Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for

A Nickel Complex of a Conjugated Bis-dithiocarbazate Schiff Base for the Photocatalytic Production of Hydrogen

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Tables

Text

Table S1. Selected bond lengths [Å] and angles [°] for **2**.

Ni(1)-S(2)	2.2222(9)
Ni(1)-S(3)	2.1358(9)
Ni(1)-N(1)	1.907(2)
Ni(1)-N(3)	1.910(2)
N(1)-N(2)	1.381(3)
N(1)-C(8)	1.314(4)
N(2)-C(9)	1.293(3)
N(3)-N(4)	1.401(3)
N(3)-C(15)	1.293(4)
N(4)-C(17)	1.307(3)
C(9)-C(14)	1.510(4)
C(14)-C(15)	1.512(4)
S(2)-Ni(1)-S(3)	96.31(3)
S(2)-Ni(1)-N(1)	73.61(8)
S(2)-Ni(1)-N(3)	174.25(7)
S(3)-Ni(1)-N(1)	163.09(8)
S(3)-Ni(1)-N(3)	88.30(7)
N(1)-Ni(1)-N(3)	102.7(1)
Ni(1)-S(2)-C(8)	76.16(9)
Ni(1)-S(3)-C(17)	94.75(9)
Ni(1)-N(1)-N(2)	135.4(2)
Ni(1)-N(1)-C(8)	98.2(2)
N(1)-N(2)-C(9)	113.8(2)
Ni(1)-N(3)-N(4)	119.7(2)
Ni(1)-N(3)-C(15)	124.1(2)
N(3)-N(4)-C(17)	111.2(2)
S(2)-C(8)-N(1)	109.0(2)
N(2)-C(9)-C(14)	122.2(2)
N(3)-C(15)-C(14)	121.4(2)
S(3)-C(17)-N(4)	125.6(2)

Table S2. Selected X-ray Crystallography Data for **2**.

Empirical formula	$C_{24}H_{19}F_3N_4NiS_5$
fw (g/mol)	639.44
color/habit	Brown block
T (K)	100(2) K
Space group	$Pna2_1$
Z	12
a (Å)	8.8108(3)
b (Å)	31.9395(9)
c (Å)	27.7375(8)
α (deg)	90
β (deg)	90
γ (deg)	90
V ($Å^3$)	7805.7(4)
Final R indices (I>2σ)	0.0218, 0.0547
Final R indices (all data)	0.0224, 0.0550
GOF	1.051
No. reflections measured	81886
No. of independent reflections	13604
R_{int}	0.0524

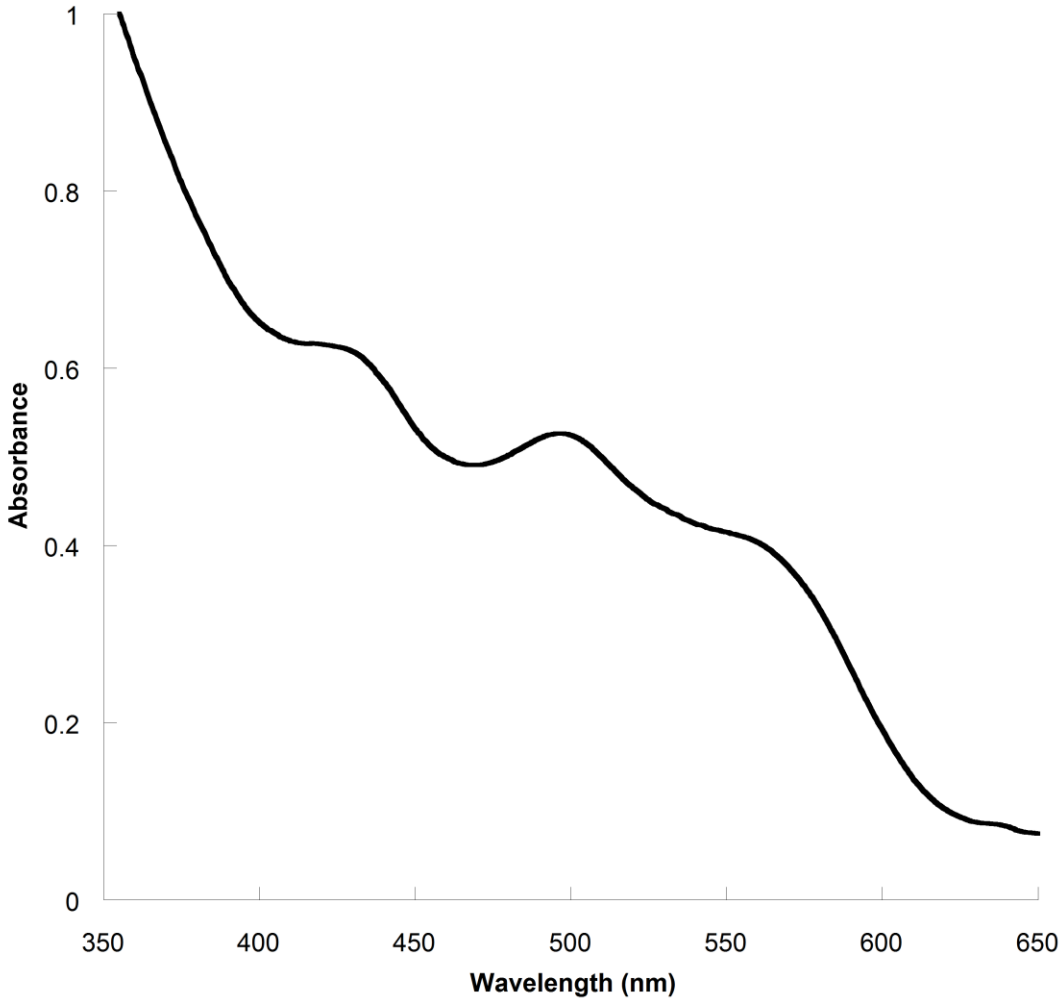

Figure S1. UV-Vis spectrum of **2** in dichloromethane.

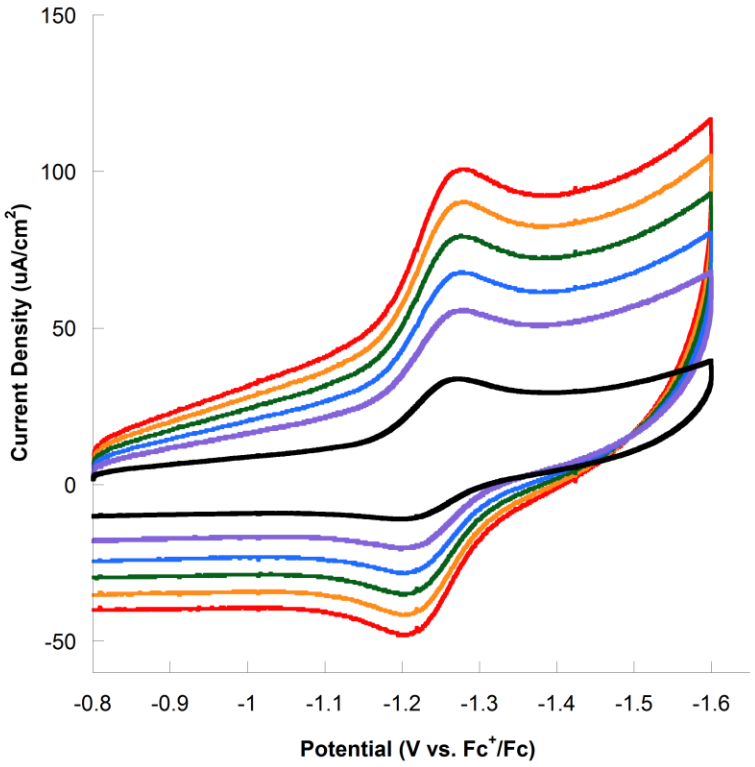

Figure S2. CVs of 0.5 mg **2** in 5 mL CH_3CN with 0.1 M $TBAPF_6$ scanned from -0.80 V vs. Fc^+/Fc to -1.60 V vs. Fc^+/Fc with no acid added at 150 mV/s (black), 300 mV/s (purple), 450 mV/s (blue), 600 mV/s (green), 750 mV/s (orange), and 900 mV/s (red).

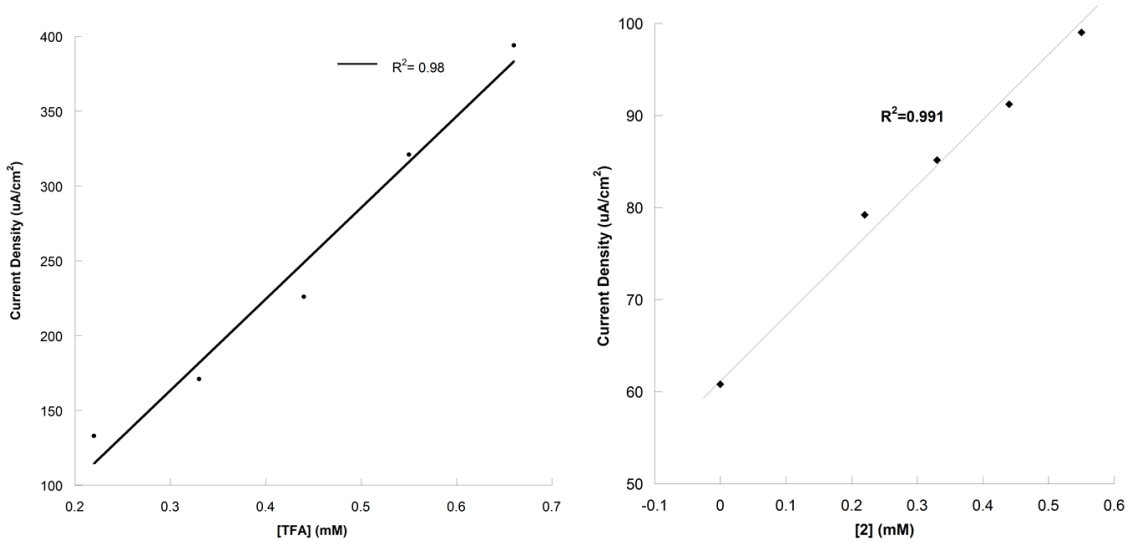

Figure S3. *Left:* Peak current density vs. [TFA] corresponding to catalytic wave at -1.7 V vs. Fc^{+}/Fc of Figure 3 in the text. *Right:* Peak current density vs. [TFA] corresponding to reduction event at -1.25 V vs. Fc^{+}/Fc of Figure 3 in the text.

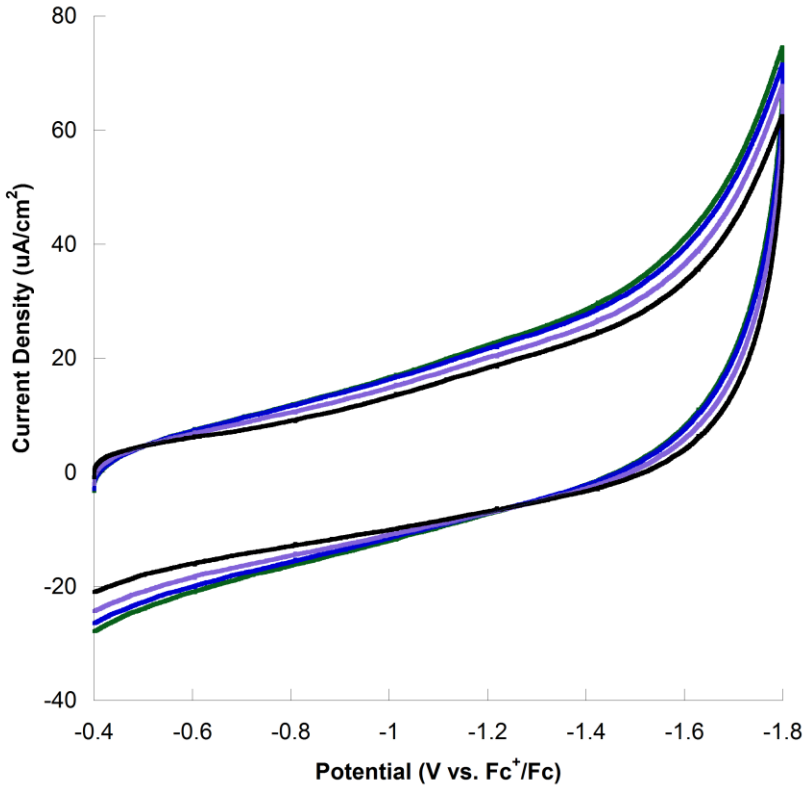

Figure S4. CVs in CH_3CN (0.1 M $TBAPF_6$) upon addition of 15 µL (black), 20 µL (purple), 25 µL (blue), and 30 µL (green) of a 0.11 M TFA solution with no catalyst.

[Fluorescein] (M)	[Catalyst] (M)	H_2 (µL)	TON
1.0×10^{-3}	1.25×10^{-6}	28.9	180
1.2×10^{-3}	1.25×10^{-6}	20.0	130
1.4×10^{-3}	1.25×10^{-6}	31.1	200
1.6×10^{-3}	1.25×10^{-6}	53.9	340
1.8×10^{-3}	1.25×10^{-6}	42.3	270

Table S3. Photocatalytic hydrogen generation with 1.25×10^{-6} M **2**, 0.36 M TEA, and various Fl concentrations in 1:1 EtOH:H_2O after 14 hours of irradiation with green LEDs (λ = 520 nm, 0.12 W).

[Fluorescein] (M)	[Catalyst] (M)	H_2 (µL)	TON
1.6×10^{-3}	7.50×10^{-7}	24.8	370
1.6×10^{-3}	1.00×10^{-6}	147.4	1600
1.6×10^{-3}	1.75×10^{-6}	125.6	800
1.6×10^{-3}	2.50×10^{-6}	42.3	190

Table S4. Photocatalytic hydrogen generation with 1.6×10^{-3} M Fl, 0.36 M TEA, and various concentrations of **2** in 1:1 EtOH:H_2O after 14 hours of irradiation with green LEDs (λ = 520 nm, 0.12 W).

[Fluorescein] (M)	[Catalyst] (M)	pH	H_2 (µL)	TON
1.6×10^{-3}	1.00×10^{-6}	12	78.3	900
1.6×10^{-3}	1.00×10^{-6}	12.5	131.4	1400
1.6×10^{-3}	1.00×10^{-6}	13	147.4	1600
1.6×10^{-3}	1.00×10^{-6}	13.5	43.7	500

Table S5. Photocatalytic hydrogen generation with 1.6×10^{-3} M Fl, 0.36 M TEA, and 1.00×10^{-6} M **2** in 1:1 EtOH:H_2O at various pHs after 14 hours of irradiation with green LEDs (λ = 520 nm, 0.12 W).

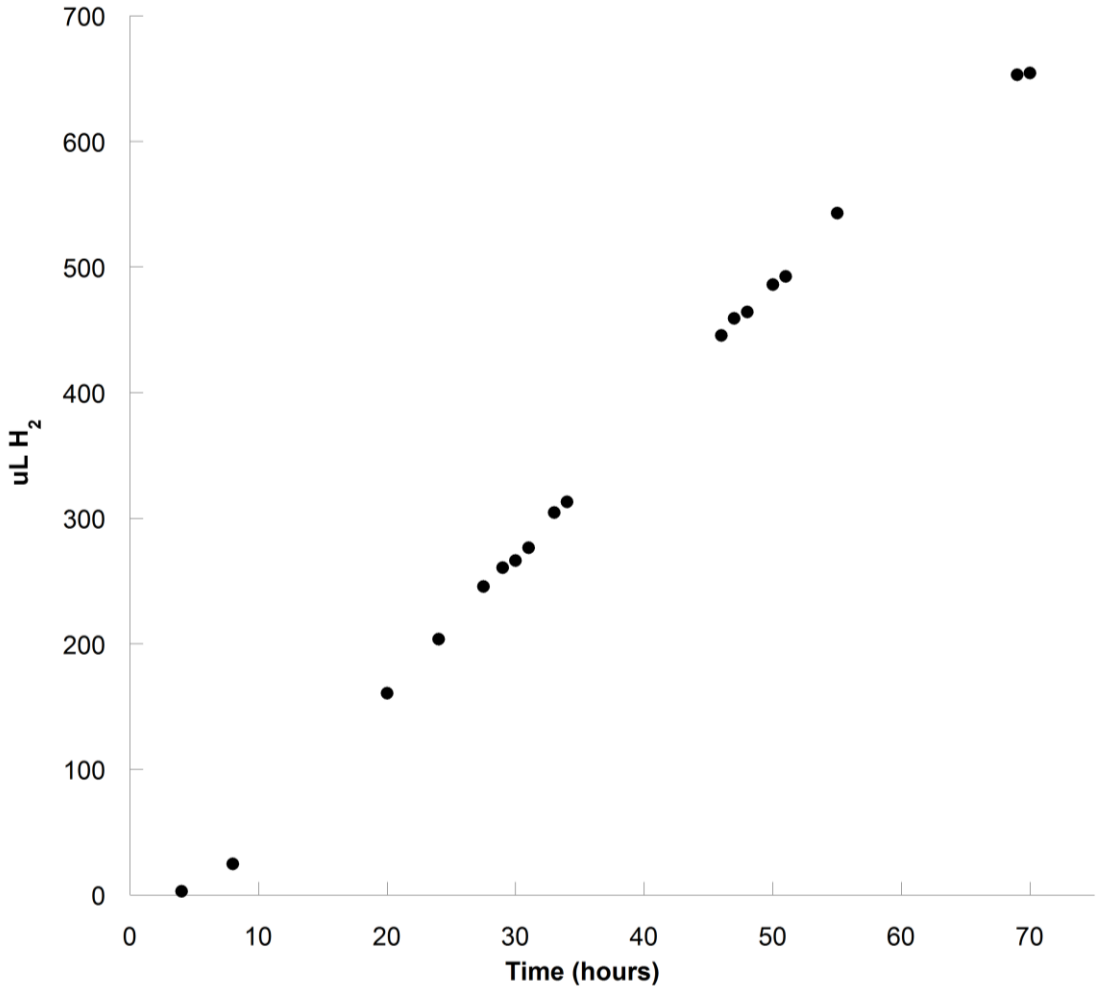

Figure S5. Photocatalytic hydrogen generation over time from a solution of Fl (5×10^{-4} M), **2** (5×10^{-5} M), and 1.96% V/V TEA in 1:1 EtOH:H_2O. 0.1% V/V TEA was added after 31 hours and 48 hours of irradiation.

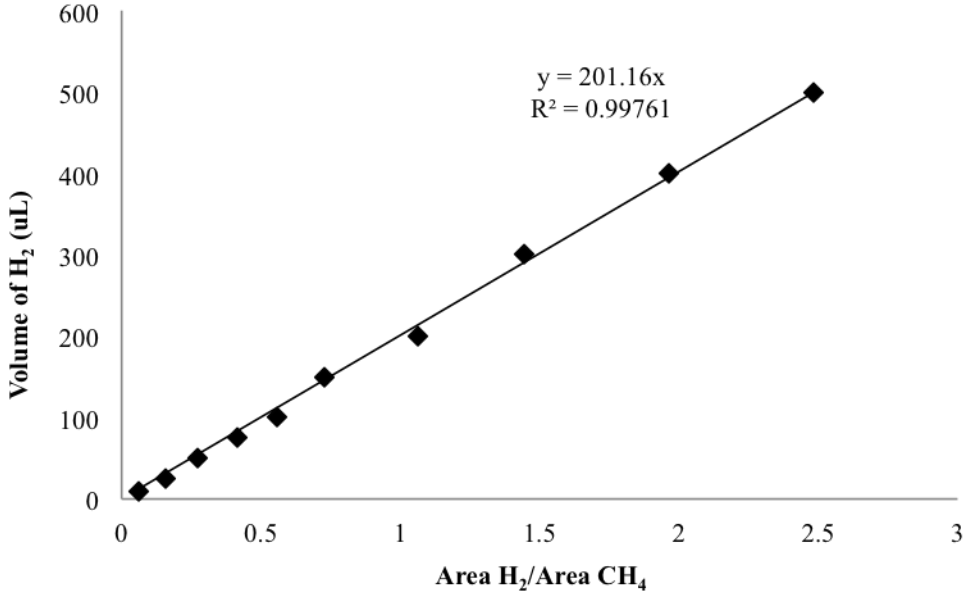

Figure S6. Calibration curve of H_2 to CH_4 peak areas used for determining photocatalytic hydrogen generation.

Calculation of Turnover Number

The turnover number for hydrogen generation by **2** can be determined using a calibration curve comparing the peak areas of H_2 and CH_4 in a gas chromatogram. Based on the calibration curve, the amount of H_2 produced (μL) is linearly related to the area ratio of H_2 to CH_4 with a slope of 201.16, as shown in equation (1).

$$(\mathbf{1})\ \mu L\ H_2 = 201.16\left(\frac{Area\ H_2}{Area\ CH_4}\right)$$

TON is defined as moles of H_2 per mole of catalyst. Moles of catalyst are determined during the experimental set-up, and moles of H_2 can be calculated from μL.

A sample calculation can be seen below:

$$\mu L\ H_2 = 201.16\left(\frac{18266.6}{29758.5}\right) = 123.5$$

$$123.5\ \mu L\ H_2\ \times \frac{1\ L}{1\ \times 10^6\ \mu L} \times \frac{1\ mol}{22.4\ L} = 5.51 \times 10^{-6} mol\ H_2$$

$$50\ \mu L\ catalyst\ \times \frac{1\ L}{1 \times 10^6\ \mu L} \times \frac{0.1\ mmol}{1\ L} \times \frac{1\ mol}{1000\ mmol} = 5 \times 10^{-9}\ mol$$

$$TON = \frac{5.51 \times 10^{-6}\ mol\ H_2}{5 \times 10^{-9}\ mol\ catalyst} = 1100$$

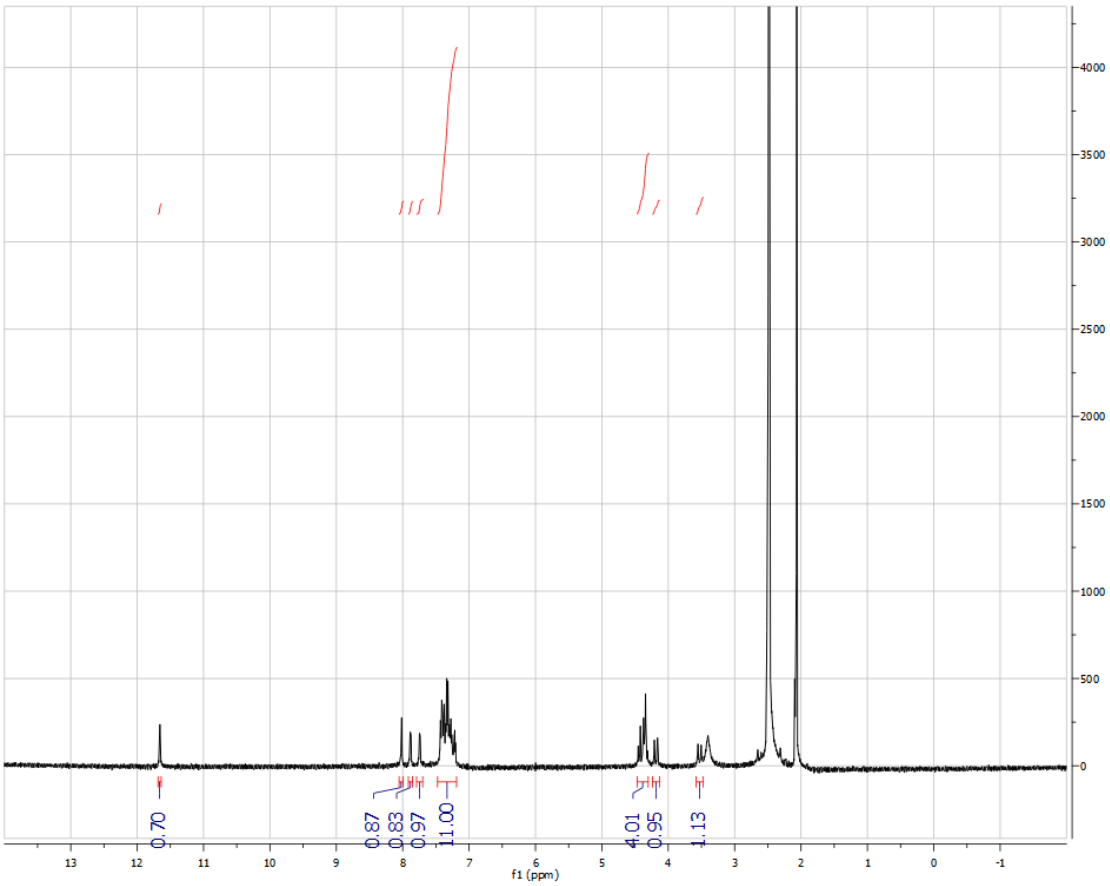

Figure S7. ^{1}H NMR of **1** in DMSO-d6.

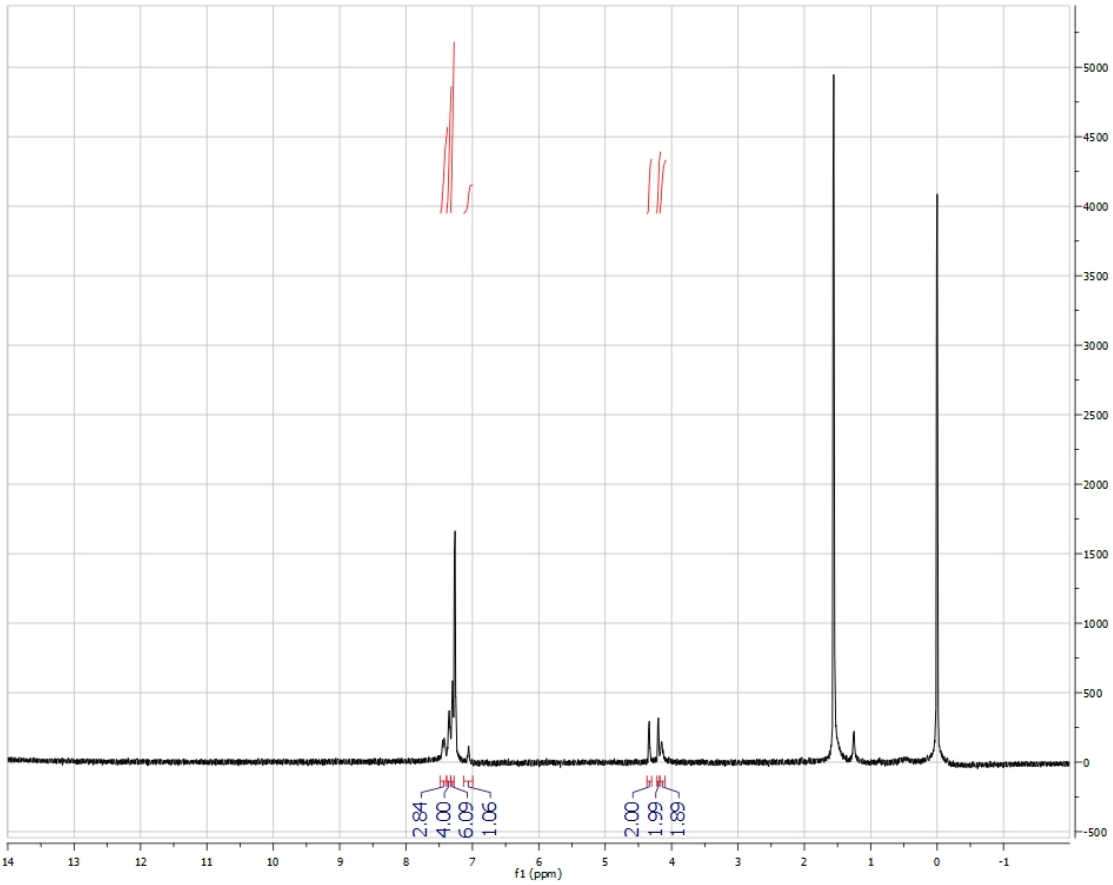

Figure S8. ^{1}H NMR of **2** in $CDCl_3$.

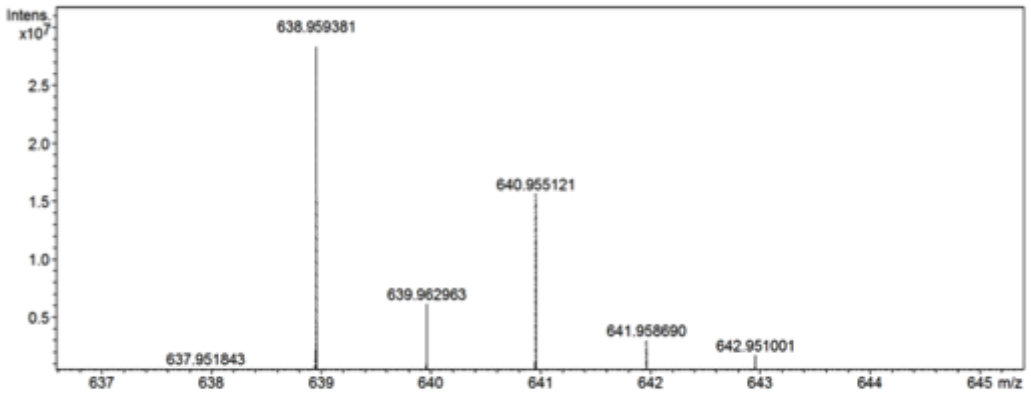

Figure S9. High-resolution mass spectrum of **2**. Analysis was completed through positive electrospray ionization on a Bruker 12 Tesla APEX-Qe FTICR-MS with an Apollo II ion source.

Figure S10. Image of the photocatalytic reaction vessel. An LED ribbon is attached to the outside of a jacketed beaker that is cooled to 20^{o}C. The samples are in test tubes that are rotated inside of the beaker.

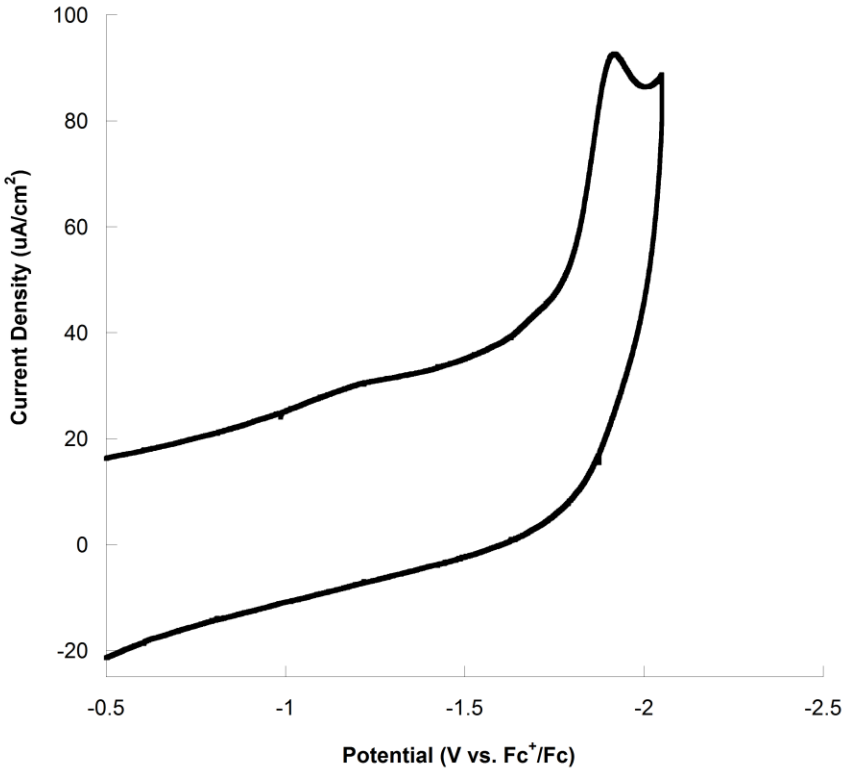

Figure S11. CV of 0.5 mg ligand **1** in a solution of 0.1 M $TBAPF_6$ in CH_3CN.

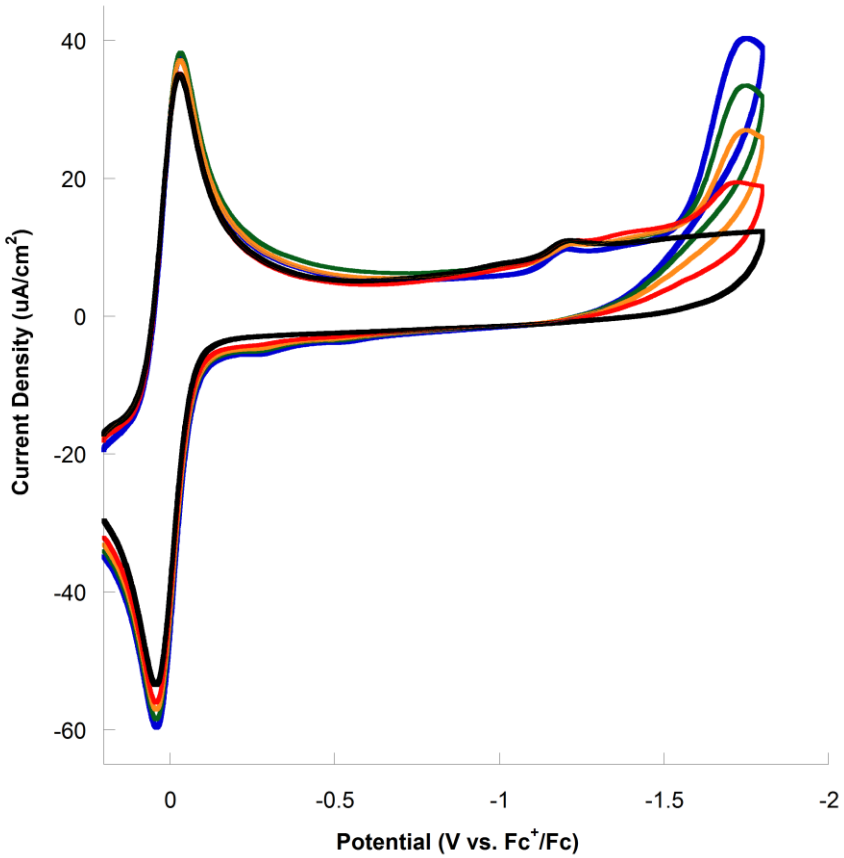

Figure S12. CVs of **2** in CH_3CN with 0.1 M $TBAPF_6$ without acid added (black), and in the presence of 0.22 mM (red), 0.33 mM (orange), 0.44 mM (green), and 0.55 mM (blue) TFA. Ferrocene was added as an internal reference and the redox couple for Fc^+/Fc was set to 0 V vs. Fc^+/Fc.

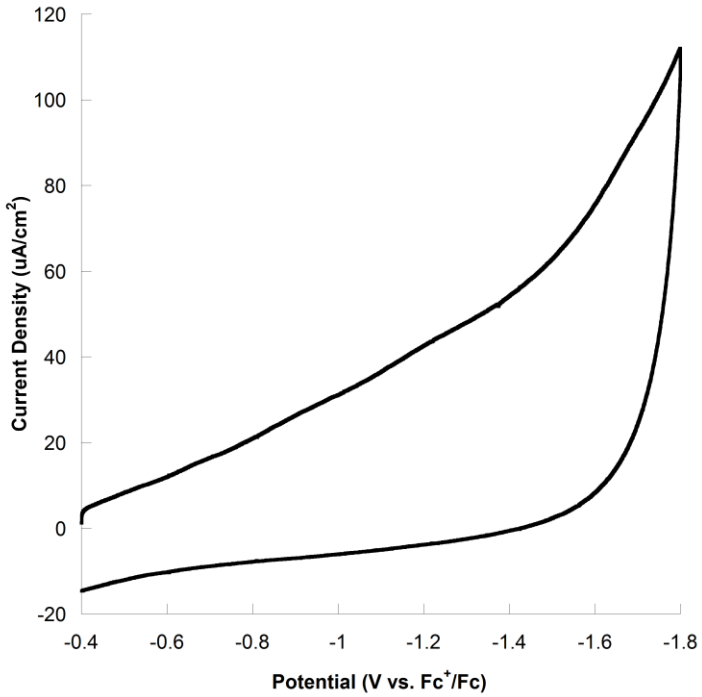

Figure S13. CV of 0.77 mM TFA in a 0.1 M solution of $TBAPF_6$ in CH_3CN using a glassy carbon working electrode that was used in a bulk electrolysis experiment. Bulk electrolysis was performed with **2** at -1.8 V vs. Fc^+/Fc for 1600 seconds. The glassy carbon working electrode was rinsed with CH_3CN (not polished) prior to obtaining this CV.