

## Supporting Information

### **Carbon Dioxide Reduction by Iron Hangman Porphyrins**

Charles G. Margarit, Christoph Schnedermann, Naomi G. Asimow, and Daniel G. Nocera

*Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA  
02138, United States*

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## Experimental methods

### General considerations

$^1\text{H}$  NMR spectra were recorded at ambient temperature on a Varian Inova 400 MHz spectrometer. All spectra were referenced to trace protonated chloroform (7.26 ppm ( $^1\text{H}$ )) or benzene (7.17 ppm ( $^1\text{H}$ )) as an internal standard (measured values for  $\delta$  are given in parts per million (ppm) and for  $J$  in Hertz (Hz)). Electrospray ionization mass spectra (ESI-MS) were obtained using a Bruker micrOTOF-QII. Absorption spectral measurements were made for each porphyrin using a Cary 5000 UV-vis-NIR spectrometer from Varian employing the software Cary WinUV. Quartz cells with a 10 mm path length were used. The microwave-assisted reactions were performed inside the cavity of a CEM Discover microwave synthesis system equipped with infrared, pressure, and temperature sensors for monitoring the synthesis. The reaction vessels were 35 mL crimp-sealed thick-wall glass tubes. The contents of each vessel were stirred with a magnetic stirrer. Automated chromatography was performed on all dibenzofuran compounds before porphyrin formation and on all metallated porphyrins using a Biotage Isolera One equipped with a UV-vis spectrometer and auto fractionation arm.

N,N-dimethylformamide (DMF) was purchased from Sigma Aldrich and purified by passage through alumina<sup>1</sup> and stored over activated 3 Å sieves under a nitrogen atmosphere for at least 24 h before use. Tetrabutylammonium hexafluorophosphate ([TBA<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]) was purchased from Sigma Aldrich and was doubly recrystallized from ethanol before being dried in vacuo at 70 °C and stored under nitrogen atmosphere inside a glovebox.

THF, methanol, pentane, acetonitrile, and dichloromethane were purified by passage through alumina.<sup>1</sup> The following chemicals were used as received: ethyl acetate, phenol (PhOH), chloroform, 4-N,N-dimethylaminopyridine (DMAP), p-toluenesulfonyl chloride (TsCl), sodium borohydride (NaBH<sub>4</sub>), tetramethylethylenediamine (TMEDA), sodium chloride (NaCl), sodium bicarbonate (NaHCO<sub>3</sub>), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), petroleum ether, n-butyl lithium (n-BuLi), pyrrole, trimethylorthoformate, 3,4,5-trimethoxybenzaldehyde, 2,6-diaminopyridine, aniline, 3-aminophenol, dibenzofuran, sulfuric acid, iron(II) chloride (FeCl<sub>2</sub>), iron(II) bromide (FeBr<sub>2</sub>), Tetraethylammonium acetate tetrahydrate ([TEA<sup>+</sup>][OAc<sup>-</sup>]) from Sigma Aldrich; chloroform-d<sub>3</sub> (CDCl<sub>3</sub>), benzene-d<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>), dimethylsulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) from Cambridge Isotope Laboratories; 3-aminobenzenesulfonic acid from TCI.

### Synthesis

Methyl-6-formyl-4-dibenzofurancarboxylate (**DBF**), 5-(4-(dibenzofuran-6-carboxylic acid))-10,15,20-tri(3,4,5-trimethoxyphenyl)-porphyrin (**HPD-CO<sub>2</sub>H**), 5-(6-(dibenzofuran-4-(3-N-carboxamido)benzenesulfonic acid))-10,15,20-tri(3,4,5-trimethoxyphenyl)porphyrin

(HPDFe-3SA) and tetrakis(3,4,5-trimethoxyphenyl) porphyrinato iron(III) chloride (**A<sub>4</sub>Fe-OMe**)<sub>3</sub>), were synthesized according to previous procedures in good yield.<sup>2,3</sup>

**5-(6-(dibenzofuran-4-N-(3-aminophenyl)carboxamide))-10,15,20-tri(3,4,5-trimethoxyphenyl)porphyrin (HPD-PhOH).** HPD-CO<sub>2</sub>H (112.5 mg, 110.5  $\mu$ mol) was added to a stirring, 100 mL DCM solution of TsCl (105 mg, 550  $\mu$ mol, 5 equiv) and DMAP (135 mg, 0.65 mmol, 10 equiv) and was allowed to stir under N<sub>2</sub> for 2 h. Dry 3-aminophenol (45 mg, 412  $\mu$ mol, 4 equiv) was added and the solution stirred overnight under N<sub>2</sub>. The volatiles were removed and the solids were dissolved in EtOAc and transferred to the separatory funnel. The organic layer was washed with HCl/H<sub>2</sub>O (2  $\times$  100 mL), H<sub>2</sub>O (1  $\times$  100 mL), and brine (1  $\times$  100 mL) before being dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to dryness. The solids were dissolved in DCM (2% NEt<sub>3</sub>) and loaded onto a silica column packed with DCM (2% NEt<sub>3</sub>), and eluted with DCM (2% NEt<sub>3</sub>). The major red fluorescent band was collected and the fraction was evaporated to dryness. The solids were dissolved in benzene and filtered through filter paper to remove Et<sub>3</sub>NH $\cdot$ Cl. The filtrate was concentrated and the product was precipitated with the addition of pentane. The solids were sonicated and washed in pentane (3  $\times$  5 mL) and dried in vacuo. <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.24 (d, J = 10.8 Hz, 4H), 9.01 (d, J = 8.9 Hz, 4H), 8.16 (dd, J = 24.7, 7.6 Hz, 2H), 7.98 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 1.4 Hz, 1H), 7.51-7.48 (m, 4H), 7.37 (s, 2H), 7.04 (s, 1H), 5.52-5.49 (m, 1H), 5.29 (t, J = 8.0 Hz, 1H), 4.87-4.85 (m, 1H), 4.69 (t, J = 1.9 Hz, 1H), 4.16 (d, J = 2.8 Hz, 3H), 4.14 (s, 6H), 3.49 (s, 9H), 3.47 (s, 4H), 3.44 (s, 6H), -1.83 (s, 2H). <sup>13</sup>C NMR (400 MHz; [C<sub>6</sub>D<sub>6</sub>]):  $\delta$  152.22, 152.10, 151.7, 146.4, 137.5, 134.9, 131.9, 128.1, 127.9, 127.6, 127.4, 125.5, 121.3, 121.1, 117.3, 116.6, 115.7, 114.6, 113.55, 113.52, 113.2, 108.9, 105.6, 60.6, 55.7. Yield = 81 mg (75%). UV-vis,  $\lambda_{\text{max}}$ /nm: 405, 423, 520, 550, 590, 650. ESI-MS [M+H]<sup>+</sup> (*m/z*) Calcd (Found): 1110.392 (1110.3895).

**5-(6-(dibenzofuran-4-(1-N-(2,3-ditertbutoxycarbonyl)guanidyl)carboxamide))-10,15,20-tri(3,4,5-trimethoxyphenyl)porphyrin (HPD-Gnd(Boc)<sub>2</sub>).** HPD-Gnd(Boc)<sub>2</sub> was synthesized according to the above procedure replacing 3-aminophenol with 2,3-ditertbutoxycarbonyl guanidine. The volatiles were removed and the solids were dissolved in EtOAc and transferred to the separatory funnel. The organic layer was washed with HCl/H<sub>2</sub>O (2  $\times$  100 mL), H<sub>2</sub>O (1  $\times$  100 mL), and brine (1  $\times$  100 mL) before being dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to dryness. The solids were used in the next step without purification.

**5-(6-(dibenzofuran-4-(1-N-guanidyl)carboxamide))-10,15,20-tri(3,4,5-trimethoxyphenyl)porphyrin (HPD-Gnd).** HPD-Gnd(Boc)<sub>2</sub> was added as a solid to a 250 mL round bottom flask and covered with neat trifluoroacetic acid and stirred for 2 h. The reaction mixture was diluted with 50 mL ethyl acetate and quenched by slowly adding 100 mL of saturated sodium bicarbonate solution. The organic layer was washed with HCl/H<sub>2</sub>O (1  $\times$  100 mL), H<sub>2</sub>O (2  $\times$  100 mL), and brine (1  $\times$  100 mL) before being dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to dryness. The solids were dissolved in DCM (2% NEt<sub>3</sub>) and loaded onto a silica

column packed with DCM (2% NEt<sub>3</sub>), and eluted with 2% MeOH in DCM (2% NEt<sub>3</sub>). The major red fluorescent band was collected and the fraction was evaporated to dryness. The solids were dissolved in benzene and filtered through filter paper to remove Et<sub>3</sub>NH·Cl. The filtrate was concentrated and the product was precipitated with the addition of pentane. The solids were sonicated and washed in pentane (3 × 5 mL) and dried in vacuo. Yield = 81 mg (75%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 9.11 (d, J = 4.7 Hz, 2H), 9.07 (d, J = 4.7 Hz, 2H), 8.85 (d, J = 4.6 Hz, 2H), 8.69 (d, J = 4.6 Hz, 2H), 7.91 (d, J = 7.2 Hz, 1H), 7.78 (d, J = 7.1 Hz, 1H), 7.52 (s, 1H), 7.41 (d, J = 1.2 Hz, 1H), 7.36 (s, 2H), 7.29 (s, 2H), 7.25 (s, 1H), 6.70 (s, 1H), 4.22 (s, 3H), 4.07 (s, 3H), 3.99 (s, 6H), 3.42 (s, 3H), 3.38 (s, 3H), 3.35 (s, 6H), 3.25 (s, 6H), -2.10 (s, 2H). <sup>13</sup>C NMR (400 MHz; [CDCl<sub>3</sub>]): δ 157.1, 155.1, 152.20, 152.11, 151.98, 139.1, 138.9, 137.6, 137.3, 133.6, 128.0, 127.7, 127.5, 126.6, 125.3, 123.3, 122.3, 122.0, 121.2, 120.9, 120.5, 113.61, 113.59, 113.46, 113.30, 60.60, 60.50, 55.78, 55.67, 55.63, 55.59, 53.0, 34.1, 22.4, 14.0. UV-vis, λ<sub>max</sub> / nm: 403, 423, 520, 551, 590, 645. ESI-MS [M+H]<sup>+</sup> (m/z) Calcd (Found): 1060.3876 (1060.3857).

**5-(6-(dibenzofuran-4-N-(3-aminophenyl)carboxamide))-10,15,20-tri(3,4,5-trimethoxyphenyl)porphyrinato iron(III) chloride (HPDFe-PhOH).** According to published procedure,<sup>3</sup> Freebase hangman porphyrin 5-(6-(dibenzofuran-4-N-(3-aminophenyl)-carboxamide))-10,15,20-tri(3,4,5-trimethoxyphenyl)porphyrin (39 mg, 35.1 μmol) and freshly ground FeCl<sub>2</sub> (88.5 mg, 0.702 mmol, 20.0 equiv) were dissolved in CH<sub>3</sub>CN and transferred to a 35 mL microwave reactor tube. A small amount of NEt<sub>3</sub> (0.05 mL) was added to the solution, the tube was capped, and microwave irradiation proceeded for 1 hr at 70 °C. The solution was analyzed by TLC and no red fluorescence (indicative of freebase porphyrin) was detected. The solution was transferred to a separatory funnel containing 100 mL EtOAc. The organic layer was washed with 1 M HCl(aq) (2 × 100 mL), H<sub>2</sub>O (1 × 100 mL), and brine (1 × 100 mL) before being dried over sodium sulfate, filtered into a round bottom flask, and dried in vacuo. The solids were dissolved in DCM and purified on a Biotage SNAP Ultra 10g column eluting with 100% DCM → 10% MeOH in DCM over twelve column volumes, collecting the brown fractions absorbing at λ = 420 nm. The volatiles were removed, solids dissolved in DCM, which was covered in 1 M HCl(aq) and the solution stirred thoroughly for 4 h. The organic layer was filtered through filter paper, the volatiles removed and the solids were sonicated in pentane (3 × 5 mL) then dried at 80°C in vacuo. Yield: 29 mg (69%). UV-vis, λ<sub>max</sub> / nm: 311, 413, 513, 570, 611, 692. ESI-MS [M - Cl]<sup>+</sup>, Calcd (Found): 1199.2804 (1199.4250).

**5-(6-(dibenzofuran-4-(1-N-(2,3-diboc)guanidyl) carboxamide))-10,15,20-tri-(3,4,5-trimethoxyphenyl)porphyrinato iron(III) chloride (HPDFe-Gnd).** According to published procedure,<sup>3</sup> freebase hangman porphyrin 5-(6-(dibenzofuran-4-(1-N-(2,3-diboc)guanidyl))-10,15,20-tri(3,4,5-trimethoxyphenyl)porphyrin (36mg, 33.9 μmol) and freshly ground FeCl<sub>2</sub> (85.5 mg, 0.679 mmol, 20.0 equiv.) were dissolved in CH<sub>3</sub>CN and transferred to a 35 mL microwave reactor tube. A small amount of NEt<sub>3</sub> (0.05 mL) was added

to the solution, the tube was capped, and microwave irradiation proceeded for 1 h at 70 °C. The solution was analyzed by TLC and no red fluorescence (indicative of freebase porphyrin) was detected. The solution was transferred to a separatory funnel containing 100 mL EtOAc. The organic layer was washed with 1 M HCl(aq) (2 × 100 mL), H<sub>2</sub>O (1 × 100 mL), and brine (1 × 100 mL) before being dried over sodium sulfate, filtered into a round bottom flask, and dried in vacuo. The solids were dissolved in DCM and purified on a Biotage SNAP Ultra 10 g column eluting with 100% DCM → 10% MeOH in DCM over twelve column volumes, collecting the brown fractions absorbing at  $\lambda = 420$  nm. The volatiles were removed, solids dissolved in DCM, which was covered in 1 M HCl(aq) and the solution stirred thoroughly for 4 h. The organic layer was filtered through filter paper, the volatiles removed and the solids were sonicated in pentane (3 × 5 mL) then dried at 80°C in vacuo. Yield: 29.5 mg (75%). UV-vis,  $\lambda_{\text{max}}$  / nm: 386, 425, 512, 583, 652, 696. Mass Spectrometry [M – Cl]<sup>+</sup>, Calcd (Found): 1149.2759 (1149.2734).

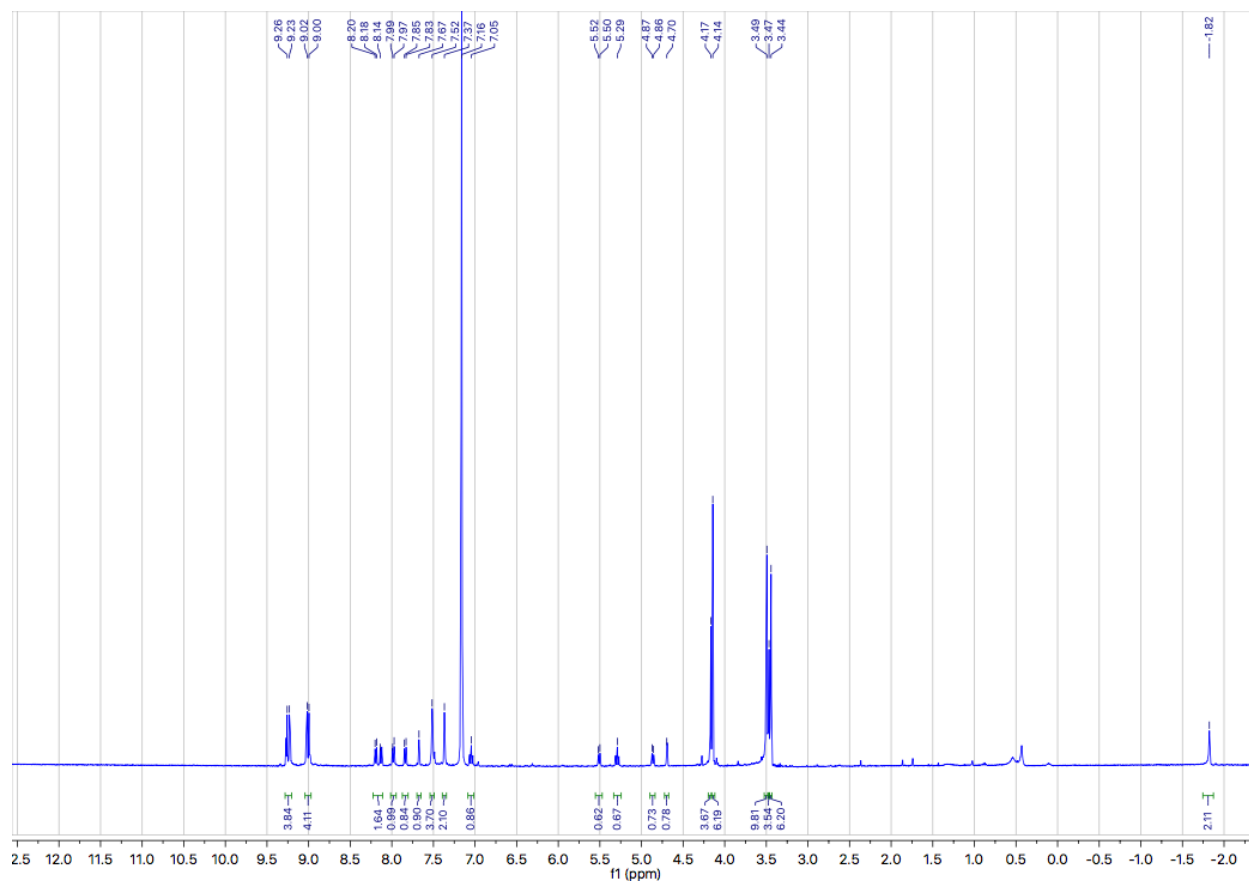
### Faradaic Efficiency Calculations

A calibration gas containing 0.5% each H<sub>2</sub>, CO, CO<sub>2</sub>, and O<sub>2</sub> in N<sub>2</sub> was used to calibrate the SRI Instruments 8610C Gas Chromatograph. Peak Simple was used to integrate the calibration peaks and these standards were used to quantify experimental products. For each run, the CO and H<sub>2</sub> peaks, if present, were integrated and then faradaic efficiency for each product gas was calculated according to eqs S1 and S2.

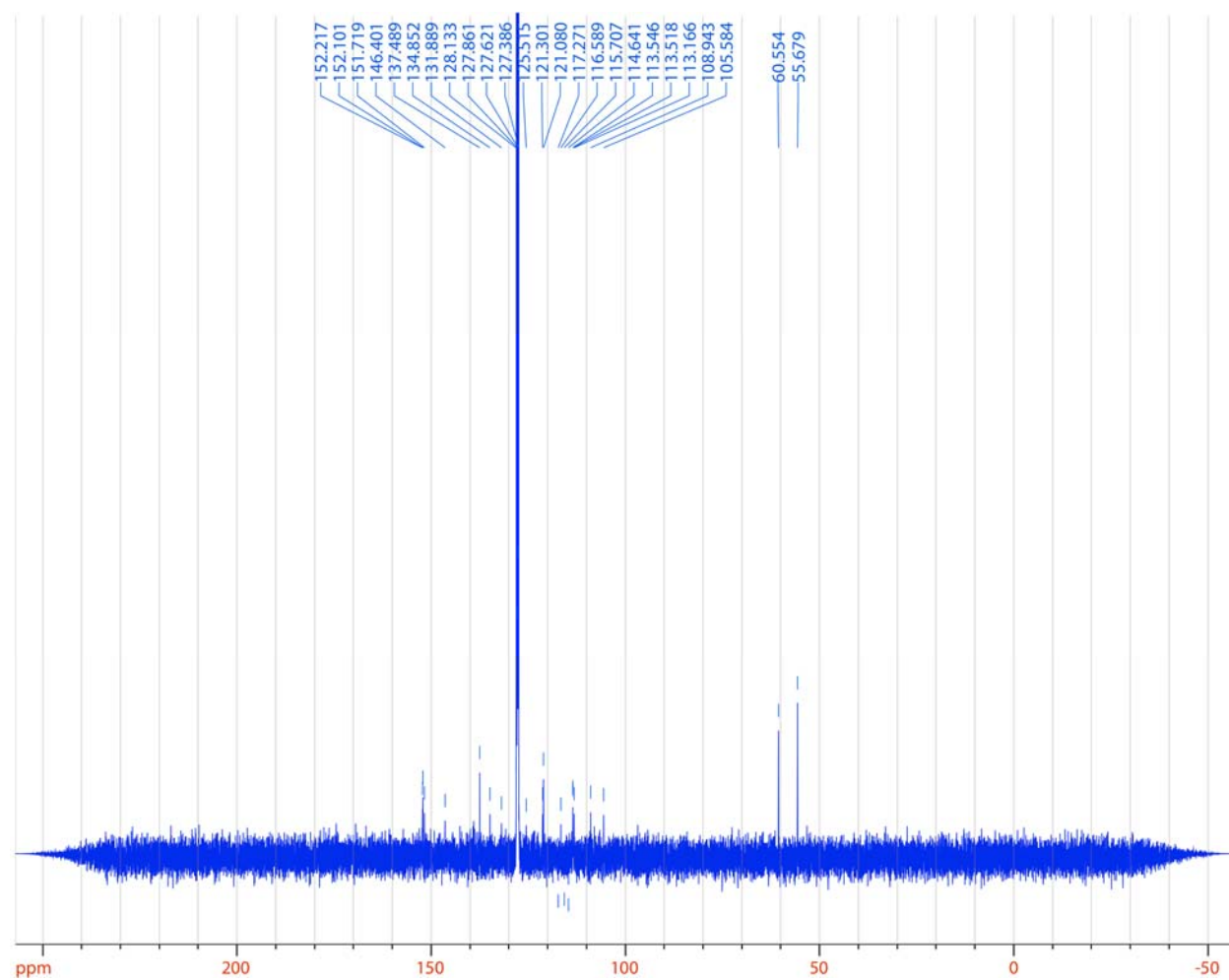
$$FE(A) = 100 \left[ \frac{\frac{Int_{exp} CF_A}{P_{atm} + P_{exp}}}{\frac{(I) \left(\frac{60s}{min}\right) \left(\frac{1}{F}\right) \left(\frac{1}{2}\right) \left(\frac{22.4L}{mol}\right)}{FR}} \right] \quad (S1)$$

$$CF_A = \frac{(P_{atm} + P_{calib})(0.005)}{Int_{calib}} \quad (S2)$$

where  $FE$  is faradaic efficiency,  $A$  is the gaseous product being quantified (CO or H<sub>2</sub>).  $Int_{exp}$  is the integration of the experimental peak measured for that gas,  $CF_A$  is the calibration factor for gas  $A$ , calculated in eq 2.  $P_{atm}$  is the atmospheric pressure in psi (14.7 psi),  $P_{exp}$  is the experimental pressure of the gas flow into the GC in psi at the time of sample collection (typically 0.02 PSI),  $I$  is the instantaneous current in amperes,  $F$  is the Faraday,  $FR$  is the flow rate of CO<sub>2</sub> through the cell at in L·min<sup>-1</sup>.  $CF_A$  is calculated by Equation 2, where  $P_{calib}$  is the pressure of the flow for the calibration gas. This pressure is multiplied by the percentage concentration of CO or H<sub>2</sub> in the calibration gas (0.005) and divided by  $Int_{calib}$ , the integration of the calibration gas peak.

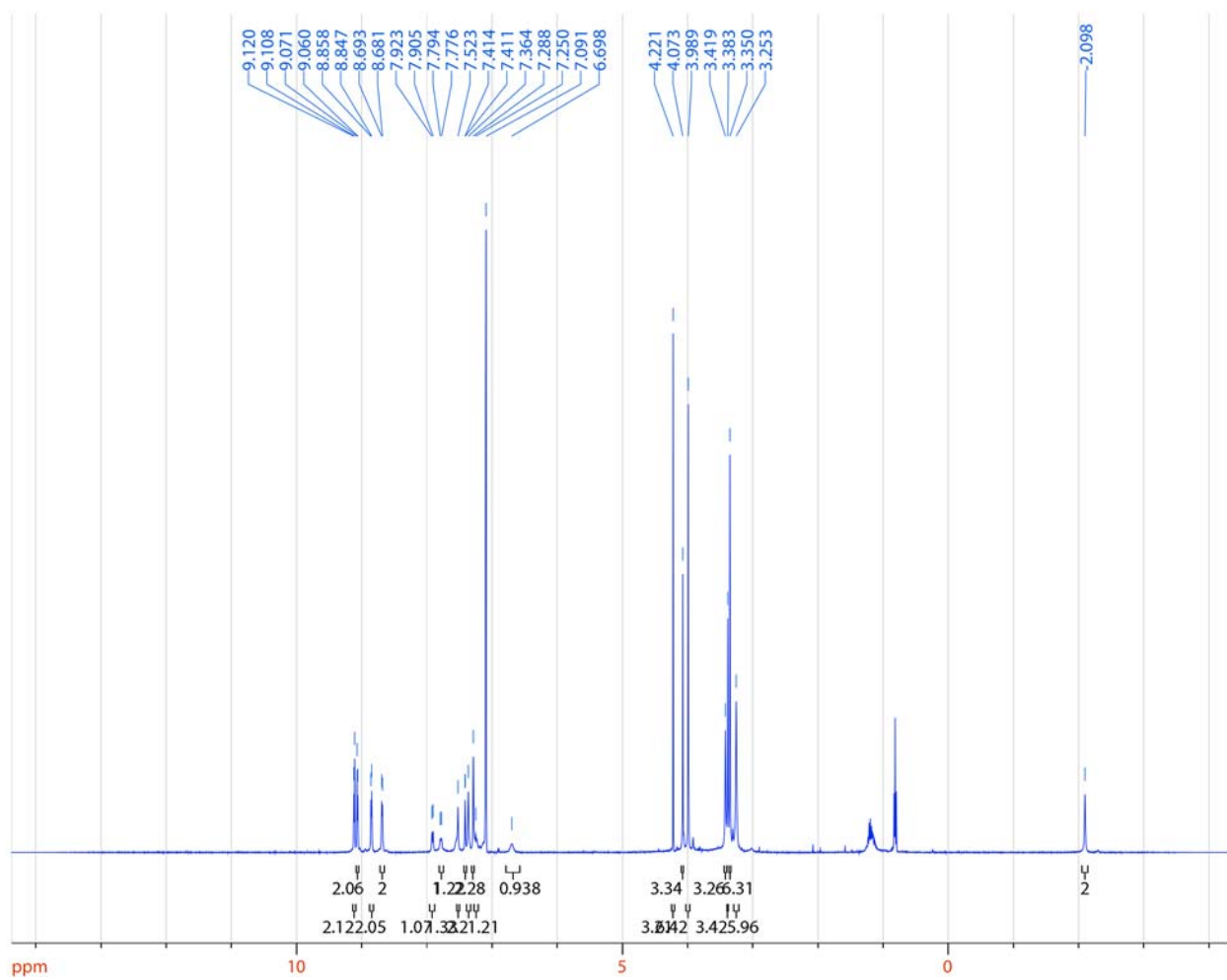


**Figure S1.**  $^1\text{H}$ -NMR spectrum of **HPD-PhOH** in  $\text{C}_6\text{D}_6$  with grease impurities around 0.5 ppm.

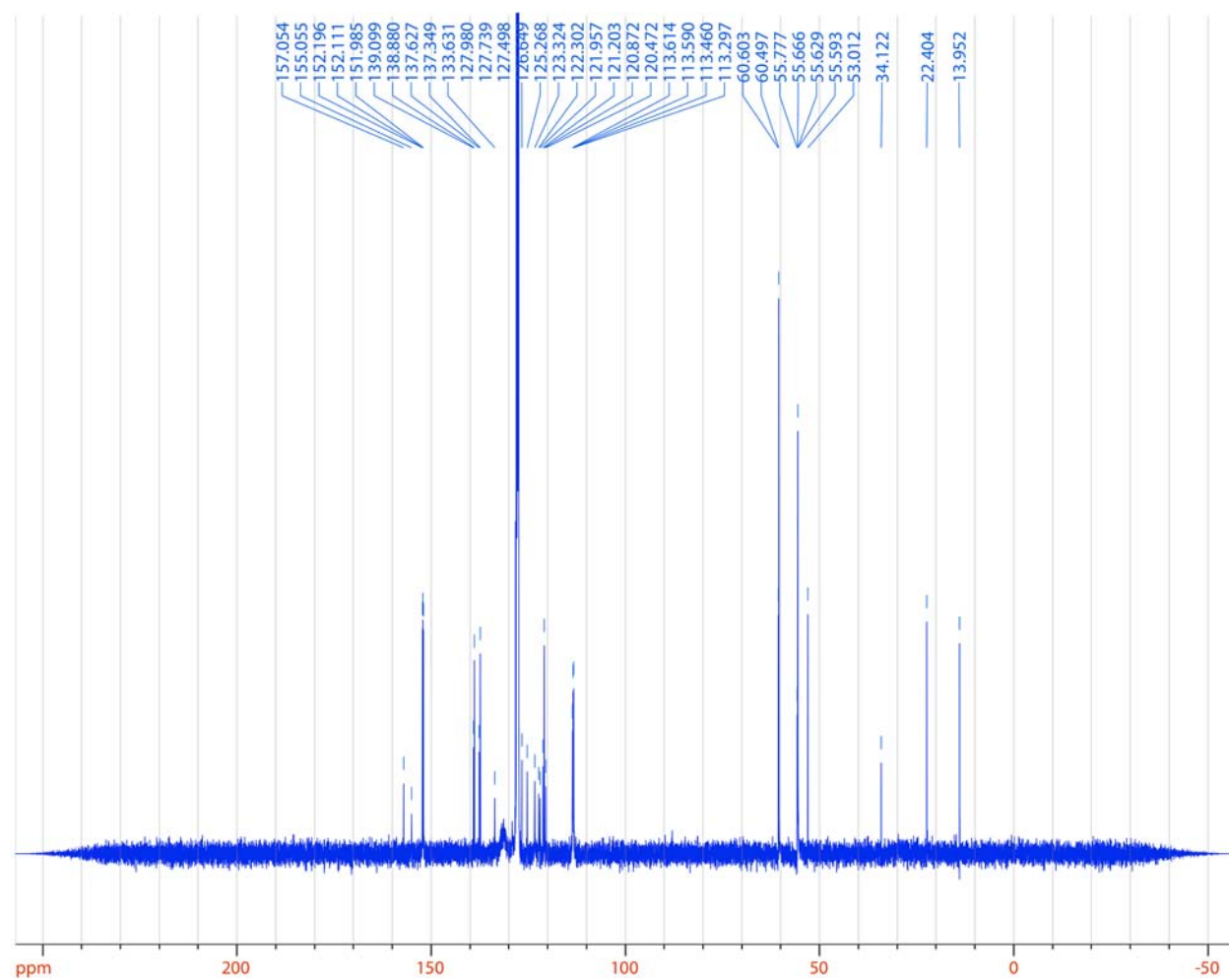


**Figure S2.**  $^{13}\text{C}$ -NMR spectrum of **HPD-PhOH** in  $\text{C}_6\text{D}_6$ .

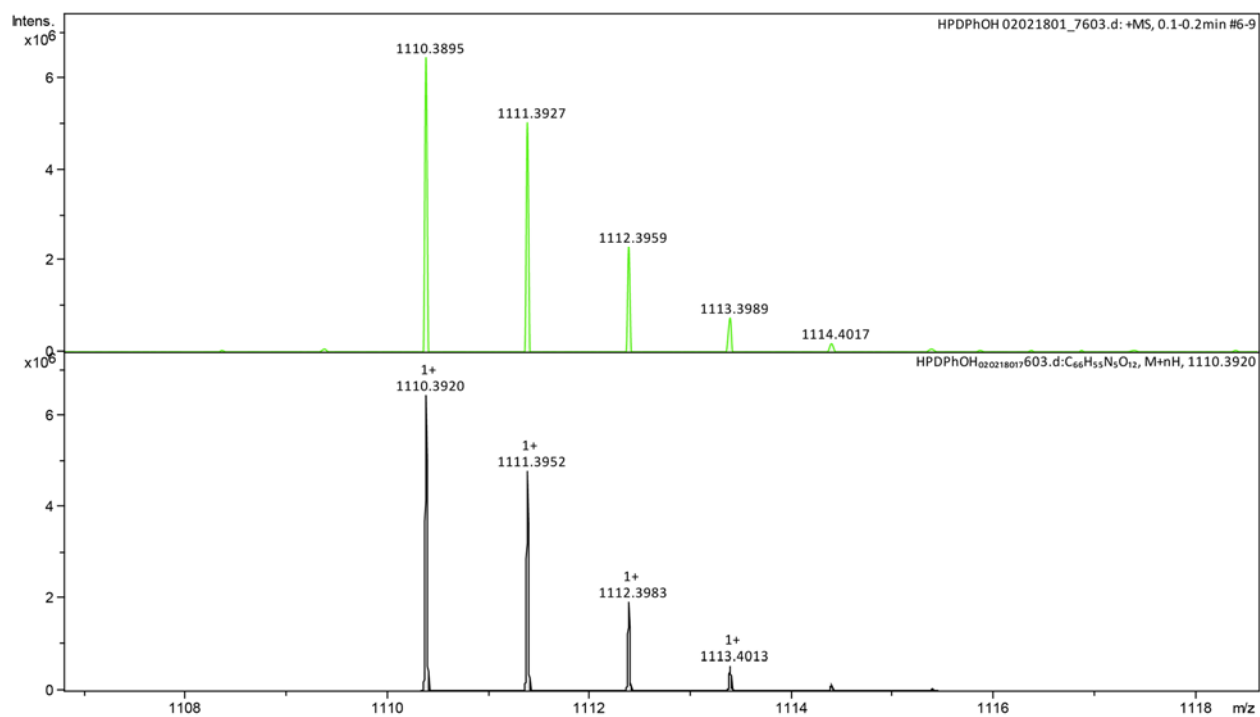




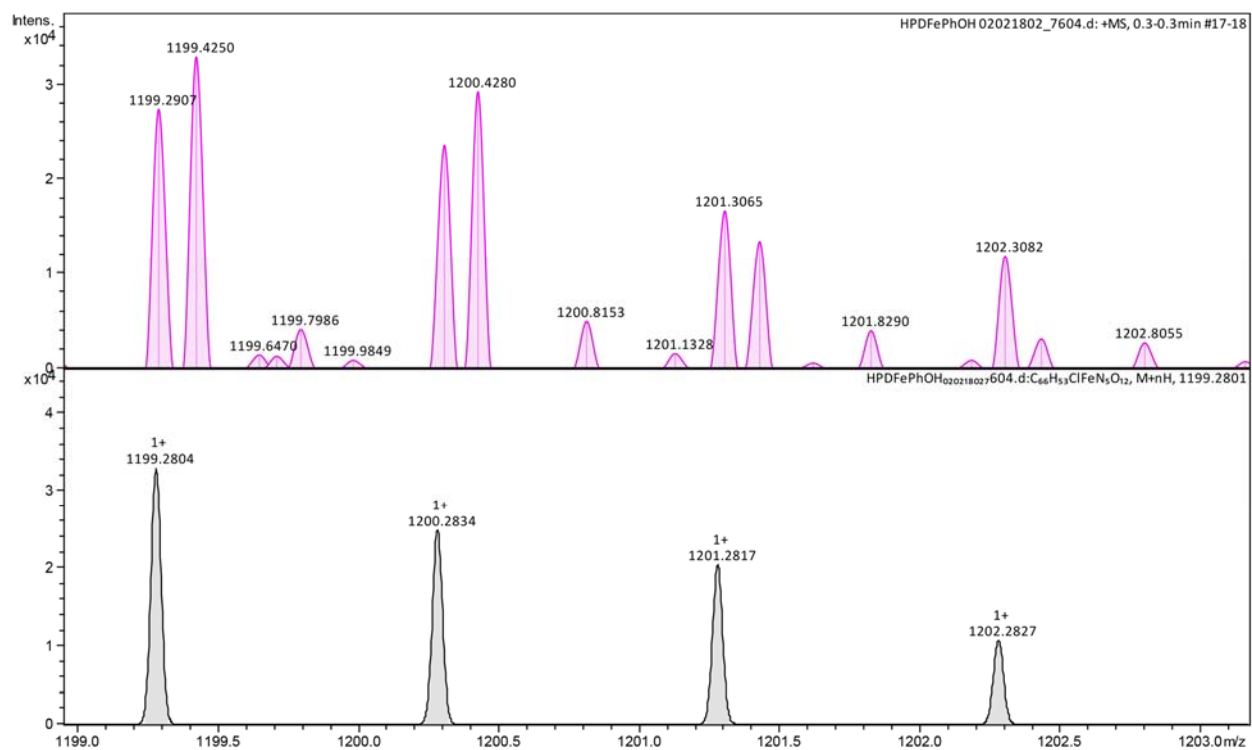
**Figure S3.**  $^1\text{H}$ -NMR spectrum of **HPD-Gnd** in  $\text{C}_6\text{D}_6$  with pentane impurity around 1 ppm.



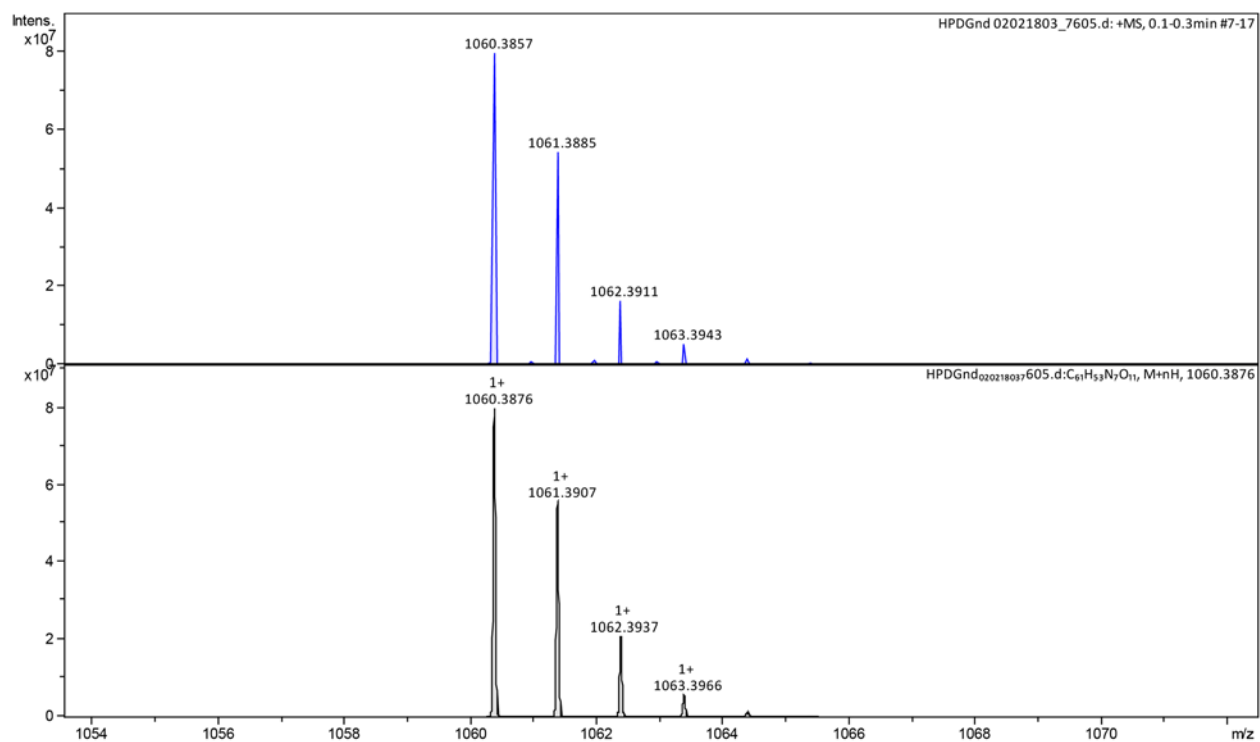
**Figure S4.**  $^{13}\text{C}$ -NMR spectrum of **HPD-Gnd** in  $\text{C}_6\text{D}_6$ .



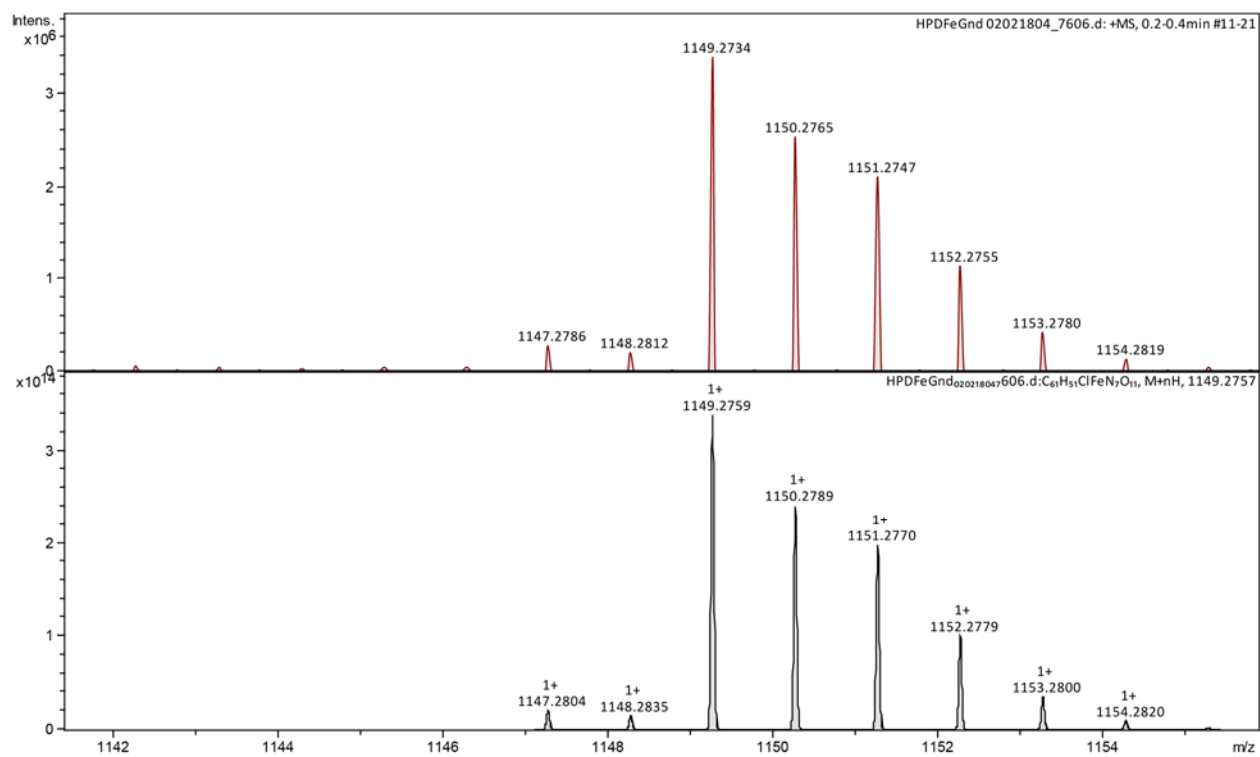
**Figure S5.** Experimental (top) and theoretical (bottom) mass spectra of **HPD-PhOH**. Error in ppm is 2.3.



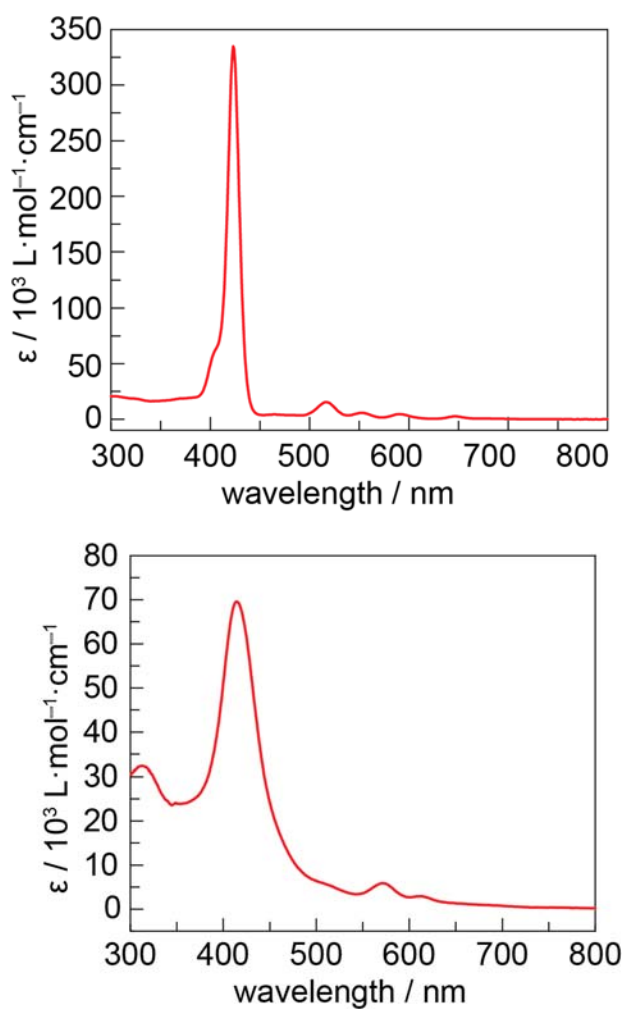
**Figure S6.** Experimental (top) and theoretical (bottom) mass spectra of **HPDFe-PhOH**. Error in ppm is 8.6.



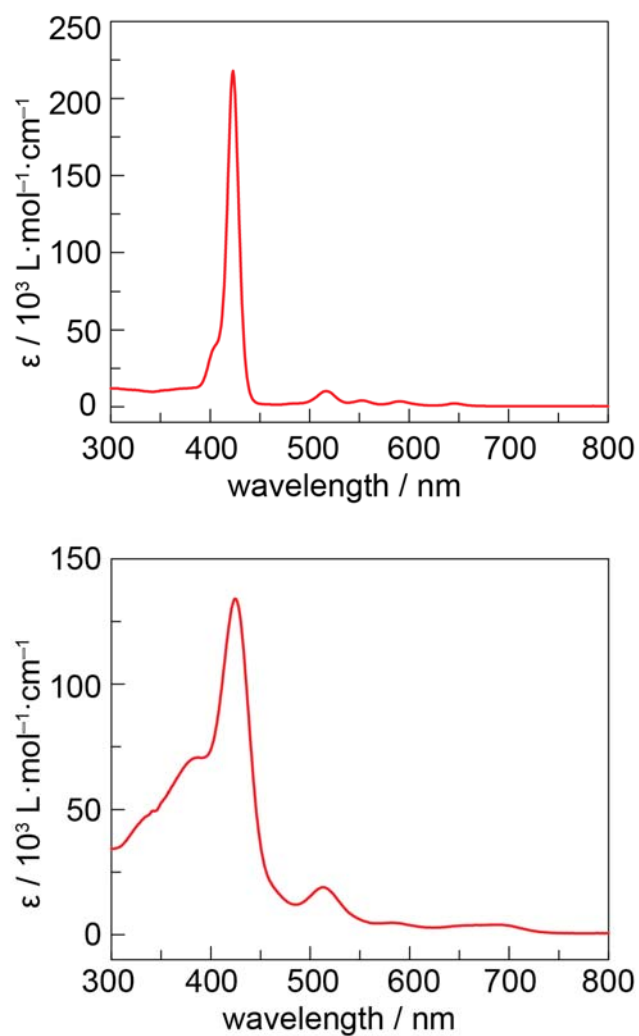
**Figure S7.** Experimental (top) and theoretical (bottom) mass spectra of **HPD-Gnd**. Error in ppm is 1.8.



**Figure S8.** Experimental (top) and theoretical (bottom) mass spectra of **HPDFe-Gnd**. Error in ppm is 2.2.

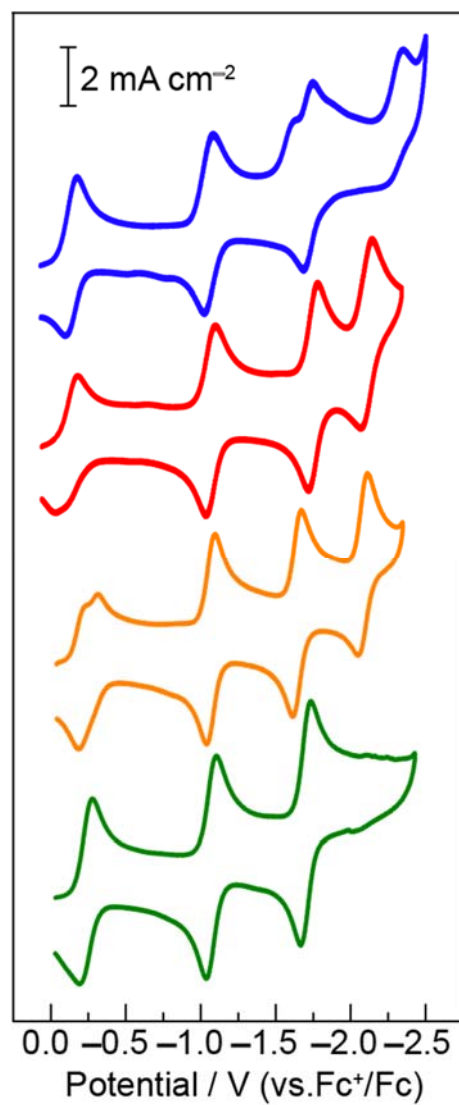


**Figure S9.** UV-vis spectrum of **HPD-PhOH** (top) and UV-vis spectrum of **HPDFe-PhOH** (bottom) in dichloromethane.

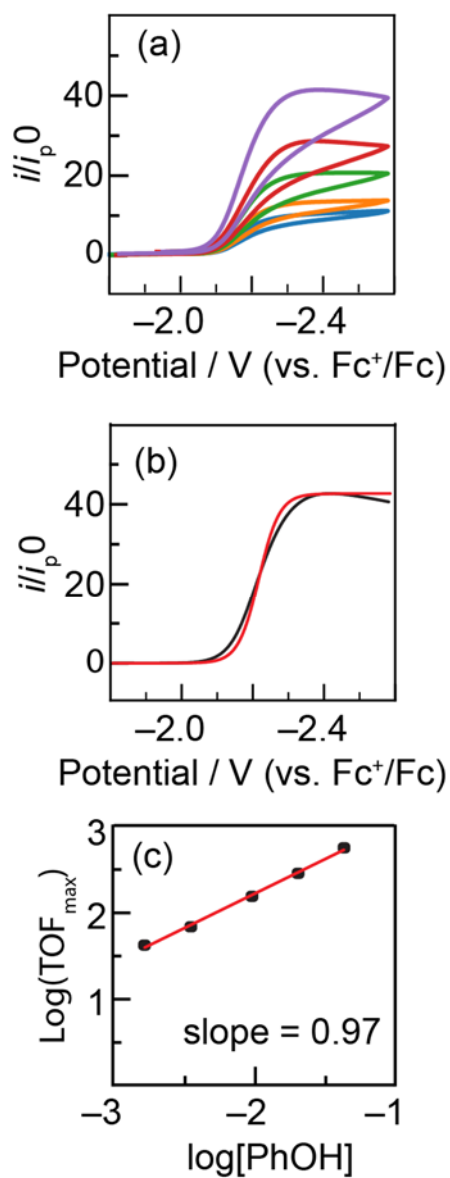


**Figure S10.** UV-vis spectrum of **HPD-Gnd** and UV-vis spectrum of **HPDFe-Gnd** in dichloromethane.





**Figure S11.** Combined CV plots of **HPDFe-Gnd** (—), **HPDFe-PhOH** (—), **HPDFe-3SA** (—), **A<sub>4</sub>Fe-(OMe)<sub>3</sub>** (—) under argon in the absence of exogenous PhOH.



**Figure S12.** (a) Cyclic voltammograms of  $A_4Fe-(OMe)_3$  with 2 mM (—), 4 mM (—), 10 mM (—), 20 mM, (—) and 40 mM (—) of added PhOH. (b) Plateau analysis for  $A_4Fe-(OMe)_3$  with  $[PhOH] = 40$  mM. Fits calculated from eq 1 (—) and overlaying cathodic trace of experimentally observed CV (—). (c) Plot of  $\log(TOF_{max})$  versus  $\log[PhOH]$  for  $A_4Fe-(OMe)_3$ , derived from plateau analysis (•) and eq (2) with linear fit.

**Table S1.** Calculated faradaic efficiencies for H<sub>2</sub> and CO over the course of the electrolysis.

Catalyst	% FE H <sub>2</sub>	% FE CO
HPDFe-PhOH	0	94%
HPDFe-Gnd	0	93%
HPDFe-3SA	0	96%
A <sub>4</sub> Fe-(OMe) <sub>3</sub>	0	99%

## References

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518.
2. Graham, D. J.; Zheng, S.-L.; Nocera, D. G. Post-Synthetic Modification of Hangman Porphyrins Synthesized on the Gram Scale. *ChemSusChem* **2014**, *7*, 2449.
3. Graham, D. J.; Nocera, D. G. Electrocatalytic H<sub>2</sub> Evolution by Proton-Gated Hangman Porphyrins. *Organometallics*. **2014**, *33*, 4994.