# **Supporting Information**

# Macromolecular Engineering of the Outer Coordination Sphere of [2Fe-2S] Metallopolymers to Enhance Catalytic Activity for H<sub>2</sub> Production

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#### 2. References

#### 1. Experimental

#### a. Materials and Characterization

Unless otherwise noted, solvents were received from Fisher Scientific as ACS grade and used without further purification.  $Fe_2S_2(CO)_6$  was prepared according to literature procedures<sup>1</sup> and sublimed before use. Fe(CO)<sub>5</sub> (99.5 %,Alfa-Aesar), NaOH (EMD, ACS grade), NH<sub>4</sub>CI (EMD, ACS grade), S<sub>8</sub> (Mallinckrodt, sublimed), Na<sub>2</sub>SO<sub>4</sub> (EMD, ACS grade), NaCNBH<sub>3</sub> (Sigma-Aldrich, 95%), Me<sub>3</sub>NO•2H<sub>2</sub>O (Sigma-Aldrich), Celite 545(VWR), and Silica Gel (SiliaFlash F60, 230-400 mesh, Silicycle) were used as received without further purification. 1,4-naphthoguinone (Alfa-Aesar, 97%, up to 5% H<sub>2</sub>O) was passed through a silica gel column with diethyl ether before use. Triethylamine (EMD. 99.5%) was distilled from KOH then stored on activated 3Å linde-type molecular sieves under argon. α-Bromoisobutyryl bromide (BIBB, Sigma-Aldrich, 98%) was initially used as received but found to decompose over time, requiring vacuum distillation (10 torr. 55°C) once it had taken on a vellow color. KCI (EMD, ACS grade) was recrystallized twice from hot 0.1 M HCl before use. Oligo(ethyleneglycol) methyl ether methacrylate (OEGMA, Mn: 475 g/mol) (Aldrich) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (Aldrich, 98%) were purified by passing through a short column of basic alumina to remove inhibitors. Copper(I) bromide (Cu(I)Br) (Aldrich, 98%) was purified by stirring overnight in glacial acetic acid, filtering, washing with ethanol and ethyl ether, and drying under vacuum before use. Alternatively, Cu(I)Br was purified by precipitation from 48% HBr followed by washing with de-ionized water, ethanol, and diethyl ether sequentially then drying under vacuum, as described in e-Eros Reagents for Organic Chemistry.<sup>2</sup> N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%), 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) (Aldrich, 97%), Dowex 50WX8-200 ion exchange resin (Aldrich), neutral alumina ( $Al_2O_3$ , activated, neutral, 50-200 µm, 60 Å, Acros Organics), basic alumina (Al<sub>2</sub>O<sub>3</sub>, powder, Baker Analyzed) tetrahydrofuran (THF) (EMD, GC grade), dichloromethane (DCM) (ACS grade), methanol (ACS grade, EMD), hexanes (ACS grade, EMD), and toluene (ACS grade, EMD) were used as received. For the synthesis of metalloinitiator (1)  $\alpha$ -Bromoisobutyryl bromide (BIBB) (Aldrich, 98%) was distilled under reduced pressure, and triethylamine (NEt<sub>3</sub>) (EMD, ACS reagent grade) was distilled at atmospheric pressure under argon. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DRX 500 MHz or a Bruker Avance III 400 MHz spectrometer. Chemical shifts were referenced to Si(Me)<sub>4</sub> ( $\delta$  0.00 ppm) for <sup>1</sup>H NMR and the CDCl<sub>3</sub> solvent peak ( $\delta$  77.0 ppm) for <sup>13</sup>C NMR. MestReNova 10.0 software was used for spectral processing. IR spectra were obtained on a Nicolet Avatar 360 FT-IR with EZ-OMNIC software for H<sub>2</sub>O and CO<sub>2</sub> correction. Resolution set to 0.964 cm<sup>-1</sup> for all IR spectra. During quantification of molar absorptivity ( $\epsilon$ ) for

Fe-CO stretches in 1 and resulting metallopolymers 128 scans were used. A Fisher Scientific FT-30 30specRFL500700\*L IRSEC cell with 0.5 mm Teflon spacer (total path length = 1 mm) and CaF<sub>2</sub> window (Alfa-Aesar) was used for quantitative IR measurements. Determination of  $\varepsilon$ for Fe-CO's was performed by preparing 10 mL of ca. 1.0 mM 1 in CHCl<sub>3</sub> using volumetric glassware. This stock was diluted to ca. 0.1 mM, 0.2 mM, 0.4 mM, and 0.6 mM in four separate 5 mL volumetric flasks using a 1 mL syringe to transfer the stock solution, then diluting to volume. The measurement was performed in triplicate and R<sup>2</sup> values for each linear regression were 0.98 or better. Qualitative IR was performed using solutions in CHCl<sub>3</sub> in thin films between NaCl plates (Fisher Scientific). Spectral processing and graphing were performed using Microsoft Excel, Origin Pro 8.0, and Prism Graph Pad 5.0. Molecular weight (M<sub>n</sub>) and molecular weight distribution  $(M_w/M_p)$  of metallopolymers were determined by gel permeation chromatography (GPC). Molecular weight and molecular weight distribution data for PDMAEMA metallopolymers and PDMAEMA-random-POEGMA metallocopolymers were collected by using GPC with a Waters 515 HPLC pump, Wyatt Optilab refractive index detector, and PSS GRAM columns containing polyester copolymer networks with 50 mM LiBr DMF solution as eluent phase at a flow rate of 1mL/min at 50 °C. The GPC analyses for POEGMA metallopolymers were performed in a THF mobile phase with a Waters 1515 isocratic pump running three 5-µm PLgel columns (Polymer Labs, pore size 10<sup>4</sup>, 10<sup>3</sup> and 10<sup>2</sup> Å) at a flow rate of 1.0 mL/min at 35 °C with a Waters 2414 differential refractometer and a Waters 2487 dual-wavelength UV-vis spectrometer. Molar masses were calculated using the Waters Empower software, calibrated against low polydispersity linear poly(methyl methacrylate) PMMA and polystyrene (PS) standards. pH measurements made using Fisher Scientific Accumet AE150 pH meter calibrated with pH 4.01, 7.00, and 10.01 standards (Sigma-Aldrich).

# b. Synthesis of [2Fe-2S]-Initiator [µ-2,3-(naphthalene-1,4-diylbis(2-bromo-2-methylpropanoate)dithiolato]bistricarbonyliron (1)

*i.* Synthetic Procedure. The starting material was synthesized as previously reported<sup>3</sup> and analyzed via <sup>1</sup>H NMR to determine what mol% had been oxidized to the guinone product by comparing the integral values for the protons at the  $C_5$  and  $C_6$  positions in both compounds. The sample was found to contain ca. 30-40% quinone catalyst, so ca. 0.4 equivalents of reducing agent were used. NaCNBH<sub>3</sub> (2.26 mg, 0.036 mmol) was weighed on a micro balance and added to a dry, argon filled Schlenk flask. The starting material ((µ-1,4-naphthoguinone-2,3dithiolato)Fe<sub>2</sub>S<sub>2</sub>(CO)<sub>6</sub>, 30-40% oxidized to naphthoquinone adduct) (45 mg, 0.090 mmol) was added to the flask. The flask was then evacuated and filled with argon twice. Anhydrous, deoxygenated THF (2 mL) was added to the flask. The solution was stirred at room temperature in the dark for 2 hours. NEt<sub>3</sub> (75  $\mu$ L, 0.54 mmol) was then added via micro syringe and the solution was stirred for 20 minutes. BIBB (30 µL, 0.22 mmol) was added via micro syringe and the solution was stirred at room temperature. TLC indicated complete consumption of the starting material 2.25 hours after the addition of BIBB. The solution was filtered through a short silica plug in a Pasteur pipette to remove precipitate. DCM was used to rinse the column until no red color was visible in the eluent. The combined organics were concentrated on rotary evaporator (23 °C, ca. 200 torr) to a red/orange solid. The solid was redissolved in minimal DCM and purified via column chromatography (SiGel, pack with 15% DCM in hexanes, elute with 3035% DCM in hexanes). The pure compound was obtained as a red band which yielded 63 mg (0.079 mmol, 87%) powdery orange solid upon removal of solvent. Subsequent syntheses produced isolated yields between 85-90% providing the BIBB reagent had not decomposed. Crystals suitable for electrochemical studies and synthesis of metallopolymers were obtained by dissolving 1 in toluene (100 mg/mL solution, 157 mg in 1.57 mL) in a narrow Schlenk tube. This solution was freeze-pump-thawed three times to degas, then the cold solution was layered with argon sparged methanol (12 mL). The solution was allowed to sit undisturbed for 72 hours, the supernatant liquid was removed via syringe and the crystals were transferred to an M porosity fritted glass funnel. Subsequent washing with ice cold methanol (3 x 0.5 mL) and drying on the funnel gave 67 mg of dark red needles (67 mg, 43%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 500 MHz, 298 K δ (ppm) 7.81 (2H, dd J = 6.5, 3.4 Hz) 7.49 (2H, dd J = 6.5, 3.4 Hz), 2.19 (12H, s). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 125 MHz, 298 K δ (ppm) 206.8 (OC-Fe), 168.3 (C=O), 143.0 (C1,4-O), 134.8 (C,2,3-S), 129.1 (C6,7-H), 128.1 (C9,10), 121.9 (C5,8-H), 54.8 (CH-Br), 31.0 (CH<sub>3</sub>). IR (CHCl<sub>3</sub>, thin film on NaCl): 3688 cm<sup>-1</sup> (w), 3619 cm<sup>-1</sup> (w, Csp<sup>2</sup>-H), 3154 cm<sup>-1</sup> (w, Csp<sup>2</sup>-H), 3019 cm<sup>-1</sup> (vs, Csp<sup>2</sup>-H), 2976 cm<sup>-1</sup> (w, Csp<sup>3</sup>-H), 2082 cm<sup>-1</sup> (Fe-CO, s), 2050 cm<sup>-1</sup> (Fe-CO, s), 2012 cm<sup>-1</sup> (Fe-CO, s) 1760 cm<sup>-1</sup> (C=O ester, w), 1522 cm<sup>-1</sup> (C=C, w), 1423 cm<sup>-1</sup> (C-H, w), 1210 cm<sup>-1</sup> (C-O, vs)

ii. <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Metalloinitiator (1)



Figure S1. <sup>1</sup>H NMR spectrum of 1



Figure S2. <sup>13</sup>C NMR spectrum of 1

iii. IR Spectra of 1



Figure S3. Full IR spectrum of 1 (solution in CHCl<sub>3</sub>, thin film on NaCl plates)



**Figure S4**. **a)** Overlay of IR spectra of Fe-CO stretching region for **1** for concentrations 0.1 mM to 1.0 mM. Baselines have been normalized to 100% transmittance. **b)** Linear regression plots for each Fe-CO peak in **1** generated from above spectra. Calculated  $\varepsilon$  values are 173.62 ± 1.92 M<sup>-1</sup> mm<sup>-1</sup> (2082 cm<sup>-1</sup>); 280.75 ± 1.11M<sup>-1</sup> mm<sup>-1</sup> (2050 cm<sup>-1</sup>); 186.4 ± 9.9 M<sup>-1</sup> mm<sup>-1</sup> (2012 cm<sup>-1</sup>)

#### iv. X-ray Crystallography of 1

**X-ray Diffraction Analysis:** Data was collected at the University of Arizona X-ray Diffraction Facility. Crystals were mounted onto a *MiTeGen* micromount under a protective film of Paratone® oil and diffraction data for all crystals were measured using a Bruker Kappa APEX II DUO diffractometer, with graphite-monochromated Mo-Kα radiation ( $\lambda = 0.71073$  Å) generated by a sealed tube, and an APEX II CCD area detector. The diffractometer was fitted with an Oxford Cryostream low-temperature device and data sets were collected using the *APEX2* software package (Bruker AXS Inc., Madison, WI, 2007). The data were corrected for absorption effects using a multi-scan method in *SADABS* (Sheldrick, G. M. University of Göttingen, Germany 1997). CCDC 1577155 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. All structures were solved by direct methods (*SHELXS-97*), and developed by full least-squares refinement based upon F<sup>2</sup> (*SHELXL*)<sup>4</sup> interfaced *via X-Seed*<sup>5</sup> and *OLEX2*<sup>6</sup> Crystallographic figures were prepared using *Mercury* (Version 3.9).



**Figure S5.** Oak Ridge thermal ellipsoid plot (ORTEP) diagram of **1** with hydrogen atoms omitted and thermal ellipsoids shown at 50% probability level. CCDC 1577155 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

#### v. Discussion of Spectroscopic Characterization of Metallopolymers

To confirm structural integrity of the [2Fe-2S] core after polymerization, IR spectroscopy of metalloinitiator **1** and metallopolymers **2-5** were conducted. The characteristic Fe-CO vibrational stretching modes in metalloinitiator **1** were observed at 2082, 2050, and 2012 cm<sup>-1</sup> and were similarly retained for the metallopolymers **2-5** with a very slight shift in of these peaks to 2080, 2050 and 2011 cm<sup>-1</sup>, along with a slight broadening of the third peak that allowed for resolution of new peaks at 2007 cm<sup>-1</sup>. These peaks, along with GPC UV-vis absorption confirmed that the [2Fe-2S] core survived atom transfer radical polymerization (ATRP) conditions. In order to estimate the concentration of [2Fe-2S] sites per mass unit of polymer, a calibration curve was constructed for the characteristic Fe-CO stretching frequencies (see **Figure S4**). Each batch of polymer was inspected via IR and a mmol.mg<sup>-1</sup> value was established using this calibration curve. This value was used to normalize metallopolymer concentrations for comparison where appropriate.

#### c. Synthesis and Characterization of PDMAEMA-g-[2Fe-2S] (2)

#### i. Synthesis of PDMAEMA-g-[2Fe-2S] (2)

 $(M)_{\circ}: (I)_{\circ}: (Cu^{I})_{\circ}: (L)_{\circ} = 100: 1: 1: 1$ 

ATRP of DMAEMA was adapted from the literature and modified for the synthesis of PDMAEMA metallopolymers.<sup>7–9</sup> A 10 mL Schlenk flask was loaded with Cu(I)Br (2.55 mg, 0.0178 mmol) and 0.20 mL of deoxygenated, anhydrous THF (DriSolv, uninhibited) was added to the flask followed by the addition of deoxygenated HMTETA (7.3 µL, 0.0267 mmol). The resulting mixture was stirred for 10 minutes to allow for the formation of the Cu-ligand complex. Then purified and deoxygenated DMAEMA (0.30 mL, 1.78 mmol) was added to the reaction flask. To a second 10 mL Schlenk flask metalloinitiator (1) (14.24 mg, 0.0178 mmol) was added and the flask was vacuumed and backfilled with argon three times. Then 0.30 mL of deoxygenated, anhydrous THF (DriSolv, uninhibited) was added in the second flask. The solution was stirred until homogeneous then the resulting metalloinitiator/THF mixture was transferred to the reaction flask and the flask was submerged in an oil bath preheated to 50 °C and the reaction was stirred at 50 °C for 90 minutes. After 90 minutes, the reaction flask was placed in an ice bath and 2.0 mL of deoxygenated THF was added to guench the polymerization. The reaction mixture was then transferred to the deoxygenated solution of Dowex resin in MeOH (700 mg in 20 mL of MeOH) and stirred for 1.5 hours to remove the copper catalyst. The red-orange solution was then filtered to remove Dowex resin and the methanol was removed on a rotary evaporator (200 torr, 23 °C). The crude, sticky solid was redissolved in a minimum amount of dichloromethane and precipitated in a rapidly stirred solution of hexanes (200 mL). The hexanes was decanted and precipitated reddish-brown polymer was rinsed with hexanes. The final solid was transferred to a vial as a solution in DCM, then solvent was removed on a rotary evaporator and dried overnight under vacuum (ca. 0.5 torr at room temperature). (66% conversion; 171 mg isolated yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K) δ (ppm) 7.63-7.43 (broad, aromatic, end group), 3.94 (2H, -OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 2.45 (2H, -OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 2.17 (6H, -OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 2.05-1.60 (2H, broad, aliphatic main chain), 1.44-1.28 (broad, methyl, end group) 1.07-0.68 (3H, broad, -CH<sub>3</sub>, main chain). IR (CHCl<sub>3</sub>, thin film on NaCl): 2950 cm<sup>-1</sup> (C-H stretching, strong), 2827 cm<sup>-1</sup> (C-H stretching of N(CH<sub>3</sub>)<sub>2</sub>, sharp), 2779 cm<sup>-1</sup> (C-H stretching of N(CH<sub>3</sub>)<sub>2</sub>, sharp), 2080 cm<sup>-1</sup> (Fe-CO, sharp), 2048 cm<sup>-1</sup> (Fe-CO, sharp), 2011 cm<sup>-1</sup> (Fe-CO, sharp), 1725 (C=O stretching, strong, sharp), 1459 cm<sup>-1</sup> (-CH<sub>2</sub>- bending, sharp), 1271 cm<sup>-1</sup> (C-O, sharp), and 1153 cm<sup>-1</sup> (C-N stretching, strong, sharp).  $M_n$ , sec = 12,700 g/mol,  $M_w/M_n$  = 1.27.

In all syntheses of PDMAEMA-*g*-[2Fe-2S] it was imperative to remove Cu species from the crude polymer as it was found to facilitate oxidative decomposition of the [2Fe-2S] core. Copper species are competently removed from POEGMA-*g*-[2Fe-2S] via neutral alumina column, however PDMAEMA is known<sup>10</sup> to complex Cu, so additional care had to be taken to ensure removal of all Cu species. After the reaction, stirring the crude polymer solution without exposing to air in degassed MeOH with Dowex-50 resin was found to be the preferred method of copper removal.

#### ii. <sup>1</sup>H NMR Spectrum of PDMAEMA-g-[2Fe-2S] (2)



Figure S6. <sup>1</sup>H NMR of 2 in CD<sub>2</sub>Cl<sub>2</sub>



**Figure S7. a)** DMF GPC of **2** ([DMAEMA]<sub>o</sub>/[**1**]<sub>o</sub>/[CuBr]<sub>o</sub>/[HMTETA]<sub>o</sub>: 100:1:1:1,  $M_{n, theo}$ = 11,176 g/mol,  $M_{n, NMR}$  = 10,050 g/mol,  $M_{n, SEC}$  = 12,700 g/mol,  $M_w/M_n$  = 1.27), **b)** overlay of IR spectra of Fe-CO stretching region for **1** *vs.* PDMAEMA-*g*-[2Fe-2S] (**2**)

#### d. Synthesis and Characterization of POEGMA-g-[2Fe-2S] (3)

i. Synthesis of POEGMA-g-[2Fe-2S] (3)

 $(M)_{\circ}: (I)_{\circ}: (Cu')_{\circ}: (L)_{\circ} = 25:1:1:1$ 

ATRP of oligo(ethylene glycol) methyl ether methacrylate (OEGMA, Mn: 475 g/mol) was adapted from the literature and modified for the synthesis of POEGMA metallopolymers.<sup>11–14</sup> A 10 mL Schlenk flask equipped with a magnetic stir bar was loaded with Cu(I)Br (2.65 mg, 0.0182 mmol), sealed with a rubber septum, evacuated and backfilled with argon three times. 0.1 mL of deoxygenated THF (DriSolv, uninhibited) via argon purged syringe was added to the flask followed by addition of deoxygenated PMDETA (3.8 µL, 0.0182 mmol). The resulting mixture was stirred for 10 minutes to allow for the formation of the light green Cu-ligand complex. Then, purified deoxygenated oligo(ethylene glycol) methyl ether methacrylate (Mn: 475 g/mol, 0.2 mL, 0.455 mmol) was added to the flask via argon purged syringe. To a second 10 mL Schlenk flask equipped with a magnetic stir bar, 1 (14.6 mg, 0.0182 mmol) was loaded and the flask was sealed with a rubber septum. The flask was evacuated and backfilled with argon three times, then 0.3 mL of deoxygenated and anhydrous THF (DriSolv, uninhibited) was added via purged syringe. The solution was stirred until homogeneous then the resulting mixture was sparged with argon for 1 min. The 1/THF mixture was transferred to the reaction flask via purged syringe and the flask was submerged in an oil bath preheated to 50 °C. The reaction was stirred for 2 hours under argon. After 2 hours, the resulting polymer mixture was diluted with 2.0 mL of DCM and passed through a short column of neutral alumina twice to remove the copper catalyst. The solvent was removed on a rotary evaporator and a red, viscous liquid polymer was obtained. The polymer was washed with 20 mL of hexanes twice and the

hexanes was decanted. The polymer was dried overnight under vacuum at room temperature. (>90% conversion; 120 mg isolated yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K)  $\delta$  (ppm) 7.58-7.36 (4H, broad, aromatic, end group), 4.09 (2H, -CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-), 3.80-3.40 (broad, -O(CH<sub>2</sub>CH<sub>2</sub>O)-), 3.34 (3H, -OCH<sub>3</sub>), 2.12-1.37 (2H, broad, aliphatic main chain), 1.33-1.20 (6H, broad, methyl, end group), 1.17-0.72 (3H, broad, methyl, main chain). IR (CHCl<sub>3</sub>, thin film on CaF<sub>2</sub>): 2878 cm<sup>-1</sup> (C-H stretching, strong), 2080 cm<sup>-1</sup> (Fe-CO, sharp), 2048 cm<sup>-1</sup> (Fe-CO, sharp), 2011 cm<sup>-1</sup> (Fe-CO, sharp), 1727 (C=O stretching, strong, sharp), 1457 cm<sup>-1</sup> (-CH<sub>2</sub>- bending, sharp), 1350 cm<sup>-1</sup> (-CH<sub>3</sub> bending, sharp), and 1100 cm<sup>-1</sup> (C-O-C stretching, strong, sharp). M<sub>n, SEC</sub> = 14,100 g/mol, M<sub>w</sub>/M<sub>n</sub> = 1.27

ii. <sup>1</sup>H NMR Spectrum of POEGMA-g-[2Fe-2S] (3)



Figure S8. <sup>1</sup>H NMR Spectrum of 3 in CD<sub>2</sub>Cl<sub>2</sub>

iii. GPC Analysis and IR Spectrum of POEGMA-g-[2Fe-2S] (3)



**Figure S9. (a)** THF GPC of **3** ([OEGMA]<sub>o</sub>/[**1**]<sub>o</sub>/[CuBr]<sub>o</sub>/[PMDETA]<sub>o</sub>: 25:1:1:1,  $M_{n, theo} = 12,675$  g/mol,  $M_{n, NMR} = 16,950$  g/mol,  $M_{n, SEC} = 14,100$  g/mol,  $M_w/M_n = 1.27$ ), **b)** overlay of IR spectra of Fe-CO stretching region for **1** *vs.* PEGMA-*g*-[2Fe-2S] **(3)** 

#### e. Synthesis and Characterization of P(DMAEMA-r-OEGMA)-g-[2Fe-2S] (4 & 5)

i. Synthesis of P(DMAEMA-r-OEGMA)-g-[2Fe-2S] (4 & 5)

(DMAEMA)<sub>o</sub> : (OEGMA)<sub>o</sub> : (I)<sub>o</sub> : (Cu<sup>I</sup>)<sub>o</sub> : (L)<sub>o</sub> = 15 : 15 : 1 : 1 : 1.5 - 50:50 Feed Ratio (4)

A 25 mL Schlenk flask equipped with a magnetic stir bar was loaded with Cu(I)Br (2.92 mg, 0.0198 mmol), sealed with a rubber septum and evacuated and backfilled with argon three times. 0.2 mL of deoxygenated THF (DriSolv, uninhibited) and HMTETA (8.07 µL, 0.0297 mmol) were added to the flask, respectively. The resulting mixture was stirred for 5-10 min to let the catalyst complex form. Monomers were purified by passing through a short column of basic alumina. Then, OEGMA (Mn: 475 g/mol, 0.130 mL, 0.297 mmol) and DMAEMA (0.05 mL, 0.297 mmol) were added to the flask using purged syringes, respectively. To a separate 10 mL Schlenk flask equipped with a magnetic stir bar, 1 (15.82 mg, 0.0198 mmol) was added. The flask was then sealed with a rubber septum and vacuumed/backfilled with argon three times. 1 was completely dissolved in 0.2 mL of deoxygenated THF (DriSolv, uninhibited) and the resulting mixture was sparged with argon for a minute. Finally, 1/THF mixture was added to the flask via purged syringe. The resulting solution was stirred in an oil bath at 50 °C for 2 hours. After the reaction, the polymer mixture was diluted with 2.0 mL of DCM. Then, the resulting solution was passed through a short column of neutral alumina. The solvent was removed in a rotary evaporator and the resulting red viscous liquid polymer was washed with 20 mL of hexanes twice. The hexanes was decanted and the polymer solution was dried under vacuum overnight at room temperature prior to use. (>90% conversion; ca. 180 mg isolated yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K) δ (ppm) 7.63-7.43 (broad, aromatic, end group), 4.06 (4H, -CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> and -CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-), 3.85-3.43 (broad, -O(CH<sub>2</sub>CH<sub>2</sub>O)-), 3.37 (3H, -OCH<sub>3</sub>), 2.56 (2H, -OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 2.28 (6H, -OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 2.08-1.33 (2H, broad, aliphatic

main chain), 1.33-1.18 (broad, methyl, end group) 1.16-0.70 (3H, broad, -CH<sub>3</sub>, main chain).  $M_{n, SEC}$  = 13.8 kg/mol,  $M_w/M_n$  = 1.61

#### (DMAEMA)<sub>o</sub> : (OEGMA)<sub>o</sub> : (I)<sub>o</sub> : (Cu<sup>I</sup>)<sub>o</sub> : (L)<sub>o</sub> = 35 : 15 : 1 : 1 : 1.5 - 70:30 Feed Ratio (5)

A 25 mL Schlenk flask equipped with a magnetic stir bar was loaded with Cu(I)Br (2.43 mg, 0.017 mmol), sealed with a rubber septum and evacuated and backfilled with argon three times. Monomers were purified by passing through a short column of basic alumina. 0.2 mL of deoxygenated THF (DriSolv, uninhibited) and HMTETA (6.92 µL, 0.025 mmol) were added to the flask, respectively. The resulting mixture was stirred for 5-10 min to let the catalyst complex form. Then, the monomers were added to the flask using purged syringes. To a separate 10 mL Schlenk flask equipped with a magnetic stir bar, 1 (13.57 mg, 0.017 mmol) was added. The flask was then sealed with a rubber septum and vacuumed/backfilled with argon three times. 1 was completely dissolved in 0.3 mL of deoxygenated THF (DriSolv, uninhibited) and the resulting mixture was sparged with argon for a minute. Finally, 1/THF mixture was added to the flask via purged syringe. The resulting solution was stirred in an oil bath at 50 °C for 2 hours. After the reaction, the polymer mixture was diluted with 2.0 mL of DCM. Then, the resulting solution was passed through a short column of neutral alumina. The solvent was removed in a rotary evaporator and the resulting red viscous liquid polymer was washed with 20 mL of hexanes twice. The hexanes was decanted and the polymer solution was dried under vacuum overnight at room temperature prior to use. (>90% conversion; 120 mg isolated yield). Mn, SEC = 13.3 kg/mol  $M_w/M_n = 1.53$ 

#### ii. <sup>1</sup>H NMR Spectra of P(DMAEMA-r-OEGMA)-g-[2Fe-2S] (4 and 5)



Figure S10. <sup>1</sup>H NMR Spectrum of 4 in  $CD_2Cl_2$  (mol % OEGMA = 44, mol % DMAEMA = 56)<sup>15</sup>



**Figure S11.** <sup>1</sup>H NMR spectrum of **5** in  $CD_2Cl_2$  (mol % OEGMA = 28, mol % DMAEMA = 72)

iii. GPC Analysis and IR Spectrum of P(DMAEMA-r-OEGMA)-g-[2Fe-2S] (4 and 5)



Figure S12. a) DMF GPC of 4 (on the left, purple line)

 $([DMAEMA]_{o}/[OEGMA]_{o}/[1]_{o}/[CuBr]_{o}/[HMTETA]_{o}=15:15:1:1:1.5, M_{n, theo}=10,283 g/mol, M_{n, SEC}=13.8 kg/mol, M_{w}/M_{n}=1.61),$ **b**) overlay of IR spectra of Fe-CO stretching region for**1**vs. P(DMAEMA-*r*-OEGMA)-*g*-[2Fe-2S] (**4**and**5**),**c**) DMF GPC of**5** $(on the right, pink line) ([DMAEMA]_{o}/[OEGMA]_{o}/[1]_{o}/[CuBr]_{o}/[HMTETA]_{o}=35:15:1:1:1.5, M_{n, theo}=13,427 g/mol, M_{n, SEC}=13,300 g/mol, M_{w}/M_{n}=1.53)$ 

## f. Electrochemical Analysis

### i. Procedures and Materials

A Gamry Interface 1000 and a Gamry Reference 3000 were used for all data collection with Gamry Framework 6 software. A custom airtight cell was designed and fabricated in house and is pictured below (Figure S13). Potentials in water were referenced to SHE using the standard conversion of +0.210 V vs. Ag/AgCI/3M KCI reference electrode. Silver wire (99.999% Alfa Aesar), KCI (99%, Alfa-Aesar, recrystallized twice from 0.1 M HCI), and Vycor frits were used to fabricate a double junction reference electrode to fit the cell. A Ag/AgCl/3M KCl pseudoreference electrode was fabricated by soaking silver wire in a commercial bleach solution (Clorox) for 16 hours. The wire was then rinsed thoroughly with 18 M $\Omega$  water and stored in 3M KCI. The reference electrode was refabricated frequently (daily up to weekly depending on use) to ensure a constant potential. A scan rate of 100 mV/s was used unless otherwise noted. Solution resistance was measured and compensated at 90% of measured cell resistance. A gold working electrode with a diameter of 0.3 cm (A = 0.071 cm<sup>2</sup>) and an edge plane graphite rod counter electrode (diameter 5 mm) were obtained from BASi. A gold amalgam electrode was prepared by immersing the tip of a 3 mm diameter gold electrode into liquid mercury for approximately 1 minute and carefully removing the excess mercury using filter paper. The mercury surface was refreshed between each scan. Aqueous solutions were prepared using 18  $M\Omega$  water purified using a Millipure water filtration system. Buffered solutions were made with NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> (VWR, ACS grade) according to literature preparations found in *Ruzin*, 1999 Plant Microtechnique and Microscopy accessed at (http://microscopy.berkeley.edu/Resources/instruction/buffers.html) and adjusted to exact pH using 1.0 M HCl or 4.0 M NaOH. A 1.6 mm diameter Pt disk electrode was used to provide comparison of HER activity at a Pt surface with HER activity of the catalysts. Aqueous solutions were prepared in air and deoxygenated in the cell by bubbling the stirred solution with argon for 30 minutes. Aerobic experiment conditions were achieved by not bubbling the solution with argon.



**Figure S13.** Cyclic voltammetry cell used for data collection. Working electrode (W.E.), reference electrode (R.E.), and counter electrode (C.E.) are all labeled, as well as the argon line into the cell.



**Figure S14.** Cyclic voltammetry of [2Fe-2S]-metallopolymers in pH 7 sodium phosphate buffer (0.75 M) in both anaerobic (blue) and aerobic (red) conditions for a) POEGMA-*g*-[2Fe-2S], **3** b) 50/50-r-copolymer-*g*-[2Fe-2S], **4** c) 70/30-r- copolymer-*g*-[2Fe-2S], and **5** d) PDMAEMA-*g*-[2Fe-2S] **2**. The scans were taken using a gold amalgam electrode and a scan rate of 50 mV/s.



**Figure S15.** a) LSV comparison of **PDMAEMA**-*g*-[2Fe-2S] (2) (red), **POEGMA**-*g*-[2Fe-2S] (3) (blue), and random copolymers (**DMAEMA**/**OEGMA** 50/50 (4), purple, and 70/30 (5), pink) in pH 7.0 sodium phosphate buffer (0.75 M) and polymer concentration of 0.2-0.3 wt% (0.1 mM [2Fe-2S] by IR. Data collected at a scan rate of 5 mV/s and stir rate of 1600 rpm. b) Tafel analysis of LSV data. c) LSV comparison of PDMAEMA (red), POEGMA (blue), and random copolymers (DMAEMA/OEGMA 70/30 = pink, 50/50 = purple) under aerobic conditions in pH 7.0 sodium phosphate buffer (0.75 M) and polymer concentration of 0.2-0.3 wt% (0.1 mM [2Fe-2S] by IR. Data collected at a scan rate of 5 mV/s and stir rate of 1600 rpm. d) Tafel analysis of LSV data.





**Figure S16.** Linear sweep voltammetry of the four metallopolymer systems under aerobic (blue) and anaerobic (red) conditions in pH 7 sodium phosphate buffer (0.75 M) a) POEGMA-*g*-[2Fe-2s], **3** b) 50/50 *r*-copolymer, **4** c) 70/30 *r*-copolymer, **5** d) PDMAEMA-*g*-[2Fe-2S], **2** 

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