## **Supplementary Information**

# Immobilization of a non-heme diiron complex encapsulated in ammonium type ionic liquid layer modified on a Au electrode: Reactivity of the electrode for O<sub>2</sub> reduction

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# Chemicals

All reagents and organic solvents were purchased from Wako Pure Chemical Industries, Ltd., TCI, Kanto Chemical Co., Inc., and Nakalai Tesque and were used without further purification. Milli-Q water was obtained using a Millipore Biocel system connected to an EYELA SA-2100E automated water distillation apparatus.

# Apparatus

<sup>1</sup>H NMR spectra were measured on a Varian Gemini 300 MHz NMR spectrometer in CDCl<sub>3</sub> or  $D_2O$  with TMS or DSS as an internal reference standard, respectively. The concentration of each sample was adjusted to about 10 mM in a sample tube ( $\emptyset$  5 mm). Fourier transform infrared (FT-IR) spectra were taken using a JASCO FT/IR-4200 spectrometer. Attenuated total reflection spectra were recorded using a JASCO ATR PRO410-S attachment. Reflection-adsorption spectra were measured using a JASCO RAS-PRO410-H attachment. Electrospray ionization-time of flight (ESI-TOF) mass spectra were obtained with a LCT ESI-TOF spectrometer (Micromass).

# Electrochemistry

Electrochemical measurements were performed using a Hokutodenko HZ-5000 electrochemical analyzer. The cyclic voltammograms were recorded using either a glassy carbon electrode or each fabricated electrode as a working electrode, a Pt wire as a counter electrode and an Ag/AgCl (3 M NaCl) as a reference electrode or  $Ag/Ag^+$ . A 0.1 M solution of NaClO<sub>4</sub>, a 0.1 M solution of tetrabutylammonium perchlorate (TBAP) or a 0.5 M solution of KOH was used as the electrolyte. Electrochemical measurements with rotating ring-disk electrode (RRDE) were carried out using a Hokutodenko RRDE system HR-301 (ring electrode: Pt, disk electrode: Au).

# Preparation of the ionic liquid with disulphide group 1

The procedures used in the preparation of 1 are summarized in Scheme S1.

#### Preparation of N-(5-hexenyl)phthalimide

6-Bromo-1-hexene (4.33 g, 26.6 mmol) was completely dissolved in N,N-dimethylformamide

(DMF) (175 mL). To the DMF solution was added potassium phthalimide (6.85 g, 37.0 mmol) and refluxed overnight. To the resultant solution was added 175 ml of distilled water. The solution was extracted with diethyl ether. The organic layer was washed with H<sub>2</sub>O (100 mL × 3) and brine (100 mL × 2). After drying over anhydrous MgSO<sub>4</sub>, a viscous pale yellow liquid was obtained by evaporation. Yield 5.42 g (89 %). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, *vs.* TMS):  $\delta$  1.44 (m, 2H, -CH<sub>2</sub>-), 1.68 (m, 2H, -CH<sub>2</sub>-), 2.08 (m, 2H, -CH<sub>2</sub>-), 3.69 (t, 2H, NCH<sub>2</sub>), 4.92-5.04 (m, 2H, =CH<sub>2</sub>), 5.77 (m, 1H, -CH=CH<sub>2</sub>), 7.72 (m, 2H, Ar), 7.83 (m, 2H, Ar).

# Preparation of hex-5-en-1-amine

*N*-(5-Hexenyl)phthalimide (5.00 g, 21.8 mmol) and H<sub>2</sub>NNH<sub>2</sub> · H<sub>2</sub>O (1.37 g, 27.3 mmol) were dissolved in 150 mL of ethanol, and the solution was refluxed for 6 hours. After adding 2.8 mL of concentrated hydrochloric acid to the resulting solution, the solution was cooled down in ice chilled water bath and filtered to remove precipitate in it. The filtrate was dried by evaporation and 100 ml of chilled water was added to the residue. The aqueous solution was filtered to remove insoluble impurities. A certain amount of sodium hydroxide was added to the filtrate until separation of organic layer. The organic layer was extracted from the aqueous solution with diethyl ether (35 mL × 5). After drying over anhydrous MgSO<sub>4</sub>, a viscous pale yellow liquid was obtained by evaporation. Yield 1.79 g (83 %). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, *vs.* TMS):  $\delta$  1.17 (s, 2H, NH<sub>2</sub>), 1.44 (m, 4H, -CH<sub>2</sub>-), 2.08 (m, 2H, -CH<sub>2</sub>-), 2.69 (t, 2H, NCH<sub>2</sub>), 4.92-5.04 (m, 2H, =CH<sub>2</sub>), 5.81 (m, 1H, -CH=CH<sub>2</sub>).

#### **Preparation of trihex-5-enylamine**

Hex-5-en-1-amine (1.00 g, 10.1 mmol) and 6-bromo-1-hexene (3.44 g, 21.1 mmol) were completely dissolved in acetonitrile (100 mL). To the acetonitrile solution was added sodium carbonate (8.49 g, 80.1 mmol), and the solution was refluxed for 2 days. After that, 200 mL of 1 M NaOH aqueous solution was added to the resultant solution. The solution was extracted with chloroform, and the organic layer was dried over with anhydrous MgSO<sub>4</sub>. The organic solution was evaporated completely. The residue was purified by silica gel column chromatography (eluent: AcOEt). After evaporation to dryness, pale yellow oil was obtained. Yield 2.00 g (75 %). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, *vs.* TMS):  $\delta$  1.41 (m, 12H, -CH<sub>2</sub>-), 2.07 (m, 6H, -CH<sub>2</sub>-), 3.38 (t, 6H, NCH<sub>2</sub>), 4.91-5.04 (m, 6H, =CH<sub>2</sub>), 5.80 (m, 3H, -CH=CH<sub>2</sub>).

## Preparation of 12-bromododecyl(trihex-5-en)ammonium bromide

1,12-Dibromododecane (2.24 g, 6.83 mmol) was completely dissolved in acetone (10 mL). An acetone solution (10 mL) of trihex-5-enylamine (1.80 g, 6.83 mmol) was added dropwise to the solution. The resultant solution was refluxed for 5 days. The reaction mixture was evaporated completely. The resulting brown oil was purified by silica gel column chromatography (eluent:

AcOEt/MeOH = 9/1). After evaporation to dryness, a highly viscous brown oil was obtained. Yield 1.61 g (40 %). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, *vs.* TMS):  $\delta$  1.27-1.85(m, 32H, -CH<sub>2</sub>-), 2.14 (m, 6H, -CH<sub>2</sub>-), 3.41 (m,10H, N<sup>+</sup>-CH<sub>2</sub>-, -CH<sub>2</sub>Br), 4.97-5.09(m, 6H, =CH<sub>2</sub>), 5.75(m, 3H, -CH=CH<sub>2</sub>). ESI-TOF MS (positive mode): m/z = 510.31 [M - Br<sup>-</sup>]<sup>+</sup>.

#### Preparation of 12-thiouroniumdoecyl(trihex-5-enyl)ammonium dibromide

Thiourea (0.23 g, 3.03 mmol) and 12-bromododecyl(trihex-5-en)ammonium bromide (1.57 g, 2.65 mmol) were dissolved in ethanol, and the solution was refluxed for 3 days. The reaction mixture was evaporated completely and the residue was dissolved in chloroform (200 mL). The organic layer was washed with water (100 mL × 3) and brine (100 mL × 1), and dried over with anhydrous MgSO<sub>4</sub>. After evaporation to dryness, a highly viscous yellow oil was obtained. Yield 0.82 g (46 %). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, *vs.* TMS):  $\delta$  1.27-1.85(m, 32H, -CH<sub>2</sub>-), 2.14 (m, 6H, -CH<sub>2</sub>-), 3.93 (m,10H, N<sup>+</sup>-CH<sub>2</sub>-, -CH<sub>2</sub>S), 4.99-5.09(m, 6H, =CH<sub>2</sub>), 5.76(m, 3H, -CH=CH<sub>2</sub>), 9.00(br, 4H, C<sup>+</sup>-NH<sub>2</sub>). ESI-TOF MS (positive mode): m/z = 253.61 [M - 2Br<sup>-</sup>]<sup>2+</sup>.

# Preparation of bis[12-(trihex-5-enylammonium)dodecyl]disulfide dibromide

12-Thiouroniumdoecyl(trihex-5-enyl)ammonium dibromide (0.79 g, 1.18 mmol) was dissolved in ethanol (30 mL). An aqueous solution (10 mL) of NaOH (0.099 g, 2.48 mmol) was added to the ethanol solution. The resultant solution was stirred for 4 days at room temperature. After evaporation, the residue was dissolved in CHCl<sub>3</sub> (80 mL) and washed with H<sub>2</sub>O (50 mL × 3) and brine (50 mL). After drying over anhydrous MgSO<sub>4</sub>, the solution was evaporated completely. The residue was purified by silica gel chromatography (eluent: CHCl<sub>3</sub>/MeOH (85/15 (v/v)). After evaporation to dryness, a yellow viscous liquid was obtained. Yield 0.19 g (14 %). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, *vs*. TMS):  $\delta$  1.27-1.72(m, 32H, -CH<sub>2</sub>-), 2.14 (m, 6H, -CH<sub>2</sub>-), 2.68 (t, 4H, -CH<sub>2</sub>S), 3.38 (m, 16H, N<sup>+</sup>-CH<sub>2</sub>-), 5.00-5.09 (m, 12H, =CH<sub>2</sub>), 5.75 (m, 6H, -CH=CH<sub>2</sub>). FT-IR (KBr, cm<sup>-1</sup>): 3073 (v<sub>C-H</sub> of the vinyl group), 2925, 2854 (v<sub>C-H</sub> of the methylene group and the methyl group), 1639 (v<sub>C=C</sub> of the vinyl group), 996, 910 ( $\delta_{C-H}$ ), 670 (v<sub>C-S</sub>). ESI-TOF MS (positive mode): m/z = 463.35 [M - 2Br<sup>-</sup>]<sup>2+</sup>.

# Preparationofbis[12-(trihex-5-enylammonium)dodecyl]disulfidebis(trifluoromethanesulfonate) (1)

Bis[12-(trihex-5-enylammonium)dodecyl]disulfide dibromide (0.15 g, 0.14 mmol) was dissolved in chloroform (5 mL). To the chloroform solution was added an ethanol solution (5 mL) of sodium trifluoromethanesulfonate (0.072 g, 0.42 mmol). The resultant mixture was stirred at room temperature for 1 day. After removal of the white precipitate (NaBr), the solution was evaporated completely. The residue was dissolved in CHCl<sub>3</sub> (30 mL) and washed with H<sub>2</sub>O (10 mL  $\times$  3). After drying over anhydrous MgSO<sub>4</sub>, the solution was evaporated completely. A pale yellow viscous

liquid was obtained. Yield 0.11 g (64 %). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, *vs.* TMS):  $\delta$  1.25-1.67(m, 32H, -*CH*<sub>2</sub>-), 2.13 (m, 6H, -*CH*<sub>2</sub>-), 2.68 (t, 4H, -*CH*<sub>2</sub>S), 3.24 (m, 16H, N<sup>+</sup>-*CH*<sub>2</sub>-), 5.00-5.08 (m, 12H, =*CH*<sub>2</sub>), 5.76 (m, 6H, -*CH*=CH<sub>2</sub>). FT-IR (KBr, cm<sup>-1</sup>): 3076 (v<sub>C-H</sub> of the vinyl group), 2926, 2855 (v<sub>C-H</sub> of the methylene group and the methyl group), 1640 (v<sub>C=C</sub> of the vinyl group), 1470 ( $\delta_{C-H}$  of the methylene group and the methyl group), 1263 (v<sub>C-F</sub> of the trifluoromethanesulfonate), 1153 (stretching vibration mode of a sulfonate group in the trifluoromethanesulfonate), 1031 (v<sub>S=O</sub> of the trifluoromethanesulfonate), 996, 912 ( $\delta_{C-H}$ ), 638 (v<sub>C-S</sub>). ESI-TOF MS (positive mode): m/z = 463.35 [M - 2TfO<sup>-</sup>]<sup>2+</sup>.

# Immobilization of the diiron complex into 1 SAM modified on Au electrode

### **Preparation of 1/Au**

Au film with a thickness of 1,000 Å was deposited onto a cleaved mica substrate ( $14 \times 14$  mm) at 1.0 Å s<sup>-1</sup> with a JIS-300AK vacuum coater (Sinku of Technology Co., Ltd.). The Au film was annealed with a hydrogen gas flame before it was dipped into each sample solution. A few drops of 1 were directly casted onto the Au film or disk electrode (Au) of a RRDE and each electrode was allowed to stand for 1 day. After removal of excess 1 by washing with EtOH and CHCl<sub>3</sub>, 1/Au was obtained. FT-IR (RAS, cm<sup>-1</sup>): 2925, 2854 (v<sub>C-H</sub> of the methylene group and the methyl group), 1640 (v<sub>C=C</sub> of the vinyl group), 1272 (v<sub>C-F</sub> of the trifluoromethanesulfonate), 1155 (stretching vibration mode of a sulfonate group in the trifluoromethanesulfonate), 1032 (v<sub>S=O</sub> of the trifluoromethanesulfonate), 996, 914 ( $\delta_{C-H}$ ), 639 (v<sub>C-S</sub>).

# Preparation of Fe<sub>2</sub>@1/Au

A few drops of 1 mM diiron complex ( $Fe_2$ ) methanol solution were directly casted onto the 1/Au and the 1/Au was allowed to stand for a couple of days under Ar atmosphere. After removal of excess  $Fe_2$  by washing with CH<sub>2</sub>Cl<sub>2</sub> and acetone,  $Fe_2@1$ /Au was obtained. FT-IR (RAS, cm<sup>-1</sup>): 2920, 2851 ( $v_{C-H}$  of the methylene group and the methyl group), 1694 ( $v_{C-O}$  of amide group in  $Fe_2$ ), 1647 ( $v_{C=C}$  of the vinyl group in 1), 1413 (pyridyl backbone in  $Fe_2$ ), 1271 ( $v_{C-F}$  of the trifluoromethanesulfonate), 1159 (stretching vibration mode of a sulfonate group in the trifluoromethanesulfonate ), 1034 ( $v_{S=O}$  of the trifluoromethanesulfonate), 956, 718 ( $\delta_{C-H}$ ), 639 ( $v_{C-S}$ ).

#### Preparation of Fe<sub>2</sub>@poly-1/Au

 $Fe_2@1/Au$  was immersed in a CH<sub>2</sub>Cl<sub>2</sub> solution (5 mL) of Grubbs catalyst 2<sup>nd</sup> generation (2 mg) at room temperature for a couple of hours. After washing the substrate with CH<sub>2</sub>Cl<sub>2</sub>,  $Fe_2@poly-1/Au$ was obtained. FT-IR (RAS, cm<sup>-1</sup>): 2916, 2849 (v<sub>C-H</sub> of the methylene group and the methyl group), 1453 (pyridyl backbone in  $Fe_2$ ), 1260, 1189 (v<sub>C-F</sub> of the trifluoromethanesulfonate), 1034 (v<sub>S=O</sub> of the trifluoromethanesulfonate), 718 ( $\delta_{C-H}$ ), 641 (v<sub>C-S</sub>).







Scheme S2. Synthetic scheme for preparation of the ammonium type ionic liquid containing terminal olefins and a disulphide group, 1.

Oxidation mechanism of Fe<sub>2</sub>



Scheme S3. Proposed oxidation and reduction mechanisms of  $Fe_2$  based on reference S1.



**Figure S1.** FT-IR spectra of **1** (ATR method) (black) and **1**/Au (IR-RAS method) (blue). (Left) C-H stretching vibration region. (Right) C-H deformation vibration regions of the counter anion, TfO<sup>-</sup>.



Figure S2. Cyclic voltammograms of the bare Au electrode (blue line) and 1/Au (red line) in 0.1 M NaClO<sub>4</sub> aq. (scan rate = 100 mV· s<sup>-1</sup>).



**Figure S3.** Liner sweep voltammograms of 1/Au (1<sup>st</sup> sweep: red line, 7<sup>th</sup> sweep: blue line) in 0.5 M KOH aq. (scan rate = 10 mV· s<sup>-1</sup>).



**Figure S4.** FT-IR spectra of **1** (ATR method) (black), **Fe**<sub>2</sub> (KBr method) (brown), **Fe**<sub>2</sub>@**1**/Au (RAS method) (green), and **Fe**<sub>2</sub>@**poly-1**/Au (RAS method) (blue). (Left) C-H stretching vibration region. (Right) C-H deformation vibration and counter anion, TfO<sup>-</sup> regions.



Figure S5. (a) Cyclic voltammogram of  $Fe_2@1/Au$  in 0.1 M NaClO<sub>4</sub> aqueous solution (scan rate = 0.1 V·s<sup>-1</sup>). (b) The plots of the peak current densities of  $Fe_2@1/Au$  towards the scan rates of CV measurement for  $Fe_2@1/Au$ .



**Figure S6.** (a) Cyclic voltammogram of  $Fe_2@poly-1/Au$  in 0.1 M NaClO<sub>4</sub> aqueous solution (scan rate = 0.1 V·s<sup>-1</sup>). (b) The plots of the peak current densities of  $Fe_2@poly-1/Au$  towards the scan rates of CV measurement for  $Fe_2@poly-1/Au$ .



**Figure S7.** Cyclic voltammogram of  $\mathbf{Fe}_2$  in 0.1 M TBAP CH<sub>2</sub>Cl<sub>2</sub> solution (scan rate = 0.1 V·s<sup>-1</sup>).



**Figure S8.** Disk and ring current densities *vs.* disk potentials of  $Fe_2@1/Au$  in 0.1 M NaClO<sub>4</sub> aqueous solution (scan rate = 5 mV·s<sup>-1</sup>, rotation rate = 100 rpm; ring potential was set to 1.0 V *vs.* Ag/AgCl in order to oxidize H<sub>2</sub>O<sub>2</sub>). Red and blue lines were measured under Ar and O<sub>2</sub> atmospheres, respectively.



**Figure S9.** Disk and ring current densities *vs.* disk potential of  $Fe_2@1/Au$  in 0.1 M NaClO<sub>4</sub> aqueous solution (scan rate = 5 mV·s<sup>-1</sup>, ring potential = 1.0 V *vs.* Ag/AgCl in order to oxidize H<sub>2</sub>O<sub>2</sub>). Rotation rate = 100 (purple lines), 400 (blue lines), 900 (sky blue lines), 1600 (green lines).



**Figure S10.** Disk and ring current densities *vs.* disk potential of  $Fe_2@poly-1/Au$  in 0.1 M NaClO<sub>4</sub> aqueous solution (scan rate = 5 mV·s<sup>-1</sup>, rotation rate = 100 rpm; ring potential was set to 1.0 V *vs.* Ag/AgCl in order to oxidize H<sub>2</sub>O<sub>2</sub>). Red and blue lines were measured under Ar and O<sub>2</sub> atmospheres, respectively.



**Figure S11.** Disk and ring current densities *vs.* disk potential of  $Fe_2@poly-1/Au$  in 0.1 M NaClO<sub>4</sub> aqueous solution (scan rate = 5 mV·s<sup>-1</sup>, ring potential was set to 1.0 V *vs.* Ag/AgCl in order to oxidize H<sub>2</sub>O<sub>2</sub>). Rotation rate = 100 (purple lines), 400 (blue lines), 900 (sky blue lines), 1600 (green lines).



**Figure S12.** Koutecky-Levich plots for  $Fe_2@1/Au$  ( $\blacktriangle$ ) and  $Fe_2@poley-1/Au$  ( $\bullet$ ) in 0.1 M NaClO<sub>4</sub> aqueous solution (scan rate = 5 mV·s<sup>-1</sup>).



**Figure S13.** Cyclic voltammograms of 1/Au in 0.1 M NaClO<sub>4</sub> aqueous solution under Ar (blue) and O<sub>2</sub> (red) conditions (scan rate =  $0.1 \text{ V} \cdot \text{s}^{-1}$ ).



**Figure S14.** Cyclic voltammograms of  $Fe_2@1/Au$  in 0.1 M NaClO<sub>4</sub> aqueous solution under Ar (blue) and O<sub>2</sub> (red) conditions (scan rate = 0.1 V·s<sup>-1</sup>).



**Figure S15.** Cyclic voltammograms of **Fe**<sub>2</sub>@**poly-1**/Au in 0.1 M NaClO<sub>4</sub> aqueous solution under Ar (blue) and O<sub>2</sub> (red) conditions (scan rate =  $0.1 \text{ V} \cdot \text{s}^{-1}$ ).

Table S1. Electrochemical data of Fe<sub>2</sub>@poly-1/Au and Fe<sub>2</sub>@1/Au

samples	E <sub>pa</sub> / V	E <sub>pc1</sub> / V	<i>E</i> <sub>pc2</sub> / V	$\Gamma_{complex}$ / mol cm <sup>-2</sup>	Ν	n <sub>app</sub>
Fe₂@poly-1/Au	0.17	0.07	-0.30	$4.4 \times 10^{-12}$	0.36	3.4
Fe <sub>2</sub> @1/Au	0.19	0.07	—	1.4 × 10 <sup>-11</sup>	0.43	2.6

Each *E* value was estimated in H<sub>2</sub>O with 0.1 M NaClO<sub>4</sub> (*vs.* Ag/AgCl at  $0.1 \text{ V s}^{-1}$ ). Each  $\Gamma_{complex}$  value stands for surface coverage of Fe<sub>2</sub> on disk electrode of RRDE and was estimated from each redox wave. Each *N* is a capture rate of H<sub>2</sub>O<sub>2</sub> on the ring electrode. Ring electrode was applied in 1.0 V *vs.* Ag/AgCl to oxidize H<sub>2</sub>O<sub>2</sub>. Each  $n_{app}$  is number of electrons related to the O<sub>2</sub> reduction on the disk electrode (*i.e.* Fe<sub>2</sub>@poly-1/Au or Fe<sub>2</sub>@1/Au).

## Notes and references

S1 H. Arii, Y. Funahashi, T. Ozawa, K. Jitsukawa, and H. Masuda, Journal of Organometallic Chemistry, 2007, 692, 343.