

Electronic Supplementary Information for

**Iron Polypyridyl Complex Adsorbed on Carbon Surfaces for
Hydrogen Generation**

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Materials and Methods

Materials

All experiments were carried out using standard Schlenk techniques under an Ar atmosphere unless otherwise indicated. All reagents were purchased from Acros Organics, Alfa Aesar, Fisher Scientific, or TCL and were used without further purification unless otherwise noted. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) was recrystallized from absolute ethanol.

Instrumentation

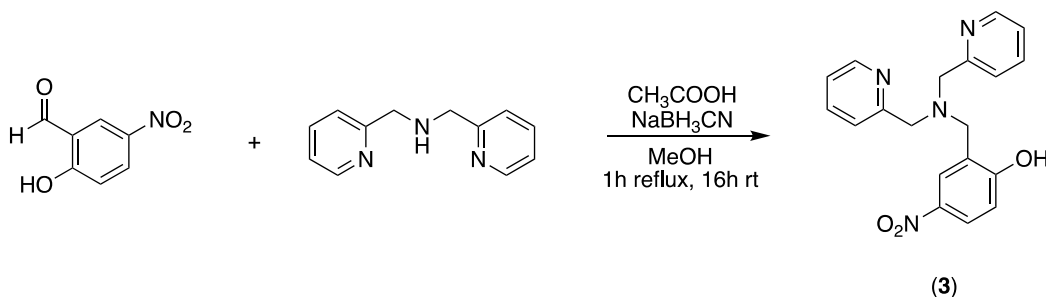
¹H and ¹³C NMR spectra were recorded on an Agilent 400MR DD2 spectrometer operating in the pulse Fourier transform mode. Chemical shifts are reported in ppm and referenced to residual solvent.

X-ray Diffraction

Data collection, structure solution, and structure refinement were conducted by William W. Brennessel at the University of Rochester's X-ray Crystallographic Facility. A single crystal was placed onto a thin glass optical fiber and mounted onto a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector. Data collection was carried out using a PhotonJet (Cu) X-ray source. The structure was solved using SHELXT and refined using SHELXL.

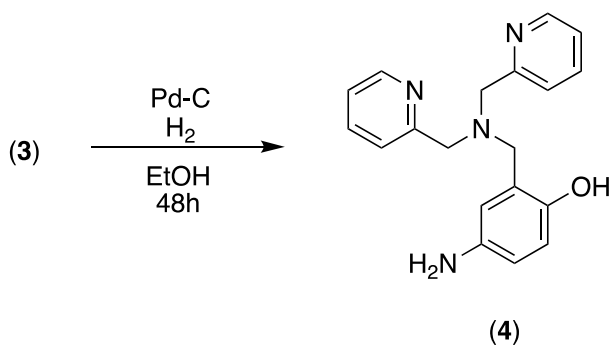
Reflection contributions from highly disordered solvent (likely dichloromethane) were fixed and added to the calculated structure factors using the SQUEEZE routine of program Platon,^{ref} which determined there to be 599 electrons in 1504 Å³ treated this way. Because the exact identity and amount of solvent were unknown, no solvent was included in the atom list or molecular formula. Thus all calculated quantities that derive from the molecular formula (e.g., F(000), density, molecular weight, etc.) are known to be inaccurate. [ref = Spek, A. L. *PLATON*, version 150216; *Acta. Crystallogr.* **2015**, *C71*, 9-18.]

Syntheses



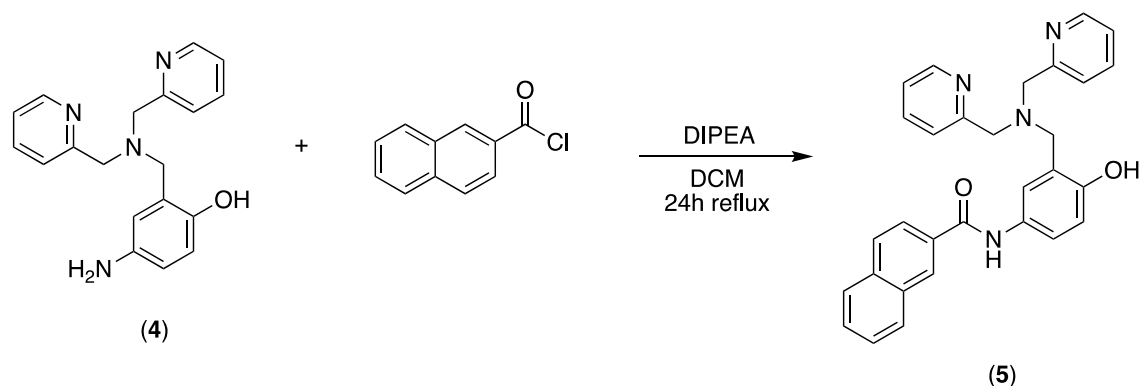
Scheme S1. Synthesis of **3**.

2-((bis(pyridin-2-ylmethyl)amino)methyl)-4-nitrophenol (3). This compound was synthesized using a modified literature procedure.¹ To a solution of 2-hydroxy-5-nitrobenzaldehyde (3.34 g, 20 mmol) in 100 mL of MeOH was added bis(pyridine-2-ylmethyl)amine (3.6 mL, 20 mmol). Glacial acetic acid (3 drops) was added followed by a solution of sodium cyanoborohydride (0.62 g, 10 mmol) in 30 mL of MeOH. After refluxing for 1 hour, the solution was stirred at room temperature overnight. 1 M HCl was added to the resulting solution until it reached pH = 4. The red solution was evaporated to dryness, dissolved in 100 mL of saturated Na₂CO₃, and extracted with chloroform (3 x 100 mL). The organic layers were combined, dried with Na₂SO₄, and filtered through celite. The solvent was removed under vacuum to yield a red oil, which was purified using silica gel chromatography with 9:1 dichloromethane:methanol to give 1.80 g of **1** (62% yield). ¹H NMR (CDCl₃): δ 8.58 (m, 2H), 8.12 (d, 1H), 8.05 (d, 1H), 7.66 (td, 2H), 7.30 (d, 2H), 7.21 (t, 2H), 6.95 (d, 1H), 3.93 (s, 4H), 3.85 (s, 2H). ¹³C NMR (CDCl₃): δ 164.27, 157.71, 148.69, 139.68, 137.06, 126.54, 125.61, 123.52, 123.08, 122.41, 117.17, 58.67, 56.10.



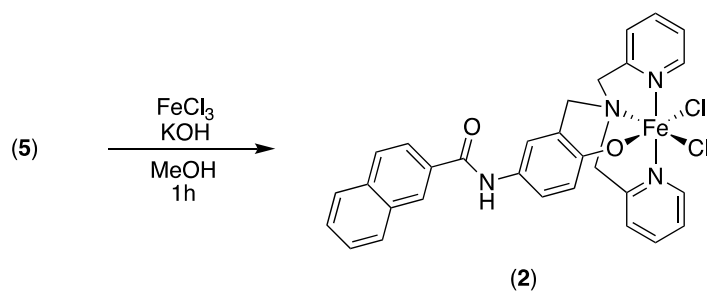
Scheme S2. Synthesis of **4**.

Synthesis of 4-amino-2-((bis(pyridin-2-ylmethyl)amino)methyl)phenol (4). Compound **4** was synthesized using a modified literature procedure.² To a solution of **3** (1 g, 2.86 mmol) in 180 mL EtOH, palladium on activated carbon (10% Pd) (0.1 g) was added. The reaction vessel was degassed, replenished with hydrogen gas, and allowed to stir at room temperature for 2 days. The brown solution was filtered through celite and evaporated to dryness to give 0.87 g of **4** (95 % yield). ¹H NMR (CDCl₃): 8.56 (m, 2H), 7.63 (td, 2H), 7.34 (d, 2H), 7.15 (m, 2H), 6.74 (d, 1H), 6.57 (dd, 1H), 6.48 (d, 1H), 3.85 (s, 4H), 3.71 (s, 2H).



Scheme S3. Synthesis of **5**.

Synthesis of *N*-(3-((bis(pyridin-2-ylmethyl)amino)methyl)-4-hydroxyphenyl)-2-naphthamide (5**).** Compound **5** was synthesized using a modified literature procedure.³ To a solution of **4** (0.80 g, 2.5 mmol) in 40 mL of DCM was added a solution of 2-naphthoyl chloride (0.48 g, 2.5 mmol) and DIPEA (0.44 mL, 2.5 mmol) dissolved in 20 mL DCM. The solution was refluxed for 24 hours before being diluted with 60 mL H₂O and extracted with DCM (3 x 60 mL). The organic layers were combined and washed with a saturated NaHCO₃ solution (3 x 60 mL). The organic layer was collected, dried with MgSO₄, and filtered. The volatiles were removed to yield a dark red oil, which was purified using silica gel chromatography with 9:1 dichloromethane:methanol to give 0.79 g of **5** (66% yield). ¹H NMR (CDCl₃): 8.57 (m, 2H), 8.36 (s, 1H), 7.90 (m, 5H), 7.64 (td, 2H), 7.57 (m, 3H), 7.36 (m, 3H), 7.15 (m, 2H), 6.94 (d, 1H), 3.90 (s, 4H), 3.82 (s, 2H). ¹³C NMR (CDCl₃): δ165.53, 158.14, 154.77, 148.86, 136.87, 134.76, 132.64, 132.37, 129.36, 128.94, 128.67, 127.79, 127.76, 127.35, 126.87, 123.58, 123.30, 123.06, 123.03, 122.28, 121.70, 116.90, 58.98, 56.80.



Scheme S4. Synthesis of **2**.

Synthesis of [FeCl₂(L-Nap)] (2**).** Compound **2** was synthesized using a modified literature procedure (Figure 2.3).⁴ To a solution of **5** (0.20 g, 0.42 mmol) and KOH (0.024 g, 0.42 mmol) in 10 mL MeOH was added a solution of FeCl₃•6H₂O (0.11 g, 0.42 mmol) in 8 mL MeOH. The solution immediately turned blue with a visible precipitate. The reaction mixture was stirred at room temperature for 1 hour and filtered. The solid was collected and washed with cold MeOH (3 x 10 mL) to give 0.18 g of **2** (72% yield). The product was crystallized by diffusion of toluene into a concentrated solution of **2** in DCM. Crystals suitable for X-ray diffraction were grown

using the same procedure but with the omission of KOH during the synthesis. Anal. Calcd for $C_{30}H_{25}C_{12}FeN_4O_2$: C, 60.02; H, 4.20; N, 9.33. Found: C, 59.93; H, 4.19; N, 9.31.

Preparation of Buffer Solutions

A citric acid/sodium phosphate buffer system was used for analyses. The buffers were prepared in batches of 20 mL using aqueous solutions of 0.1 M citric acid and 0.2 M Na_2HPO_4 .

Table S1. Preparation of Buffer Solutions.

pH	Citric Acid (0.1 M, mL)	Na_2HPO_4 (0.2 M, mL)
3.8	12.90	7.10
4.6	10.65	9.35
5.4	8.85	11.15
6.2	6.78	13.22

Cyclic Voltammetry General Procedure

All electrochemical experiments were performed under an atmosphere of Ar using a CH Instruments 620D potentiostat with a CH Instruments 680 Amp booster. Cyclic voltammograms were acquired using a standard three-electrode cell. A saturated calomel reference electrode (SCE) was used for all experiments. Prior to each acquisition, the platinum auxiliary electrode was polished using 0.05 μ m alumina powder paste on a cloth-covered polishing pad, followed by rinsing with water and acetonitrile. The glassy carbon working electrode (diameter = 0.30 cm) was polished in the same manner and was subsequently added to either the electrochemical cell or catalyst-soak solution depending on the experiment (specific details below). Ferrocene was used as an internal standard to correct for drifting of the reference electrode.

Scan Rate Dependence Study

A polished glassy carbon electrode was soaked overnight in a 0.5 mM solution of **2** in acetonitrile. The electrode was thoroughly rinsed with acetonitrile and added to an electrochemical cell containing 5 mL of 0.1 M TBAPF₆ in CH₃CN. Cyclic voltammograms were taken at a scan rate of 1000, 800, 600, 400, and 200 mV/s respectively.

Adsorption Time-Dependence Study

A polished glassy carbon electrode was soaked in a 0.5 mM solution of **2** in acetonitrile for time periods ranging from 1 – 1710 minutes. After soaking, the electrode was thoroughly rinsed with acetonitrile and added to an electrochemical cell containing 5 mL of 0.1 M TBAPF₆ in CH₃CN. Cyclic voltammograms were taken at a scan rate of 200 mV/s 5 minutes after adding the glassy carbon electrode to the cell.

Solvent-Stability Study

A polished glassy carbon electrode was soaked overnight in a 0.5 mM solution of **2** in acetonitrile. The electrode was thoroughly rinsed with acetonitrile followed by the solvent (CH₃CN, DCM, acetone, pentane, EtOH, or water) used in the subsequent soak. The electrode was suspended in 15 mL of a particular solvent (CH₃CN, DCM, acetone, pentane, EtOH, or water) for 30 minutes before being removed, rinsed with acetonitrile, and added to an electrochemical cell containing 5 mL of 0.1 M TBAPF₆ in CH₃CN. Cyclic voltammograms were taken at a scan rate of 200 mV/s 2 minutes after adding the glassy carbon electrode to the cell.

Catalyst Adsorption Control Study

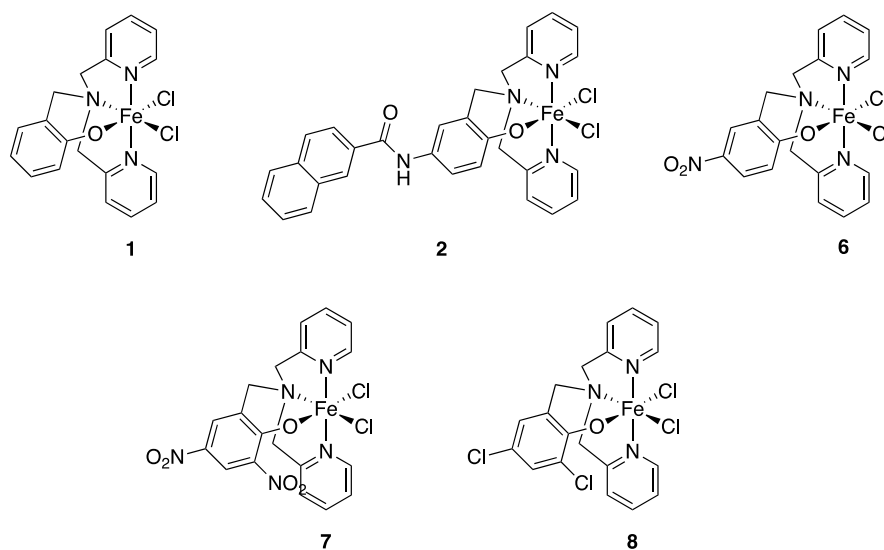


Figure S1. Structure of catalysts used in the adsorption control study.

Polished glassy carbon electrodes were soaked overnight in a 0.5 mM solution of either **1**, **2**, **6**, **7**, or **8** in acetonitrile. After soaking, the electrodes were thoroughly rinsed with acetonitrile and added to respective electrochemical cells containing 5 mL of 0.1 M TBAPF₆ in CH₃CN. Cyclic

voltammograms were taken at a scan rate of 200 mV/s 10 minutes after adding the glassy carbon electrode to the cell.

Acid Addition Studies

A polished glassy carbon electrode was soaked overnight in a 0.5 mM solution of **2** in acetonitrile. The electrode was rinsed with acetonitrile and added to an electrochemical cell containing 5 mL of 0.1 M TBAPF₆ in CH₃CN. Cyclic voltammograms, which were taken 10 minutes after addition of the working electrode, were taken without acid and after additions of 10, 20, 30, and 40 μL of either trifluoroacetic acid (0.2 M) or p-toluenesulfonic acid (0.2 M). The working electrode was polished and resoaked overnight in **2** before each scan.

pH Dependence Study

A polished glassy carbon electrode was soaked overnight in a 0.5 mM solution of **2** in acetonitrile. The electrode was rinsed with acetonitrile and water before it was added to an electrochemical cell containing 5 mL of an aqueous buffer solution (pH = 3.8 – 6.2), which served as the electrolyte. Cyclic voltammograms, which were run 2 minutes after addition of the electrode, were taken at 100 mV/s from 0.0 to -1.4 V for pH = 3.8 and from 0.0 to -1.6 V for pH = 4.6 – 6.2.

Supplementary Text

Determination of Overpotential

The overpotential in acetonitrile was calculated according to a literature procedure.⁵ E_{ref} for 1 mM TFA in CH₃CN, which is given in the literature to be -0.71 V vs. Fc⁺/Fc, can be subtracted from $E_{1/2}$ of **2** in the presence of 1 mM TFA, which is determined to be -1.19 V vs. Fc⁺/Fc as demonstrated in Fig S2.⁶ Therefore, the overpotential is calculated as such:

$$\begin{aligned} \text{Overpotential} &= |E_{1/2} - E_{ref}| \\ &= |(-1.19 \text{ V vs } Fc^+/Fc) - (-0.71 \text{ V vs } Fc^+/Fc)| \\ &= 480 \text{ mV} \end{aligned}$$

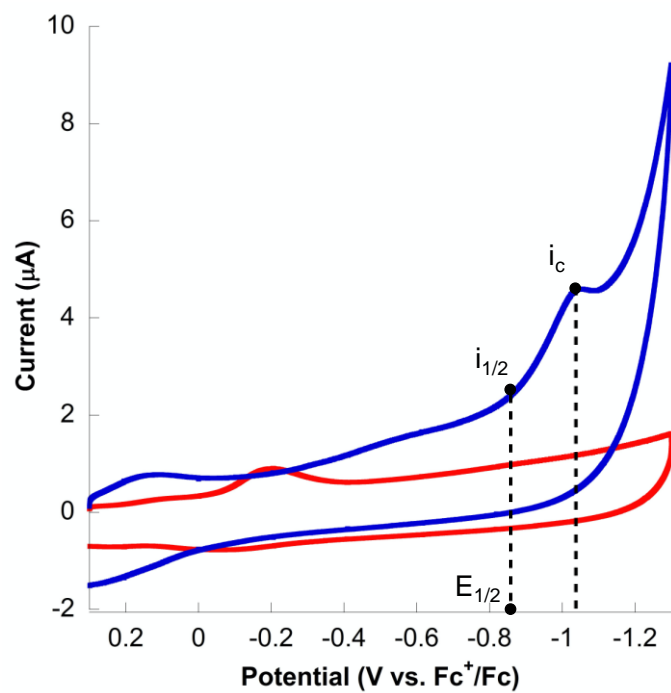


Figure S2. Cyclic voltammograms of surface-adsorbed **2** in 5 mL of 0.1 M TBAPF₆ in CH₃CN at 200 mV/s without acid (red) and in the presence of 1.6 mM TFA (blue) with i_c , $i_{1/2}$, and $E_{1/2}$ highlighted.

Calculation of i_c/i_p

The i_c and i_p values were found as demonstrated in Fig S3 and the i_c/i_p value was calculated as such:⁴

$$\frac{i_c}{i_p} = \frac{4.231}{0.774} = 5.46$$

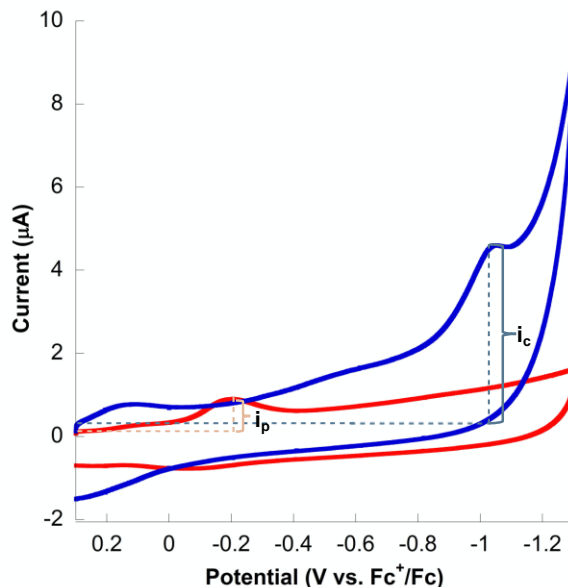


Figure S3. Cyclic voltammograms of surface-adsorbed **2** in 5 mL of 0.1 M TBAPF₆ in CH₃CN at 200 mV/s without acid (red) and in the presence of 1.6 mM TFA (blue) with i_c and i_p , highlighted.

Surface Coverage Calculation

Using the relationship between peak current and potential sweep rate for a surface-adsorbed analyte, the surface coverage of **2** on the glassy carbon electrode (0.30 cm diameter) at 298 K can be calculated as such:⁷

$$i_p = \frac{n^2 F^2}{4RT} v A \Gamma^*$$

$$i_p = \frac{1^2 * 96,485^2}{4 * 8.314 * 298} * v * 0.071 * \Gamma^* = (6.64 * 10^5) * v * \Gamma^*$$

$$\frac{i_p}{v} = slope = 5.09 * 10^{-6} = (6.64 * 10^5) * \Gamma^*$$

$$\Gamma^* = 7.7 * 10^{-11} \text{ mol/cm}^2$$

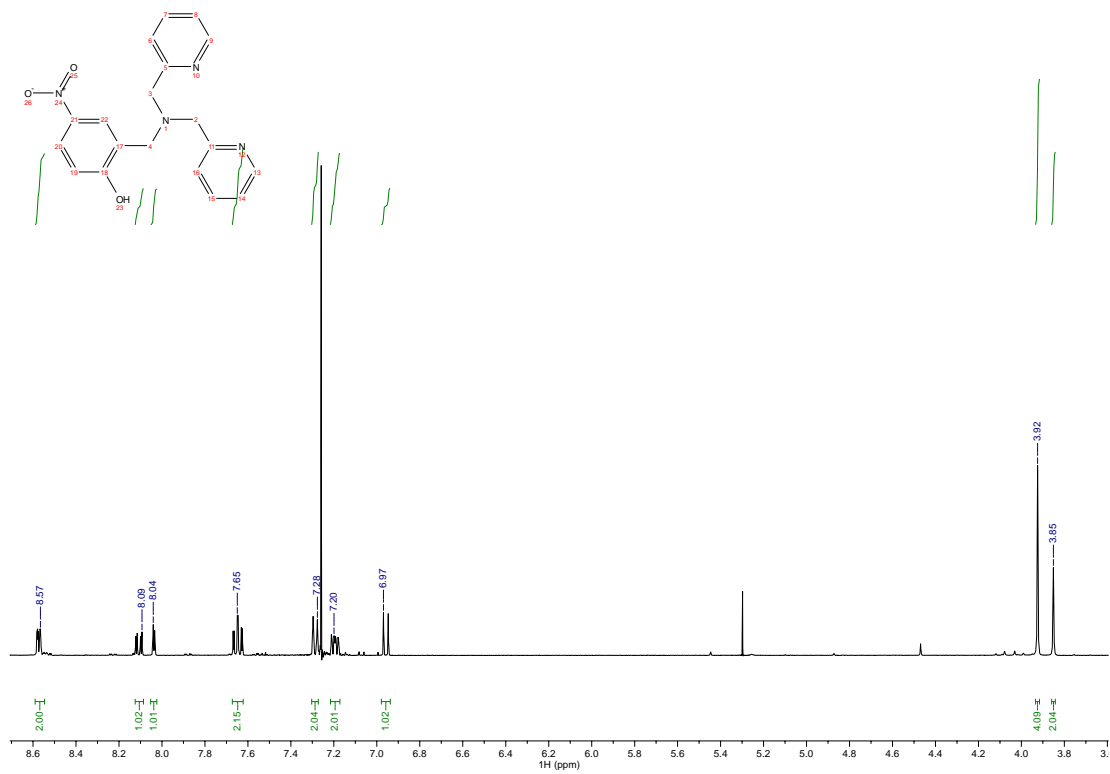


Figure S4. ¹H NMR spectrum of **3** with integrals in green.

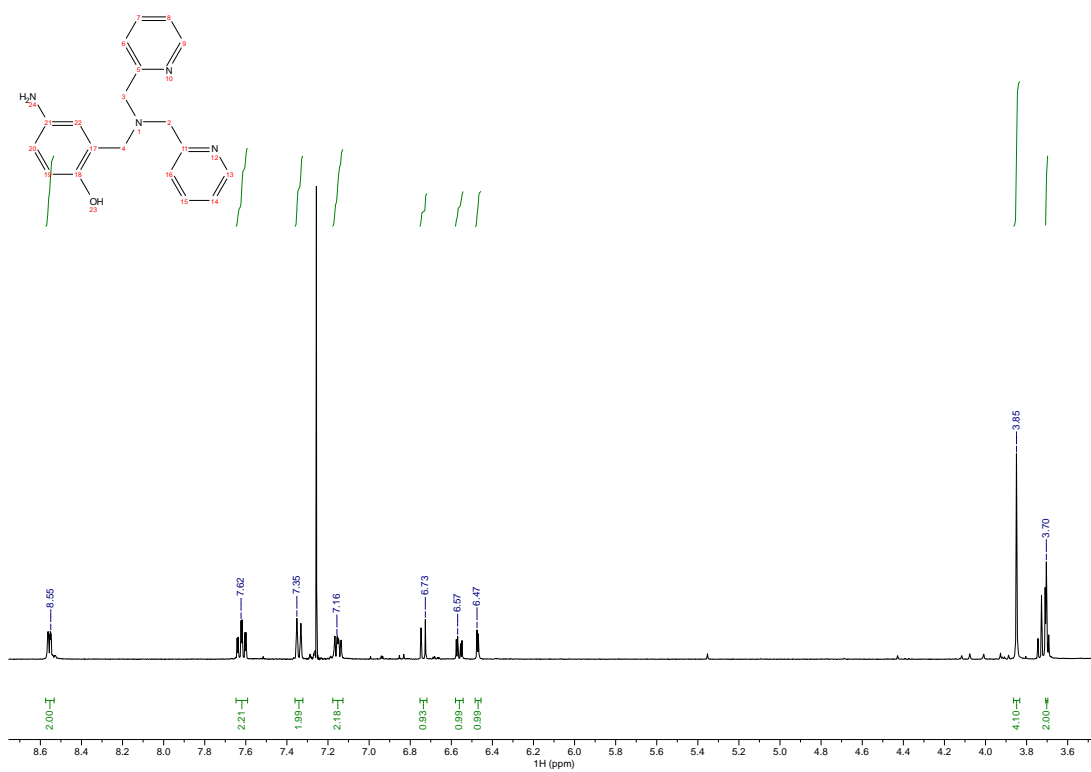


Figure S5. ¹H NMR spectrum of **4** with integrals in green.

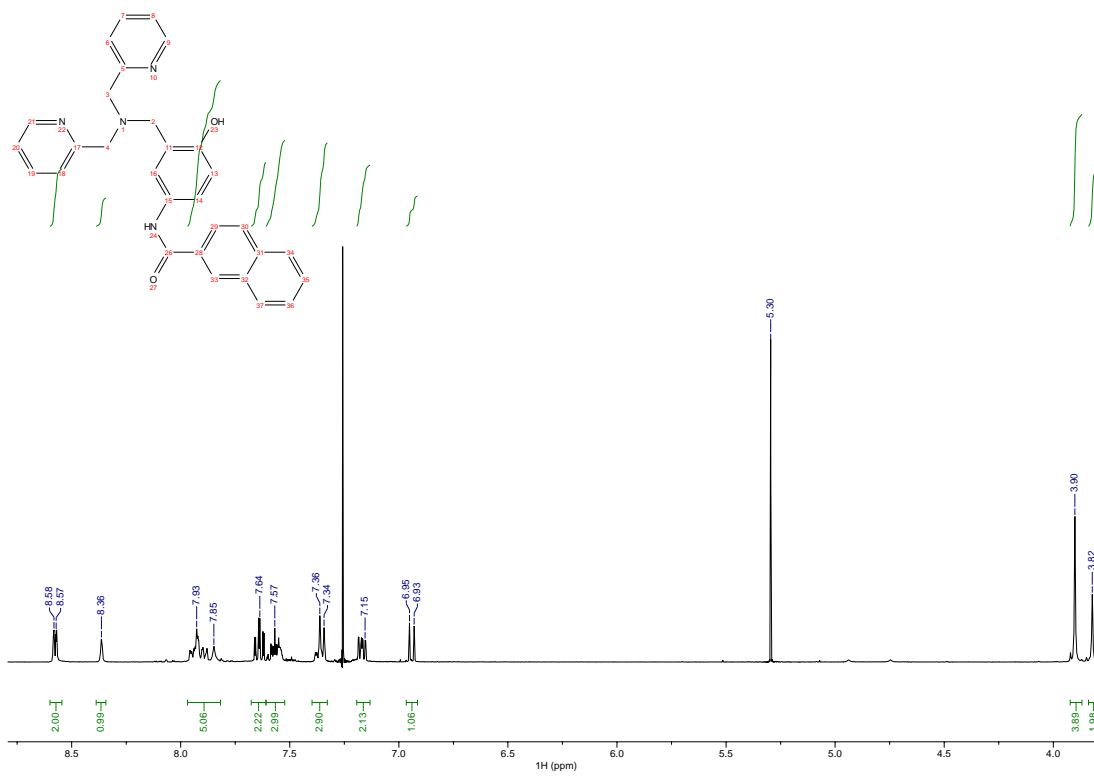


Figure S6. ¹H NMR spectrum of **5** with integrals in green.

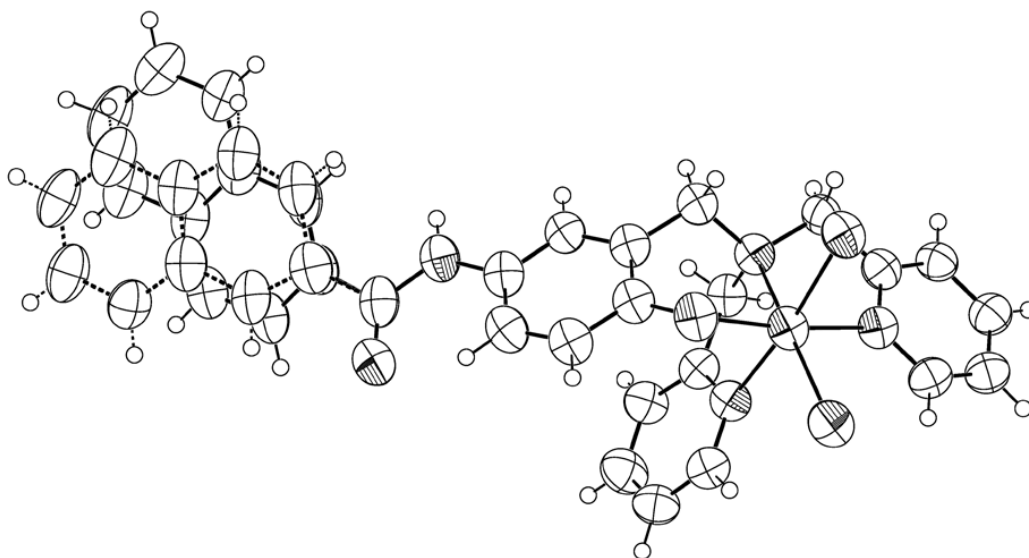


Figure S7. ORTEP diagram of **2** with disorder visible in the naphthalenyl group.

Table S2. Crystal data and structure refinement for **2**.

Empirical formula	C30 H25 Cl2 Fe N4 O2
Formula weight	600.29
Temperature	99.98(10) K
Wavelength	1.54184 Å
Crystal system	orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	$a = 11.4056(2)$ Å $b = 22.8180(4)$ Å $c = 25.3841(5)$ Å
Volume	$6606.3(2)$ Å ³
Z	8
Density (calculated)	1.207 Mg/m ³
Absorption coefficient	5.388 mm ⁻¹
<i>F</i> (000)	2472
Crystal color, morphology	blue, plate
Crystal size	0.19 x 0.102 x 0.028 mm ³
Theta range for data collection	3.482 to 78.003°
Index ranges	-14 ≤ <i>h</i> ≤ 13, -28 ≤ <i>k</i> ≤ 25, -30 ≤ <i>l</i> ≤ 32
Reflections collected	41178
Independent reflections	6941 [<i>R</i> (int) = 0.0590]
Observed reflections	5181
Completeness to theta = 74.504°	99.7%
Absorption correction	Multi-scan
Max. and min. transmission	1.00000 and 0.35954
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	6941 / 250 / 447
Goodness-of-fit on <i>F</i> ²	1.049
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0556, <i>wR</i> 2 = 0.1556
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0724, <i>wR</i> 2 = 0.1695
Largest diff. peak and hole	0.768 and -0.692 e.Å ⁻³

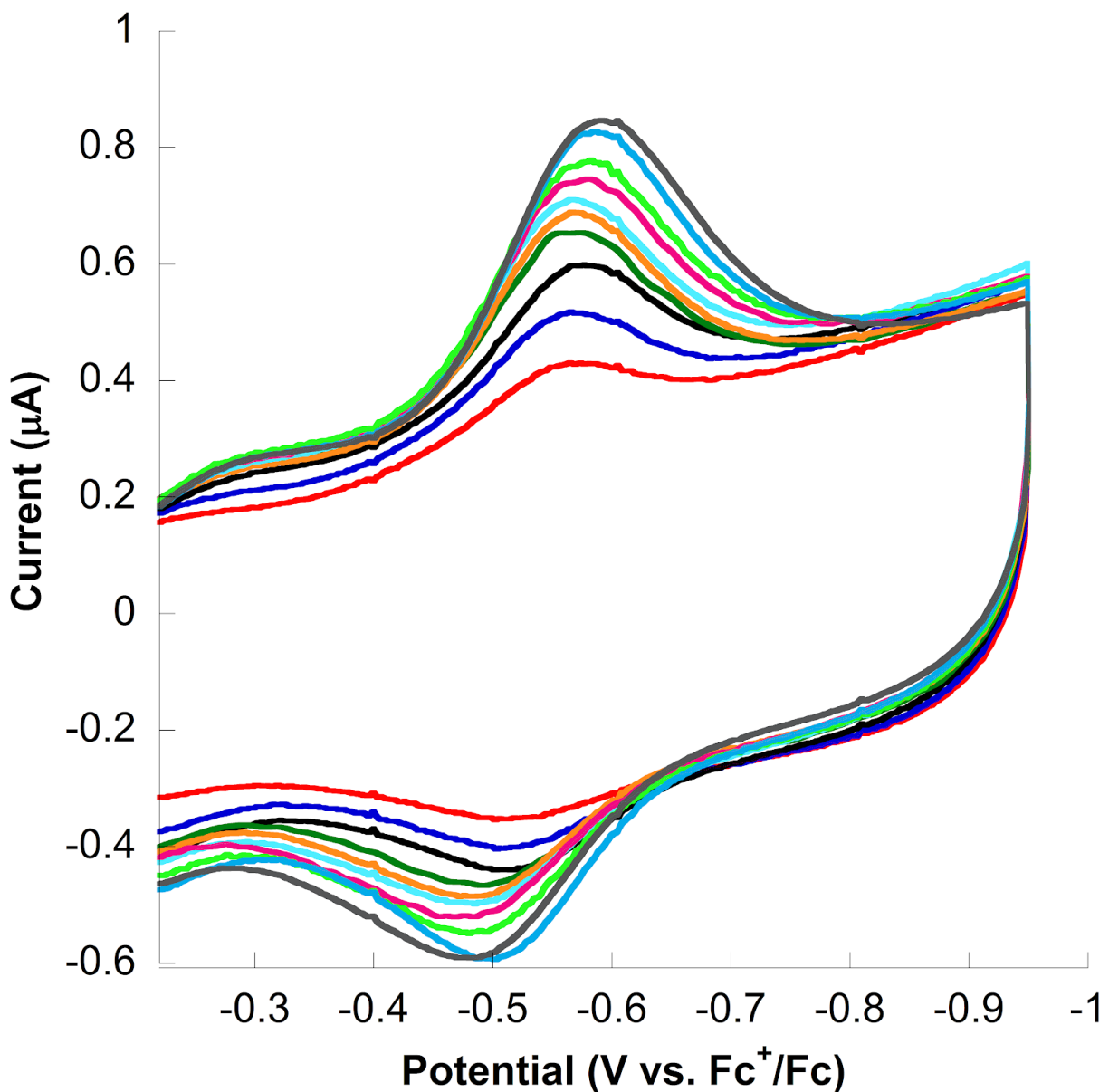


Figure S8. Adsorption time-dependence study: cyclic voltammograms, taken in 5 mL of 0.1 M TBAPF₆ in CH₃CN at 200 mV/s, for the time-dependent soak study of **2**. Time periods, in minutes, include 1 (red), 5 (blue), 10 (black), 20 (green), 30 (orange), 60 (cyan), 120 (magenta), 180 (light green), 360 (light blue), and 720 (grey).

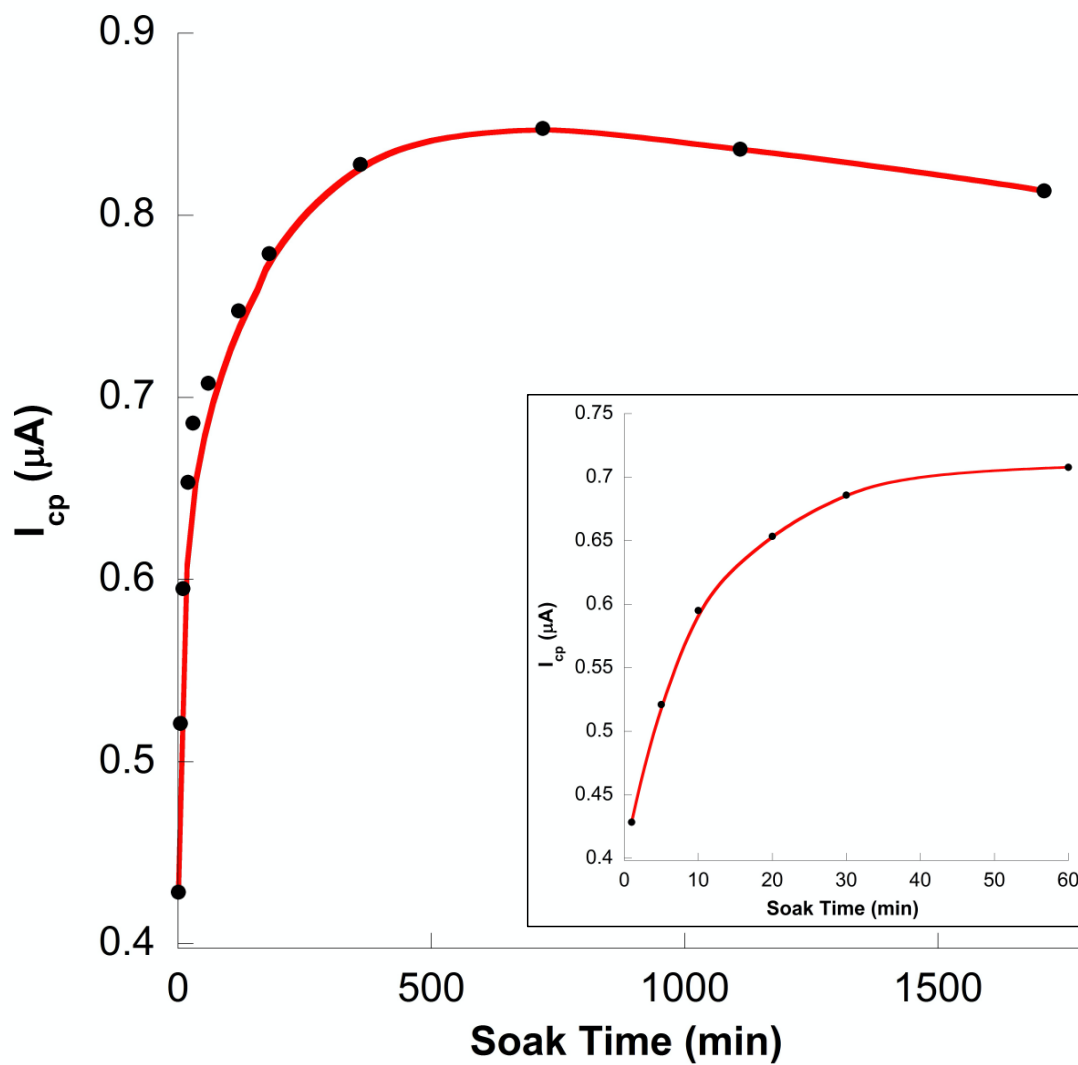


Figure S9. Adsorption time-dependence study: adsorption kinetics of **2** as a function of time. Inset plot highlights rapid adsorption during the first 60 minutes.

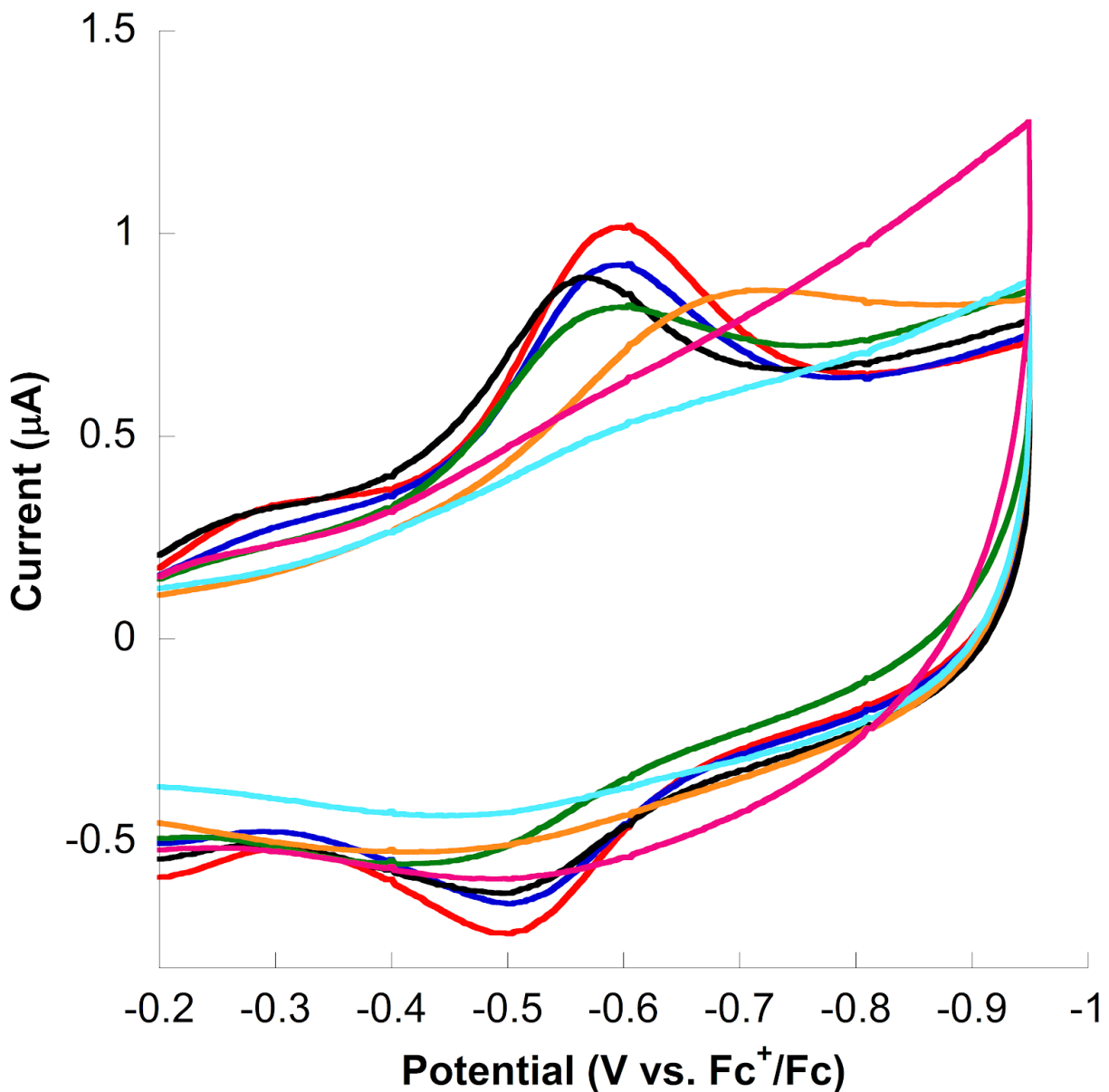


Figure S10. Solvent-stability study: impact of 30-minute solvent soaks on the adsorption of **2** to the surface of a glassy-carbon electrode. Cyclic voltammograms were scanned at 200 mV/s in 5 mL of 0.1 M TBAPF₆ in CH₃CN for the control (red) and after 30-minute electrode soaks in acetonitrile (blue), dichloromethane (black), pentane (green), acetone (orange), ethanol (cyan), and water (magenta).

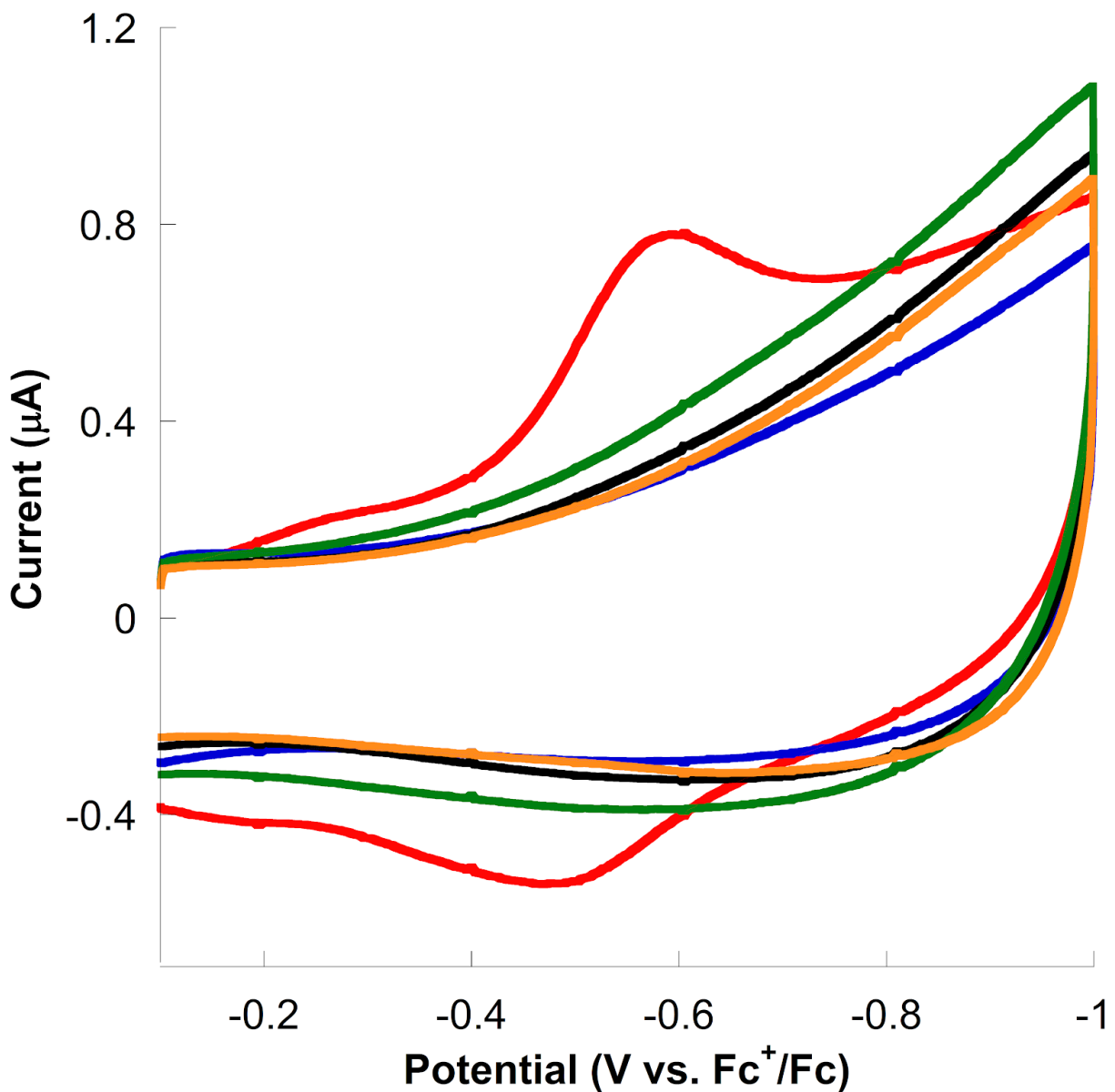


Figure S11. Catalyst adsorption control study: cyclic voltammograms were scanned at 200 mV/s in 5 mL of 0.1 M TBAPF₆ in CH₃CN following overnight soaking of the glassy carbon working electrode in **1** (blue), **2**, (red), **6** (black), **7** (green), and **8** (orange).

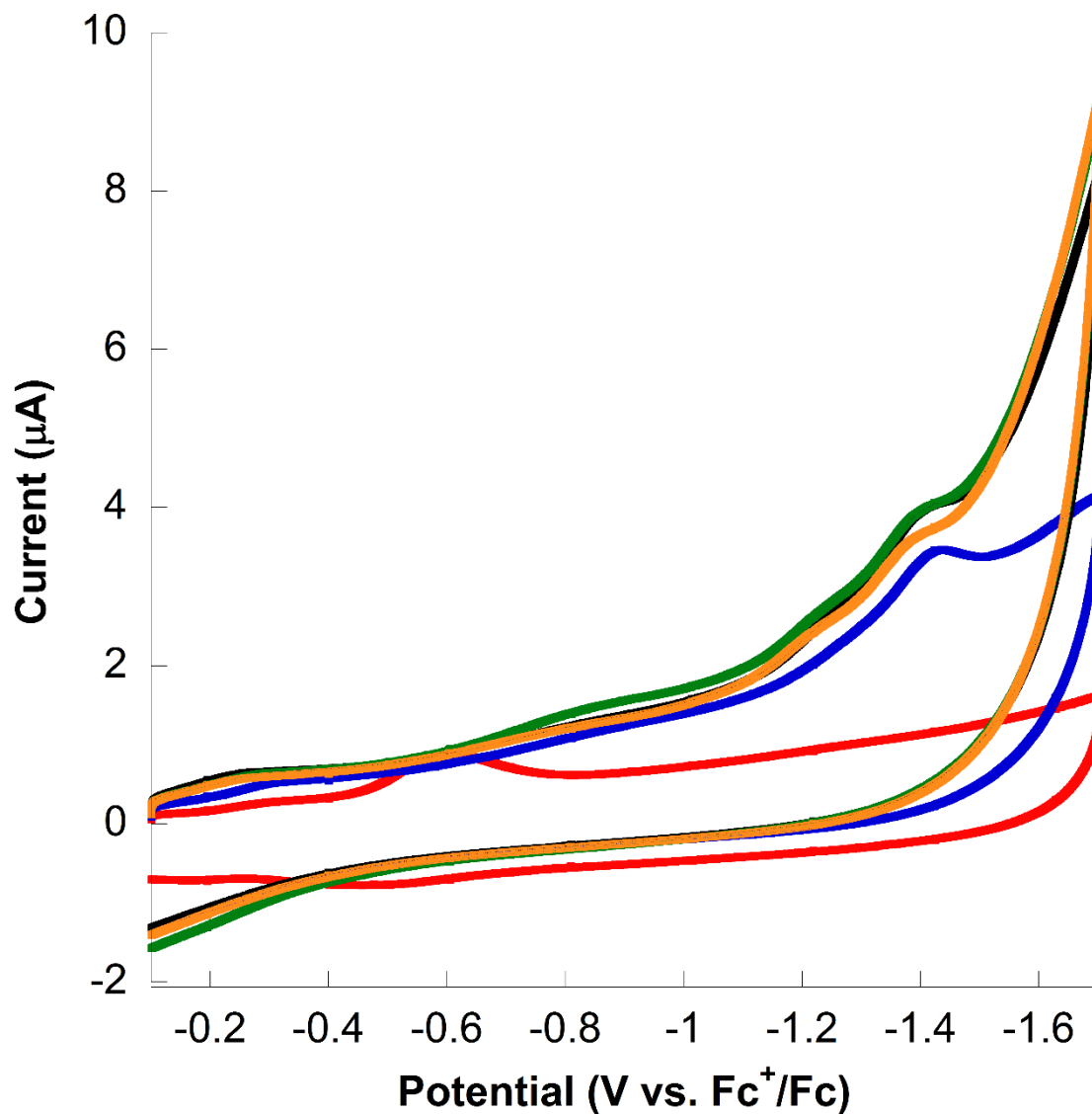


Figure S12. Cyclic voltammograms of surface adsorbed **2** in 5 mL of 0.1 M TBAPF₆ in CH₃CN in the presence of no acid (red), 0.4 mM (blue), 0.8 mM (black), 1.2 mM (green), and 1.6 mM (orange) tosic acid at 200 mV/s.

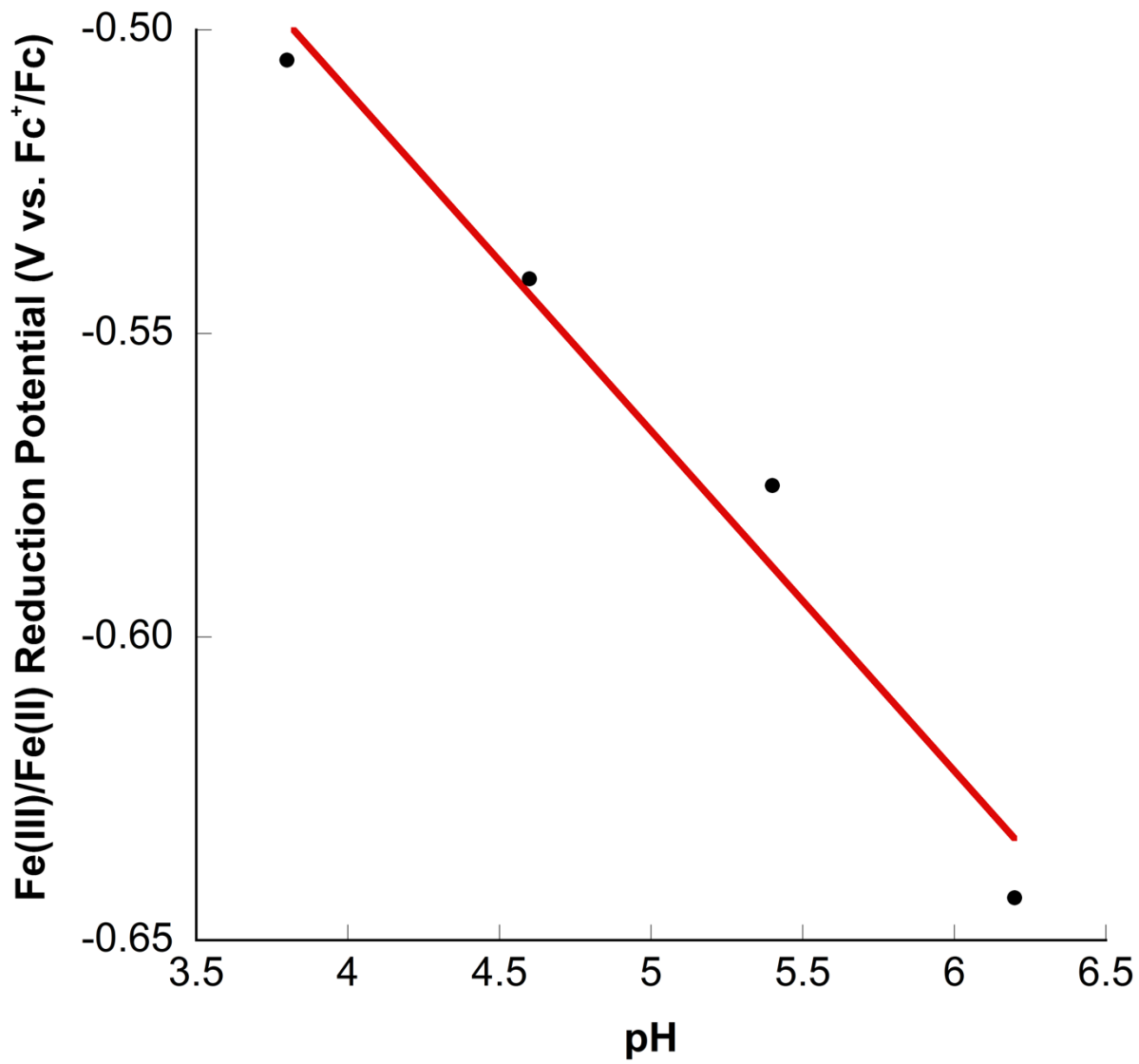


Figure S13. Linear relationship ($R^2 = 0.991$) between Fe(III)/Fe(II) reduction potential and pH with a slope of 52 mV.

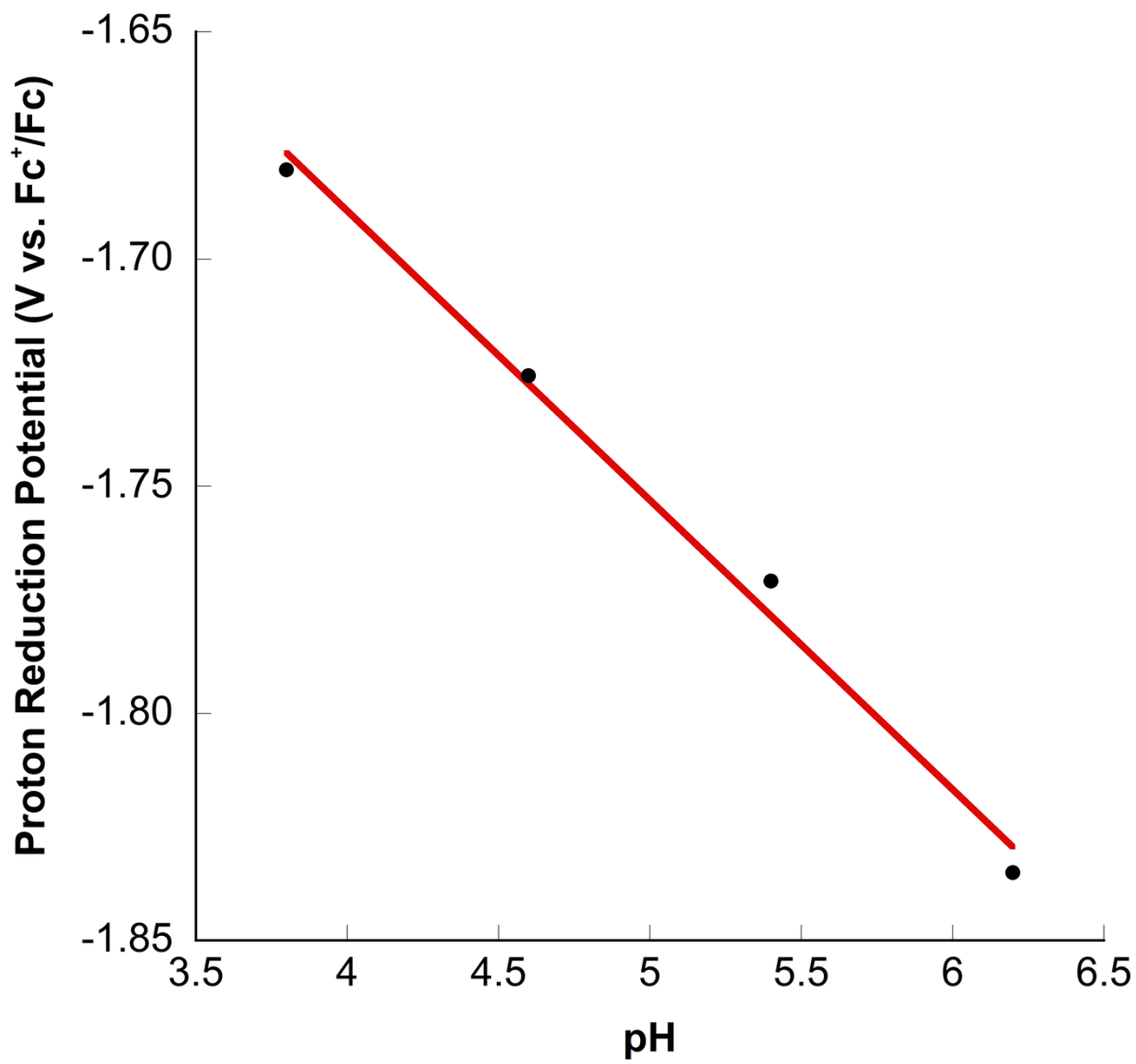


Figure S14. Linear relationship ($R^2 = 0.996$) between catalytic proton reduction wave potential and pH with a slope of 64 mV.

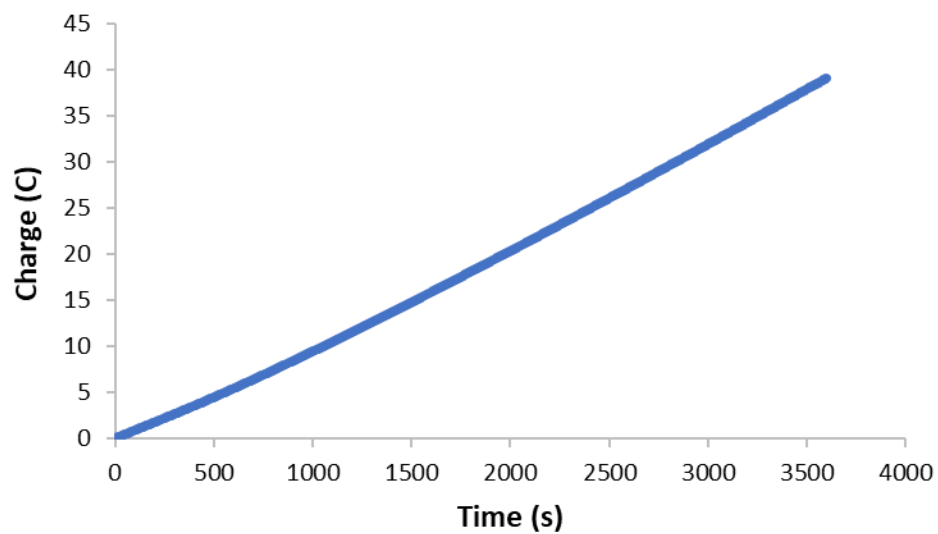


Figure S15. Bulk Electrolysis using glassy carbon electrode soaked in 0.5 mM **2** for 720 minutes. The bulk electrolysis was run in a 0.1 M solution of TBAPF₆ in CH₃CN with 65 mM TFA. The potential was held at -1.6 V vs. Fc⁺/Fc for 1800 seconds resulting in a charge of 39.1 C. A GC of the headspace gases corresponded to a faradaic yield of 99%.

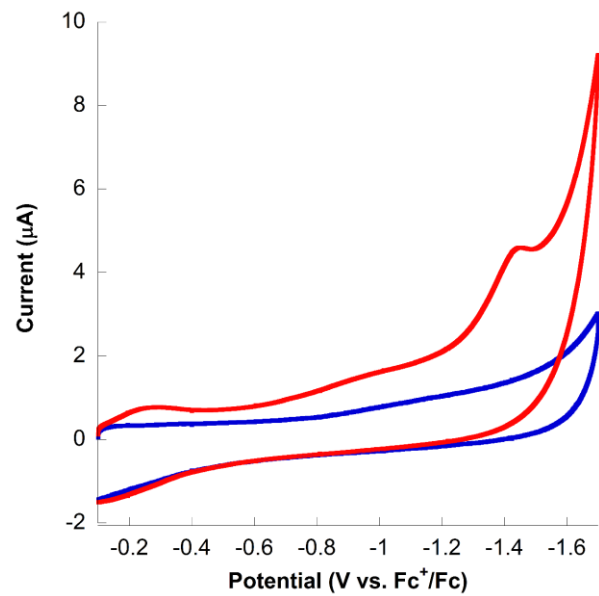


Figure S16. CVs of 1.6 mM TFA in CH₃CN for catalyst modified glassy carbon electrode (red) and a clean glassy carbon electrode without catalyst (blue).

References

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