Electronic Supplementary Information for PCCP

Supplementary Data

A photo- and electrochemical investigation of BODIPY-cobaloxime complexes for hydrogen production, coupled with quantum chemical calculations.

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1. Photocatalytic Hydrogen Turnover Number Experiment

1×10^{-4} M solutions of the catalysts/ photosensitisers were prepared in completely dry and deaerated THF. 1.2 mL of the catalyst/ photosensitiser solution, 0.2 mL (10%) H_2O and 0.6 mL (33%) TEA were added to a suitable gas tight vial and irradiated at various (350, 470 or > 470 nm) wavelengths for an average of 20 hours. Alternatively for the 0% water experiments 0.2 mL of THF was added to replace the water. For the photolysis reaction in THF, the septa capped deoxygenated photolysis reaction vial (5 mL full volume) containing 2 mL of the reaction solution was used. The solutions were photolysed using an LED light arrays. After 20 h photolysis time, the amount of hydrogen produced was measured by gas chromatography using gas tight syringe. Samples of the syringe (500 µL) were injected into a series CP-3800 Gas Chromatograph equipped with a 5 Å molecular sieves column and polymer supported silica column purchased from Varian Inc. (UK) using ultra-high purity nitrogen as the carrier gas. The signals were amplified with a Varian Star Workstation Chromatography Data system. The system was calibrated for hydrogen signal sensitivity by hydrogen standard measurements. The total amount of hydrogen produced in a photolysis experiment was obtained by the sum of hydrogen found in the gas phase (hydrogen found in the solution phase was assumed to be negligible).

Photocatalytic Hydrogen Turnover Number Calculations

- To calculate the concentration (in ppm) of hydrogen generated:

$$\frac{\text{Average Area of } H_2 \text{ Peak}}{\text{x ppm}} = \frac{\text{Area of standard } H_2 \text{ peak}}{\text{Conc. in ppm of } H_2 \text{ standard}}$$

- To calculate the number of moles of H_2 produced the ideal gas law is applied ($PV = nRT$):

- TON:

$$\frac{\text{No. moles of } H_2 \text{ produced}}{\text{No. moles catalyst used}}$$

2. Electrocatalytic Hydrogen Turnover Number (TON) Experiment

All electrocatalytic experiments were carried out in a 2 necked V-shaped electrochemical cell, using a glassy carbon working electrode with an area of 0.07cm^2, a platinum wire counter electrode and a Ag/AgCl reference electrode filled with 3 M KCl.

A 1x10^{-4} M solution of each sample was prepared in dimethylformamide (DMF). 1.5 µL of this sample was then drop cast on the surface of the glassy carbon electrode and allowed to dry overnight is complete darkness. The V-shaped cell was filled with 15 mL of 0.1 M NaH_2PO_4 buffer at pH 2.0. The sample coated glassy carbon electrode, along with the platinum wire counter and Ag/AgCl reference electrodes, were placed into the cell and the cell was sealed with a suba-seal in each neck. The buffer was degassed with BIP grade argon for 20 min prior to each experiment. Bulk electrolysis experiments were carried out -1.2 V vs. Ag/AgCl.

Electrocatalytic Hydrogen Turnover Number Calculations

- Electrochemical calculation of number of moles of H_2 produced:

After bulk electrolysis the current change (I_t) over the duration of the experiment can be measured. According to Faraday's laws of electrolysis:

$$n = \left(\frac{It}{F}\right)\left(\frac{1}{z}\right)$$

n = number of moles of H_2 produced.

F = Faraday's constant (96485 C mol^{-1}).

z = the valence number of ions of the substance (electrons transferred per ion).

- Electrochemically determined H_2 generation TON:

$$\text{TON} = \frac{\text{No. moles of } H_2 \text{ produced}}{\text{No. moles catalyst used}}$$

- GC determined H_2 generation TON:

As with the photocatalytic studies the GC was used to determine the electrocatalytic TON of H_2.

- **Determination of the Efficiency of the System:**

The efficiency of the system refers to the efficacy of the system to produce H_2 relative to the current passed during the experiment. This is measured by calculating the TON which has been determined using Faradays law of electrolysis, and comparing this result with the TON which has been calculated through injection of the headspace into the GC, measuring the actual number of moles of H_2 gas produced.

The efficiency =

$$\frac{\text{Electrochemically Determined TON}}{\text{GC Determined TON}} \times 100$$

- **Determination of Current Density:**

Current density is a measurement of the flow of current per unit area. During a bulk electrolysis experiment the average current throughout the experiment is measured. The area of the electrode surface has been measured to be 0.07 cm^2.

Therefore the current density =

$$\frac{\text{Average Current During Bulk Electrolysis (mA)}}{\text{Area of Electrode Surface } (cm^2)}$$

- **Electrocatalysis results.**

Complex	Onset of catalytic current (V)	Moles H_2 (echem)[a] (x 10^{-6})	TON (echem)[b] (x 10^3)	Moles H_2 (GC)[c] (x 10^{-6})	TON (GC)[d] (x 10^3)	Efficiency[e] %	Current Density ($mAcm^{-2}$)
1	-1.00	0.8	5.5	0.78	5.2	98	0.49
2	-0.95	0.9	5.8	0.83	5.5	95	0.81
1a	-0.80	3.3	22.0	2.48	16.5	75	1.51
2a	-0.90	2.7	18.3	1.62	10.8	59	1.46
Co-Ox	-0.98	0.24	15.7	12.0	8.0	51	2.18

Table 2. Results of electrocatalytic studies for all BODIPY-cobaloxime complexes. Bulk electrolysis experiments were carried out at -1.2 V vs. Ag/AgCl. All TON are quoted ± 30%. [a] number of moles of H_2 produced was determined from the charge produced over the length of the experiment, [b] electrochemically determined turnover number (TON), [c] number of moles of H_2 produced was determined using GC measurements, [d] GC determined TON, [e] efficiency refers to (GC determined TON/ electrochemically determined TON).

3. Quantum Chemical Calculations

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Tight Optimisation of BODIPYoxime B3LYP/6-311G(d)

Created by GaussView 3.09
 86 90  0  0  0  0  0  0  0  0  0    0
   -4.6930    1.2425    0.1364 N   0  0  0  0  0  0  0  0  0  0  0
0
   -3.2975    1.2164    0.1342 C   0  0  0  0  0  0  0  0  0  0  0
0
   -5.1023    2.5149    0.2773 C   0  0  0  0  0  0  0  0  0  0  0
0
   -2.8365    2.5672    0.2870 C   0  0  0  0  0  0  0  0  0  0  0
0
   -3.9737    3.3699    0.3781 C   0  0  0  0  0  0  0  0  0  0  0
0
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0
   -5.1221   -2.5060   -0.2794 C   0  0  0  0  0  0  0  0  0  0  0
0
   -3.3073   -1.2213   -0.1390 C   0  0  0  0  0  0  0  0  0  0  0
0
   -4.0003   -3.3695   -0.3815 C   0  0  0  0  0  0  0  0  0  0  0
0
   -2.8569   -2.5754   -0.2922 C   0  0  0  0  0  0  0  0  0  0  0
0
   -2.6226   -0.0051   -0.0028 C   0  0  0  0  0  0  0  0  0  0  0
0
   -1.1313   -0.0102   -0.0029 C   0  0  0  0  0  0  0  0  0  0  0
0
   -0.4039    0.1526   -1.1809 C   0  0  0  0  0  0  0  0  0  0  0
0
   -0.4052   -0.1759    1.1754 C   0  0  0  0  0  0  0  0  0  0  0
0
    0.9818    0.1454   -1.1394 C   0  0  0  0  0  0  0  0  0  0  0
0
   -0.9085    0.2860   -2.1304 H   0  0  0  0  0  0  0  0  0  0  0
0
    0.9804   -0.1692    1.1354 C   0  0  0  0  0  0  0  0  0  0  0
0
   -0.9110   -0.3083    2.1245 H   0  0  0  0  0  0  0  0  0  0  0
0
    1.5568    0.2794   -2.0429 H   0  0  0  0  0  0  0  0  0  0  0
0
    1.5546   -0.3023    2.0397 H   0  0  0  0  0  0  0  0  0  0  0
0
    1.6808   -0.0108   -0.0015 N   0  0  0  0  0  0  0  0  0  0  0
0
    3.7021    0.0041    0.0015 Co  0  0  0  0  0  0  0  0  0  0  0
0
    5.9666    0.0298    0.0056 Cl  0  0  0  0  0  0  0  0  0  0  0
0
    3.7728   -1.3430    1.3843 N   0  0  0  0  0  0  0  0  0  0  0
0
```

```
    3.7839   -1.1578   -1.5208 N   0  0  0  0  0  0  0  0  0  0  0
0
    3.7506    1.1665    1.5334 N   0  0  0  0  0  0  0  0  0  0  0
0
    3.7463    1.3526   -1.3915 N   0  0  0  0  0  0  0  0  0  0  0
0
    3.9252   -0.8761    2.6050 C   0  0  0  0  0  0  0  0  0  0  0
0
    3.9356    0.5826    2.6767 C   0  0  0  0  0  0  0  0  0  0  0
0
    4.1500    1.3356    3.9516 C   0  0  0  0  0  0  0  0  0  0  0
0
    3.3310    1.1632    4.6570 H   0  0  0  0  0  0  0  0  0  0  0
0
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0
    4.2196    2.4019    3.7526 H   0  0  0  0  0  0  0  0  0  0  0
0
    4.1019   -1.8058    3.7625 C   0  0  0  0  0  0  0  0  0  0  0
0
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0
    3.3498   -2.5981    3.7295 H   0  0  0  0  0  0  0  0  0  0  0
0
    5.0759   -2.3033    3.7046 H   0  0  0  0  0  0  0  0  0  0  0
0
    3.7239    2.5221    1.4685 O   0  0  0  0  0  0  0  0  0  0  0
0
    3.7100    2.7162    0.4766 H   0  0  0  0  0  0  0  0  0  0  0
0
    3.7234   -2.5993    1.1360 O   0  0  0  0  0  0  0  0  0  0  0
0
    3.9598   -0.5773   -2.6665 C   0  0  0  0  0  0  0  0  0  0  0
0
    3.9197    0.8812   -2.6099 C   0  0  0  0  0  0  0  0  0  0  0
0
    4.2064   -1.3670   -3.9122 C   0  0  0  0  0  0  0  0  0  0  0
0
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0
    4.2169   -0.7351   -4.7987 H   0  0  0  0  0  0  0  0  0  0  0
0
    5.1701   -1.8790   -3.8326 H   0  0  0  0  0  0  0  0  0  0  0
0
    4.0840    1.7791   -3.7953 C   0  0  0  0  0  0  0  0  0  0  0
0
    3.3066    1.6202   -4.5503 H   0  0  0  0  0  0  0  0  0  0  0
0
    4.0322    2.8129   -3.4589 H   0  0  0  0  0  0  0  0  0  0  0
0
    5.0521    1.6230   -4.2813 H   0  0  0  0  0  0  0  0  0  0  0
0
    3.8191   -2.5133   -1.4676 O   0  0  0  0  0  0  0  0  0  0  0
0
    3.7887   -2.7175   -0.4785 H   0  0  0  0  0  0  0  0  0  0  0
0
```

```
    3.6493    2.6036   -1.1306 O   0  0  0  0  0  0  0  0  0  0  0
0
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0
   -7.0493   -2.5990    0.6387 H   0  0  0  0  0  0  0  0  0  0  0
0
   -7.0903   -2.2949   -1.0852 H   0  0  0  0  0  0  0  0  0  0  0
0
   -6.7146   -3.9254   -0.4897 H   0  0  0  0  0  0  0  0  0  0  0
0
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0
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0
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0
   -1.4396   -4.1646   -0.5265 H   0  0  0  0  0  0  0  0  0  0  0
0
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0
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0
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0
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0
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0
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0
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0
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0
   -4.0689   -4.8651   -0.5288 C   0  0  0  0  0  0  0  0  0  0  0
0
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0
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0
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0
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0
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0
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   -4.1654   -6.6969    0.6574 H   0  0  0  0  0  0  0  0  0  0  0
0
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0
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0
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0
   -6.4290   -0.1196    1.1394 F   0  0  0  0  0  0  0  0  0  0  0
0
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  1  3  4  0  0  0  0
  1 84  1  0  0  0  0
  2  4  4  0  0  0  0
  2 11  4  0  0  0  0
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  5 73  1  0  0  0  0
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  6 84  1  0  0  0  0
  7  9  4  0  0  0  0
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  8 11  4  0  0  0  0
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 22 27  1  0  0  0  0
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 26 38  1  0  0  0  0
 27 42  2  0  0  0  0
 27 53  1  0  0  0  0
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66	67	1	0	0	0	0
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70	71	1	0	0	0	0
70	72	1	0	0	0	0
70	76	1	0	0	0	0
73	74	1	0	0	0	0
73	75	1	0	0	0	0
73	80	1	0	0	0	0
76	77	1	0	0	0	0
76	78	1	0	0	0	0
76	79	1	0	0	0	0
80	81	1	0	0	0	0
80	82	1	0	0	0	0
80	83	1	0	0	0	0
84	85	1	0	0	0	0
84	86	1	0	0	0	0

Functional	Basis set	Diffuse (Y/N)	Solvent	Multiplicity	Energy (Hartrees)	1st λ_{max} (nm)	CPU time (min)
B3LYP	6-31G*	N	None	Singlet	-3918.98081199	448.17	470
B3LYP	6-31+G*	Y	None	Singlet	-3919.07628506	445.64	2665
B3LYP	6-31G*	N	DCM	Singlet	-3919.00533678	449.49	569
B3LYP	Tzvp	N	DCM	Singlet	-3919.92273536	453.89	2237
BP86	6-31G*	N	None	Singlet	-3919.24619333		
BP86	6-31G*	N	None	Triplet	-3919.21575923		
B3LYP	6-311G*	N	None	Singlet	-3919.58493699	440.70	
B3LYP	6-311G*	N	None	Triplet	-3919.54497815		
B3LYP	6-311G*	N	None	Quintet	-3919.51516374		

Table 3 Selected results of various calculations investigating the effect of functional choice, Basis set, solvent and multiplicity.

4. Cyclic Voltammetry

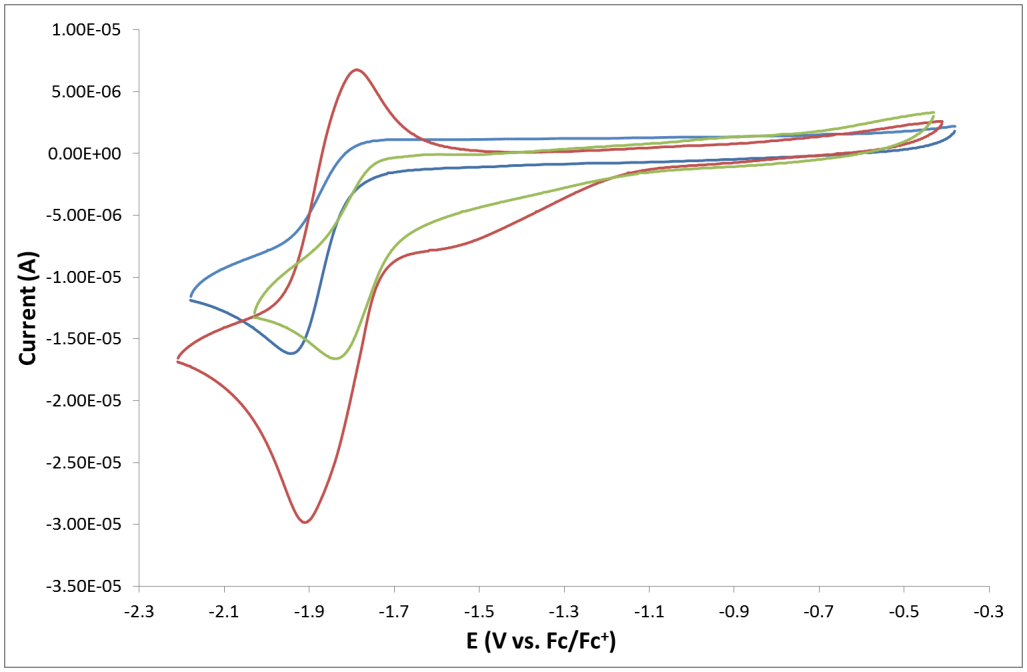

Figure S1. Cyclic voltammogram of **1** (blue line), **1a** (red line), and cobaloxime (green line) in 0.1 M $TBAPF_6$/ DCM illustrating their reduction processes. Scan rate 0.1 $Vsec^{-1}$.

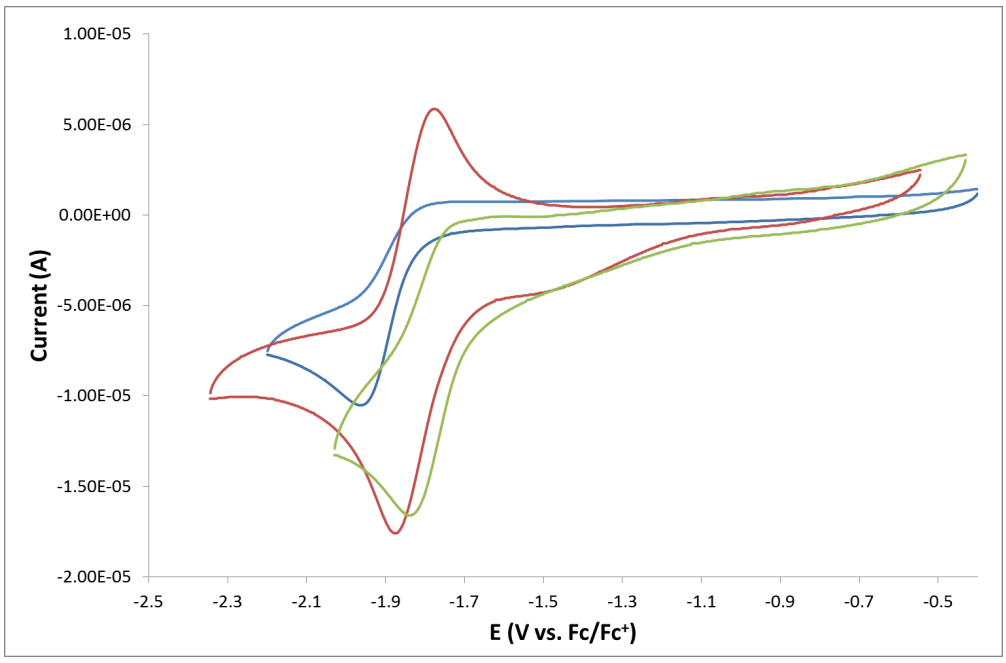

Figure S2. Cyclic voltammogram of **2** (blue line), **2a** (red line), and cobaloxime (green line) in 0.1 M $TBAPF_6$/ DCM illustrating their reduction processes. Scan rate 0.1 $Vsec^{-1}$.

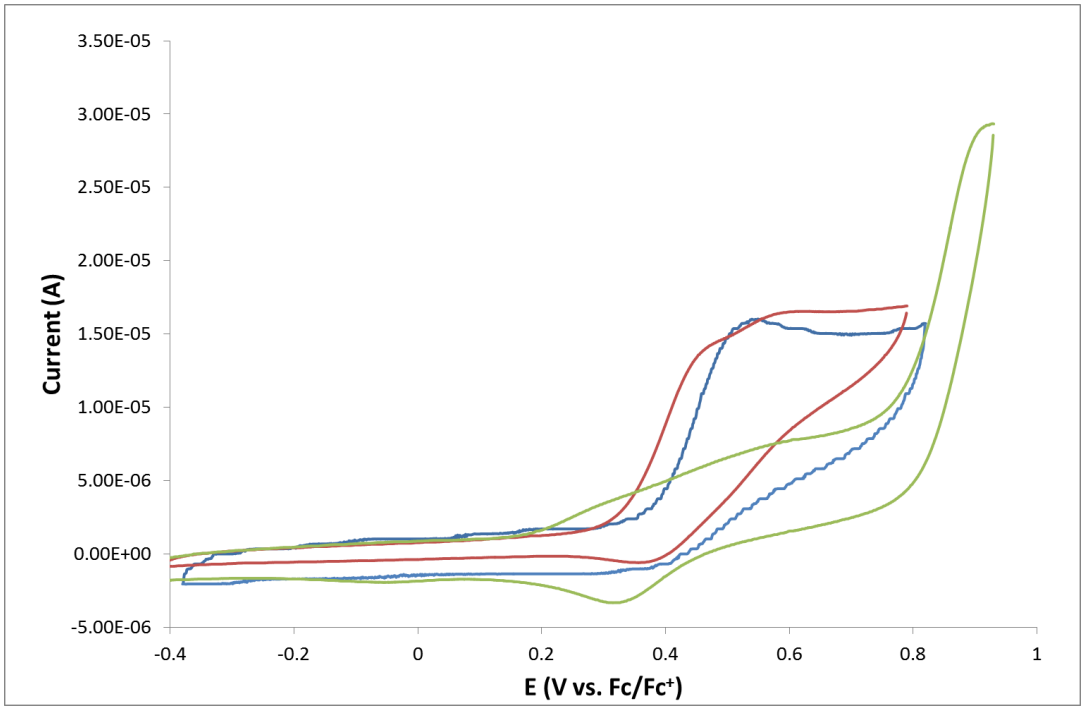

Figure S3. Cyclic voltammogram of **1** (blue line), **1a** (red line), and cobaloxime (green line) in 0.1 M $TBAPF_6$/ DCM illustrating their oxidation processes. Scan rate 0.1 $Vsec^{-1}$. Scans to more positive potentials lead to fouling of the electrode and therefore are not shown.

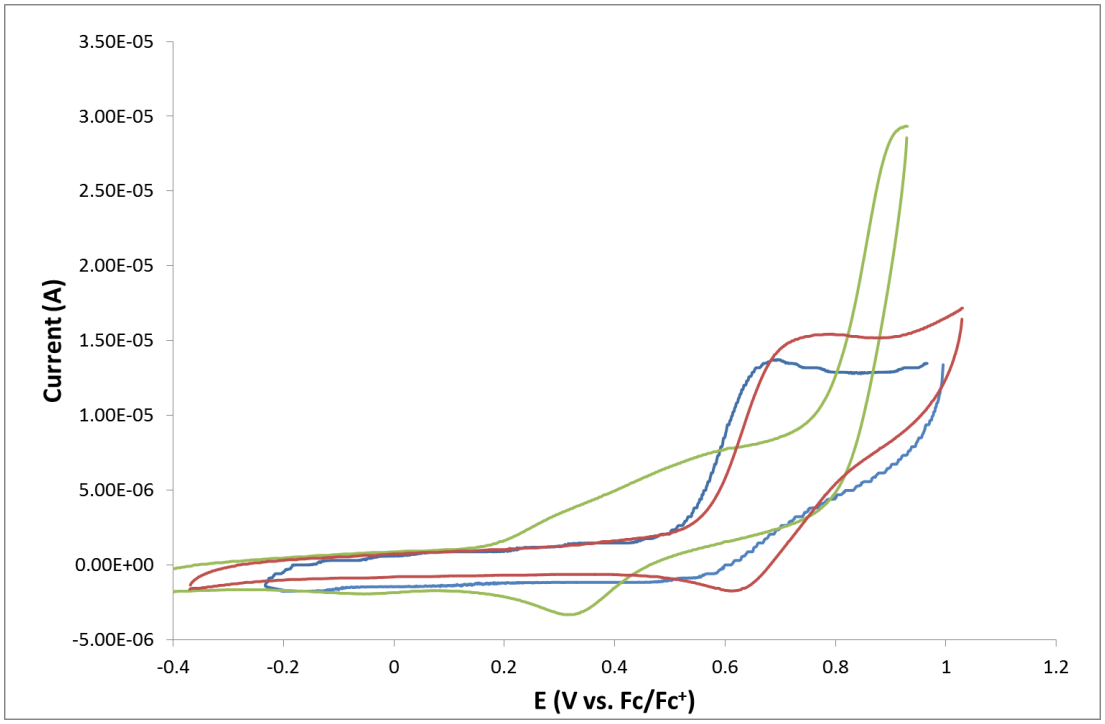

Figure S4. Cyclic voltammogram of **2** (blue line), **2a** (red line), and cobaloxime (green line) in 0.1 M $TBAPF_6$/ DCM illustrating their oxidation processes. Scan rate 0.1 $Vsec^{-1}$. Scans to more positive potentials lead to fouling of the electrode and therefore are not shown.