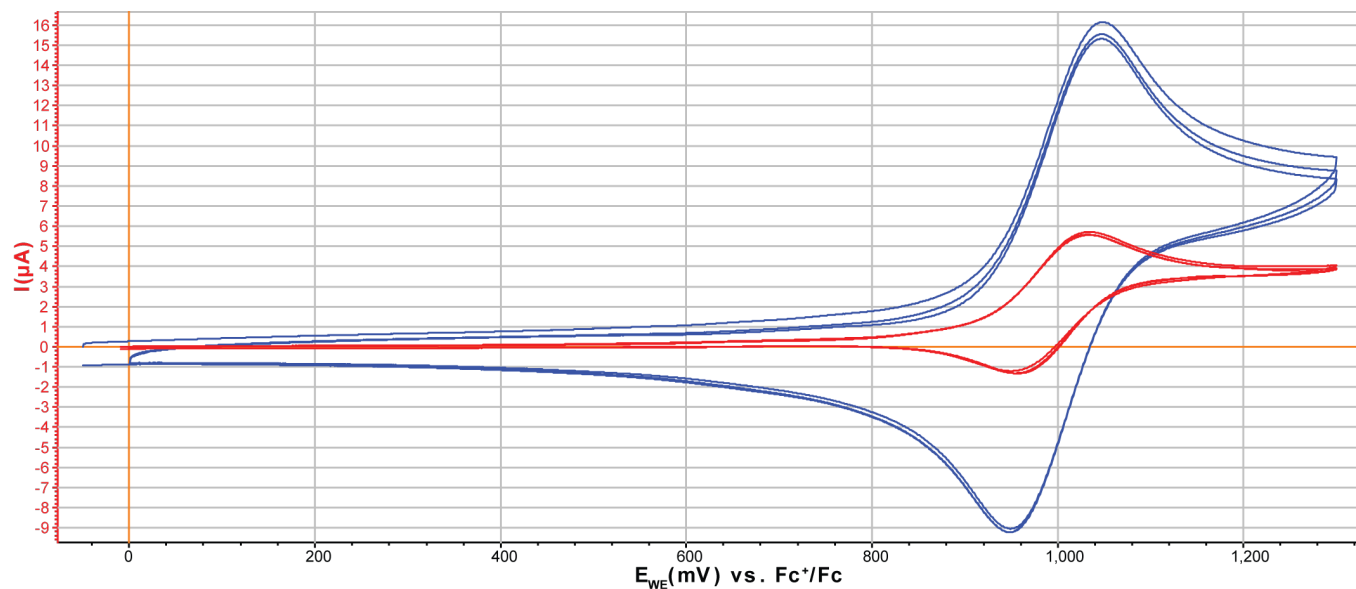


Figure S10: Cyclic voltammograms of Pd(dppf)bpy (1.80 mM) Fc-centered oxidation event at scan rates of 100 mV s^{-1} (blue) and 10 mV s^{-1} (red). Shown are 3 cycles starting from E_{oc} in DCM (100 mM TBAPF_6).

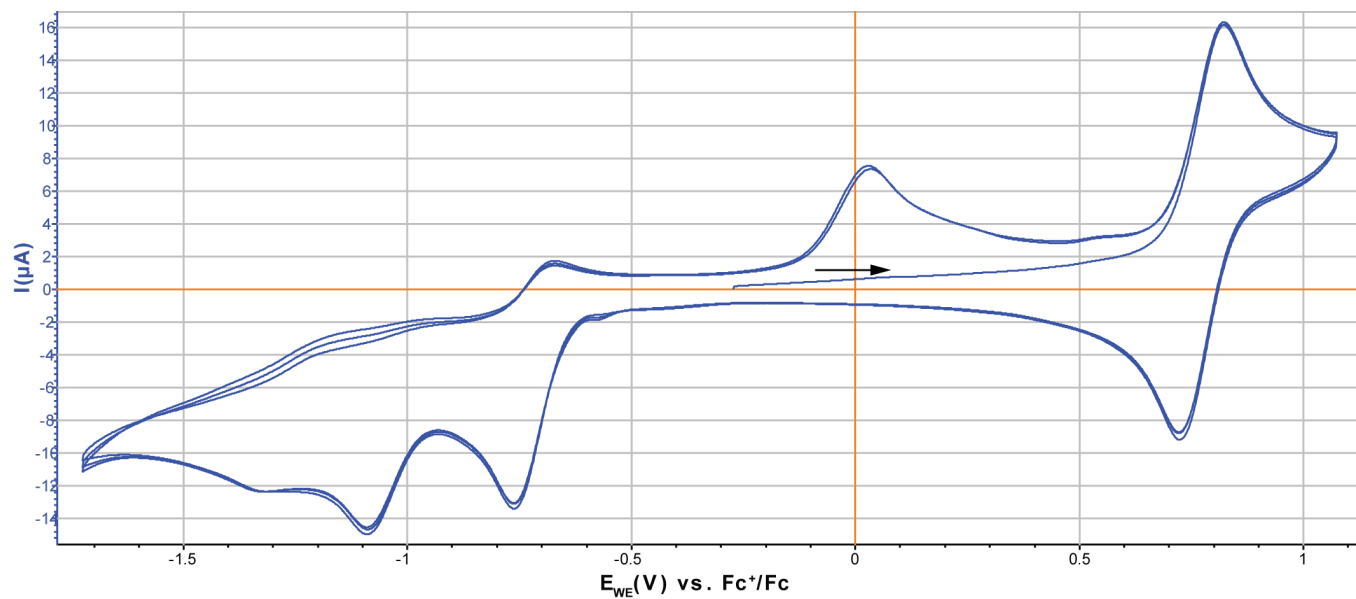


Figure S11: Cyclic voltammograms of Pd(dppf)bpy (1.80 mM). Shown are 3 cycles starting from E_{oc} at 100 mV/s in DCM (100 mM TBAPF_6).

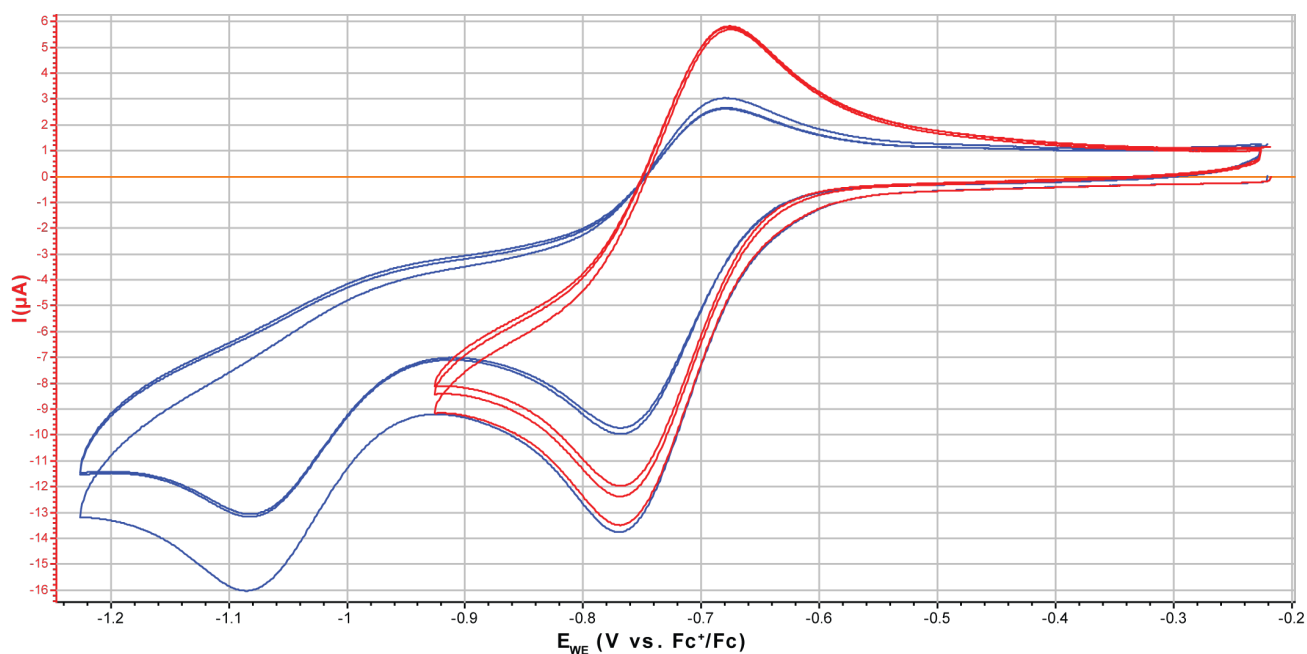


Figure S12: Cyclic voltammograms of Pd(dppf)bpy reduction events with varying potential windows. Shown are 3 cycles starting from E_{oc} at 100 mV/s in DCM (100 mM TBAPF₆).

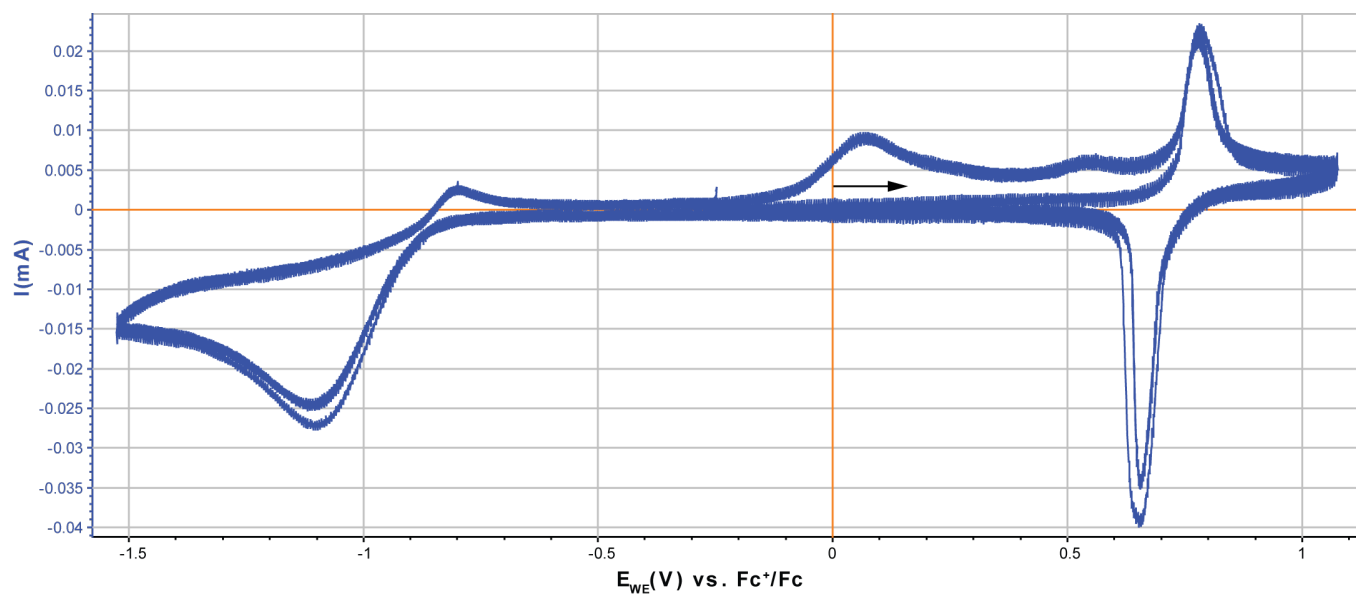


Figure S13: Cyclic voltammograms of Pd(dppf)TPT (0.30 mM). Shown are 3 cycles starting from E_{oc} at 100 mV/s in DCM (100 mM TBAPF₆).

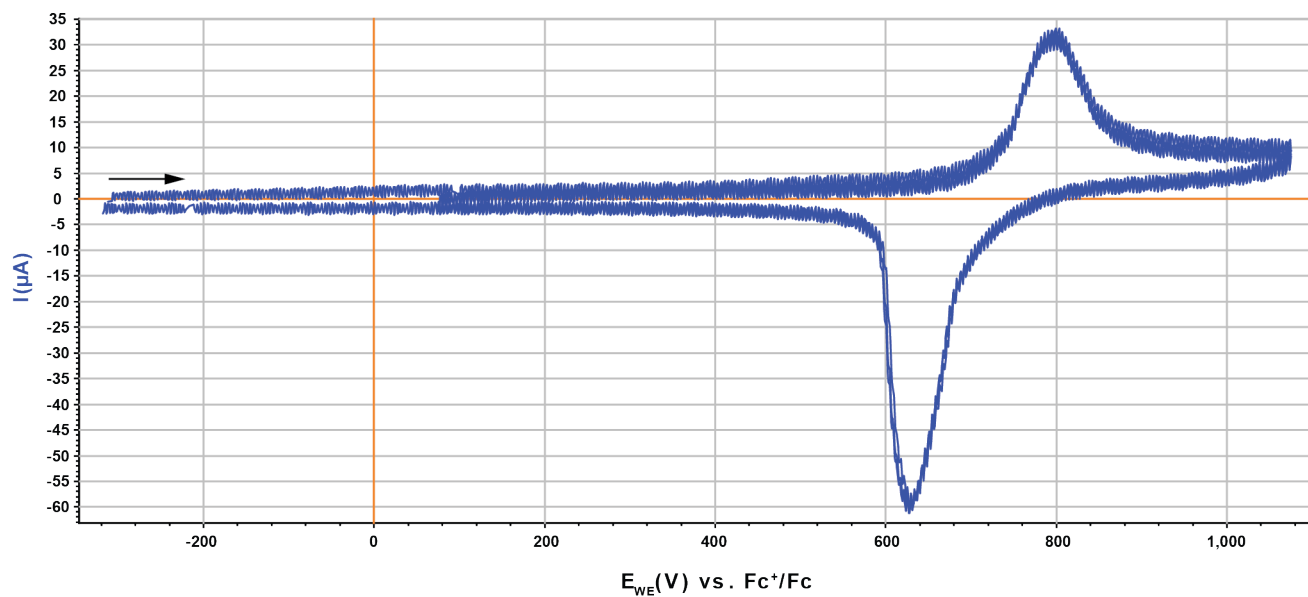


Figure S14: Cyclic voltammograms of **Pd(dppf)TPT** (0.30 mM). Shown are 3 cycles starting from E_{oc} at 250 mV/s in DCM (100 mM TBAPF₆).

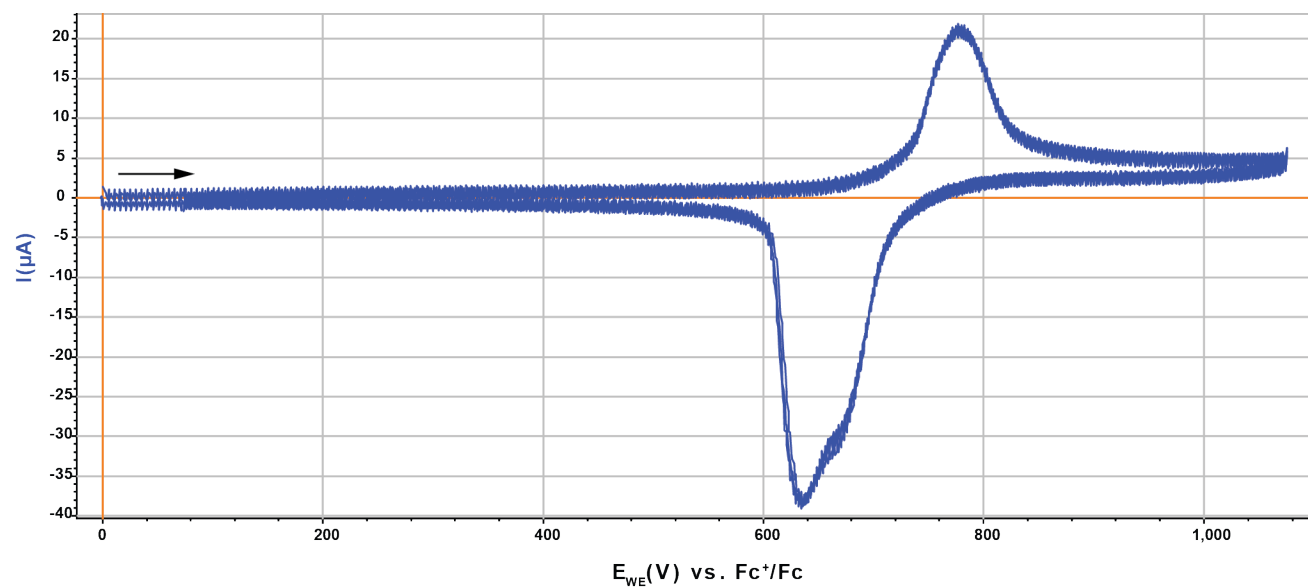


Figure S15: Cyclic voltammograms of **Pd(dppf)TPT** (0.30 mM). Shown are 3 cycles starting from E_{oc} at 100 mV/s in DCM (100 mM TBAPF₆).

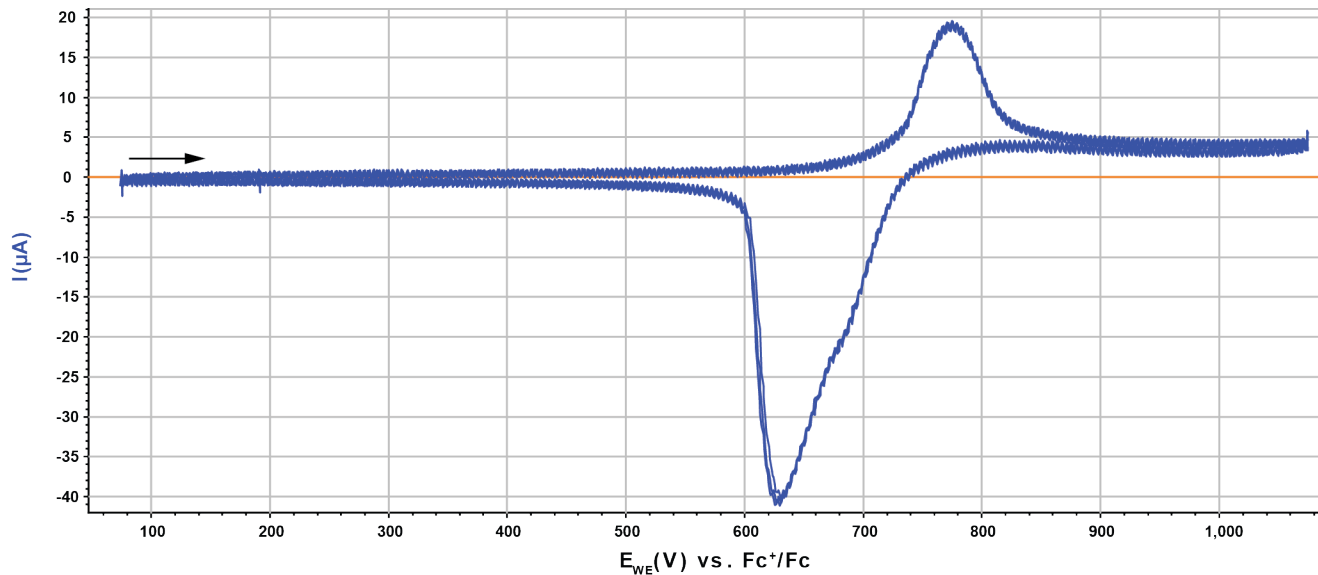


Figure S16: Cyclic voltammograms of **Pd(dppf)TPT** (0.30 mM). Shown are 3 cycles starting from E_{oc} at 80 mV/s in DCM (100 mM TBAPF₆).

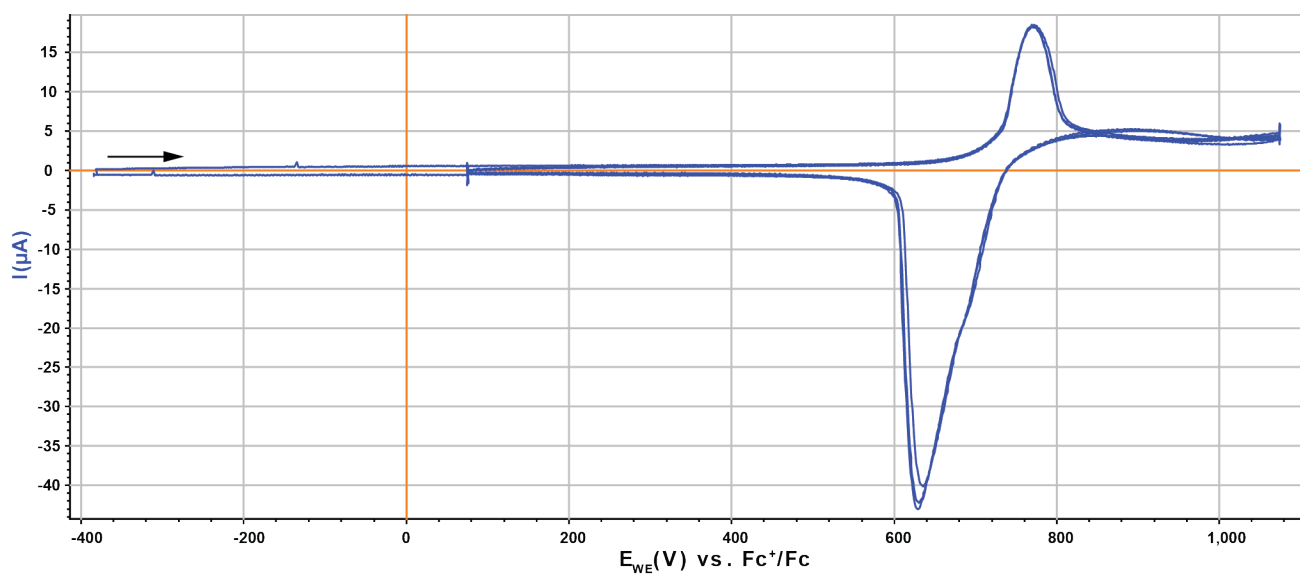


Figure S17: Cyclic voltammograms of **Pd(dppf)TPT** (0.30 mM). Shown are 3 cycles starting from E_{oc} at 60 mV/s in DCM (100 mM TBAPF₆).

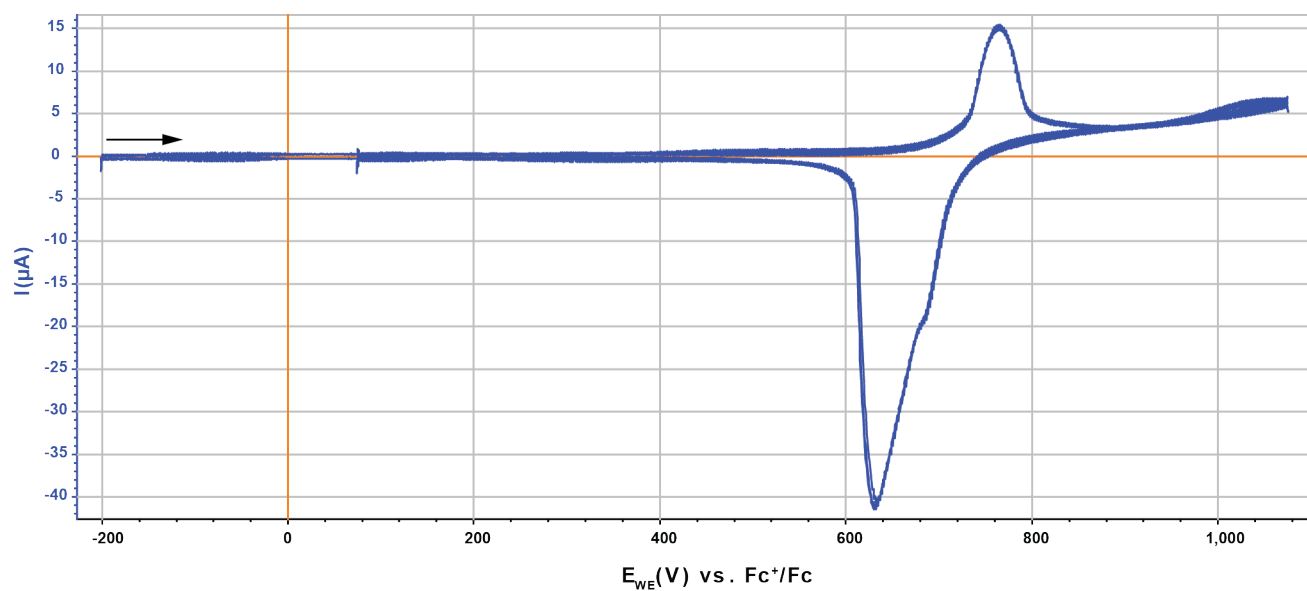


Figure S18: Cyclic voltammograms of **Pd(dppf)TPT** (0.30 mM). Shown are 3 cycles starting from E_{oc} at 40 mV/s in DCM (100 mM TBAPF₆).

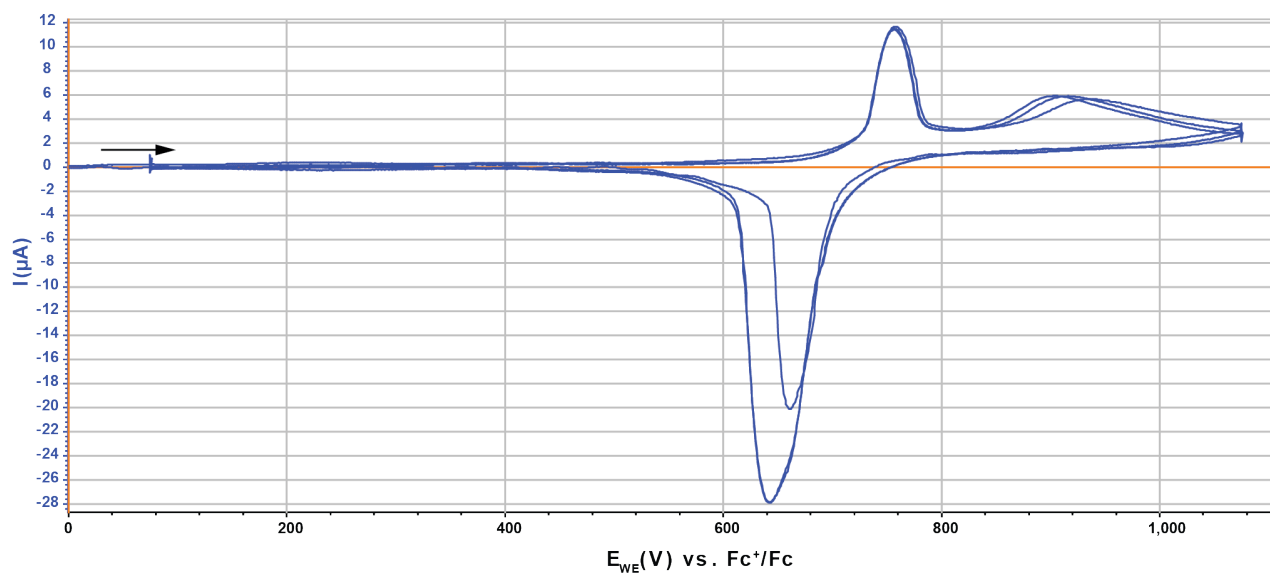


Figure S19: Cyclic voltammograms of **Pd(dppf)TPT** (0.30 mM). Shown are 3 cycles starting from E_{oc} at 20 mV/s in DCM (100 mM TBAPF₆).

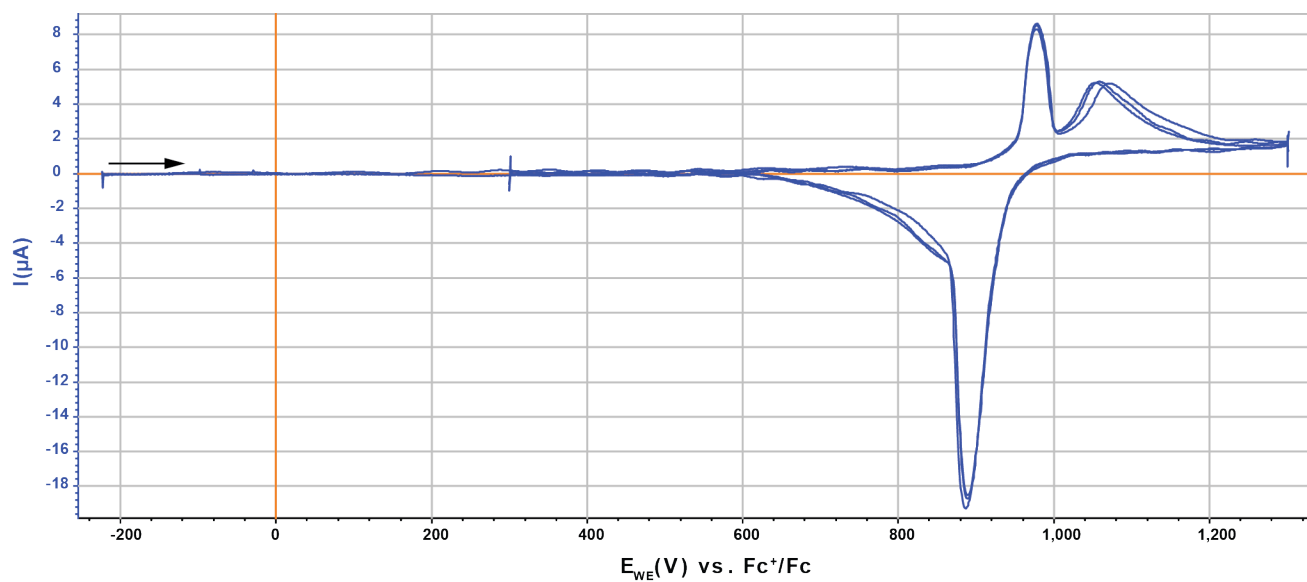


Figure S20: Cyclic voltammograms of **Pd(dppf)TPT** (0.30 mM). Shown are 3 cycles starting from E_{oc} at 10 mV/s in DCM (100 mM TBAPF₆).

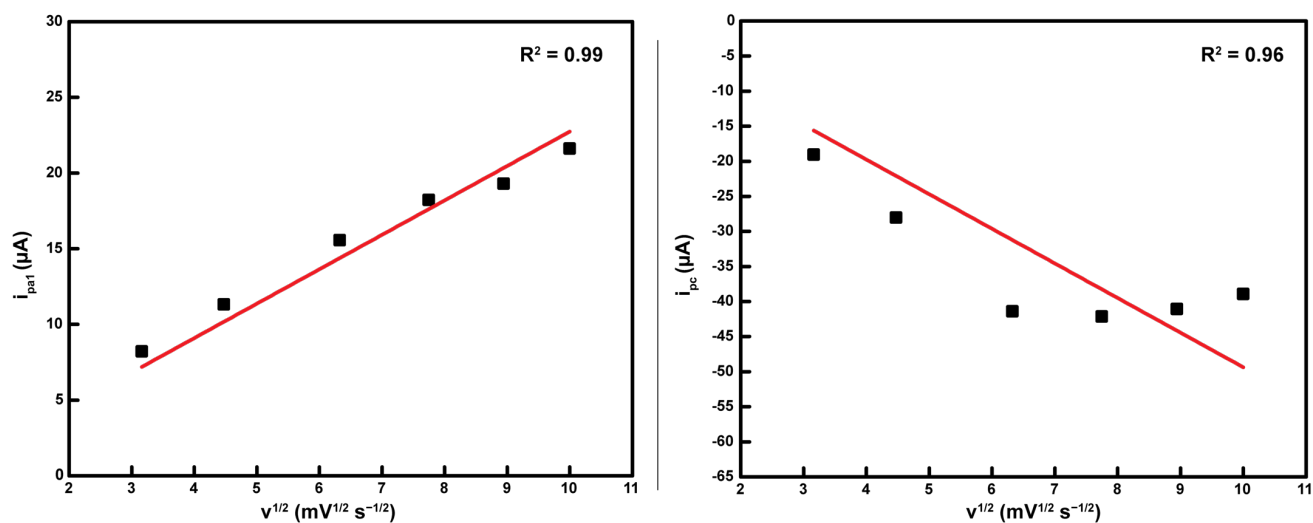


Figure S21: Relationship between peak current (i) and the square root of scan rate ($v^{1/2}$) from cyclic voltammograms of 0.30 mM **Pd(dppf)TPT** in DCM (100 mM TBAPF₆) for the first anodic peak (left) and the cathodic peak (right). Linear fits are shown in red.

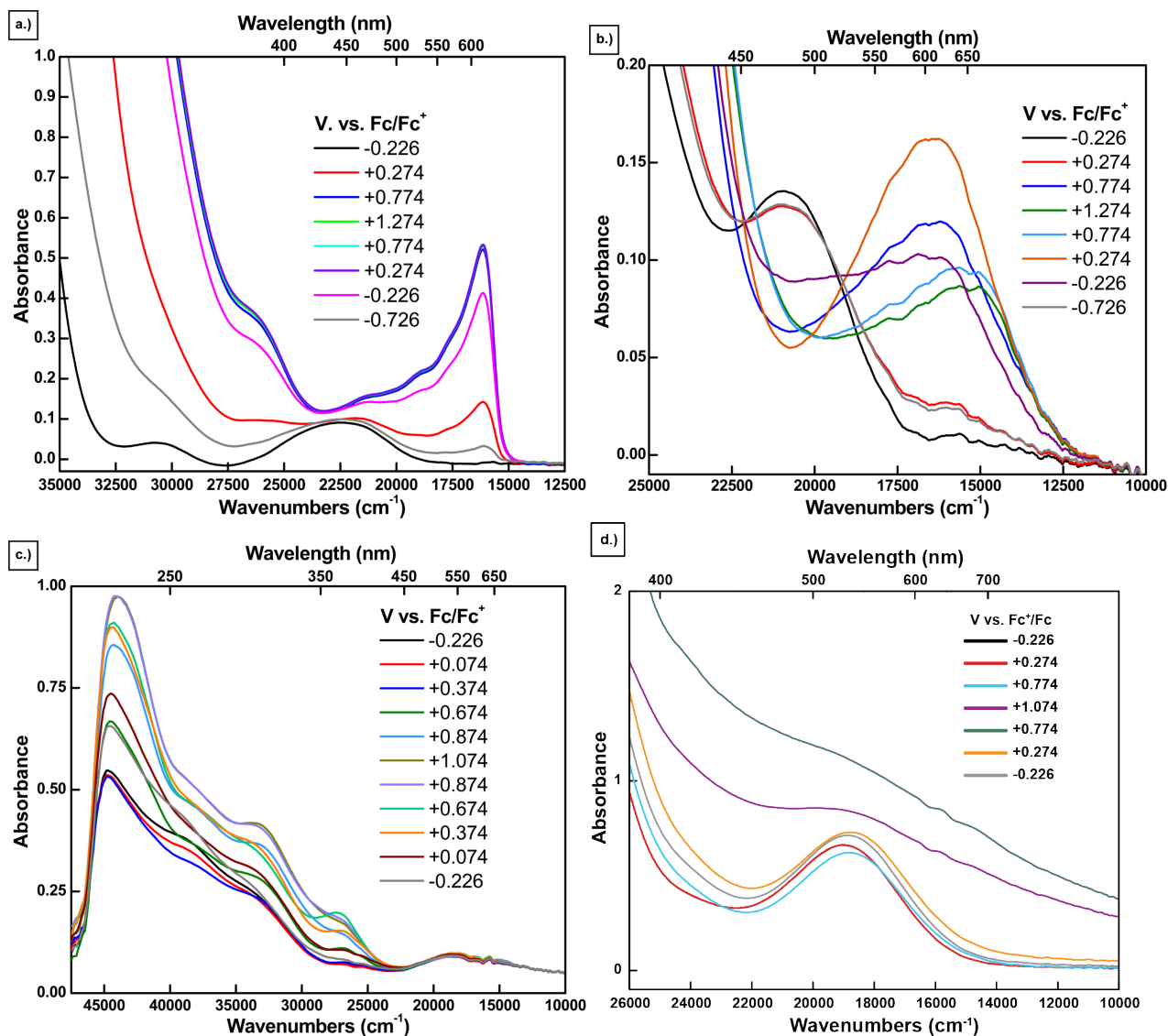


Figure S22: UV-Vis absorbance spectra acquired from spectroelectrochemical experiments probing the Fc-centered oxidation events of a.) **Fc** (1.8 mM), b.) **Pd(dppf)Cl₂** (1.8 mM), c.) **Pd(dppf)TPT** (0.04 mM), and d.) **Pd(dppf)TPT** (0.30 mM). All solutions were prepared in dry DCM (100 mM TBAPF₆).



Figure S23: Photographs of FTO working electrode used in diffuse reflectance spectroelectrochemical experiments. The FTO films shown are following: (1) the bulk oxidation and deposition of **Pd(dppf)TPT** (left), and (2) the subsequent bulk rereduction of the **Pd(dppf)TPT**-modified film (right).