

Supplementary Information

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. ^1H NMR spectra were measured on a Varian Gemini 300 MHz NMR spectrometer in CDCl_3 or D_2O with TMS or DSS as internal reference standards. The concentration of each sample was adjusted to about 10 mM in a sample tube (\varnothing 5 mm). Fourier transform infrared (FT-IR) spectra were measured using a JASCO FT/IR-4200 spectrometer. Attenuated total reflection spectra were measured 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 SAM as a working electrode, a Pt wire as a counter electrode and an Ag/AgCl (3 M NaCl) as a reference electrode. A 0.1 M solution of NaClO_4 was used as the electrolyte.

Detailed preparation of the ionic liquid with disulphide group 1. The procedures used in the preparation of **1** are summarized in Scheme S1.

Preparation of 12-bromododecyl(trihexyl)phosphonium bromide. 1,12-dibromododecane (18.3 mmol) was completely dissolved in toluene (60 mL) under Ar. A toluene solution (60 mL) of trihexylphosphine (18.3 mmol) was added dropwise to this solution over the course of 2 h. The resultant solution was stirred for 68 h under Ar at room temperature and then the reaction mixture was evaporated completely. The resulting highly viscous yellow oil was purified by silica gel column chromatography (eluent: $\text{AcOEt}/\text{MeOH} = 9/1$). After evaporation to dryness, a viscous yellow oil was obtained. Yield 46.3%. ^1H -NMR (300 MHz, CDCl_3 , vs. TMS): δ 0.90 (m, 9H, $-\text{CH}_3$), 1.20-2.30 (m, 44H, $-\text{CH}_2-$), 2.45 (m, 8H, $-\text{P}^+\text{CH}_2-$), 3.42 (t, 2H, BrCH_2-). FT-IR (ATR (Ge), cm^{-1}): 2954, 2926, 2855 ($\nu_{\text{C-H}}$ of the methylene group and the methyl group), 1457 ($\delta_{\text{C-H}}$ of the methylene group). ESI TOF-MS (positive mode): $m/z = 535.5$ [$\text{M} - \text{Br}$] $^+$.

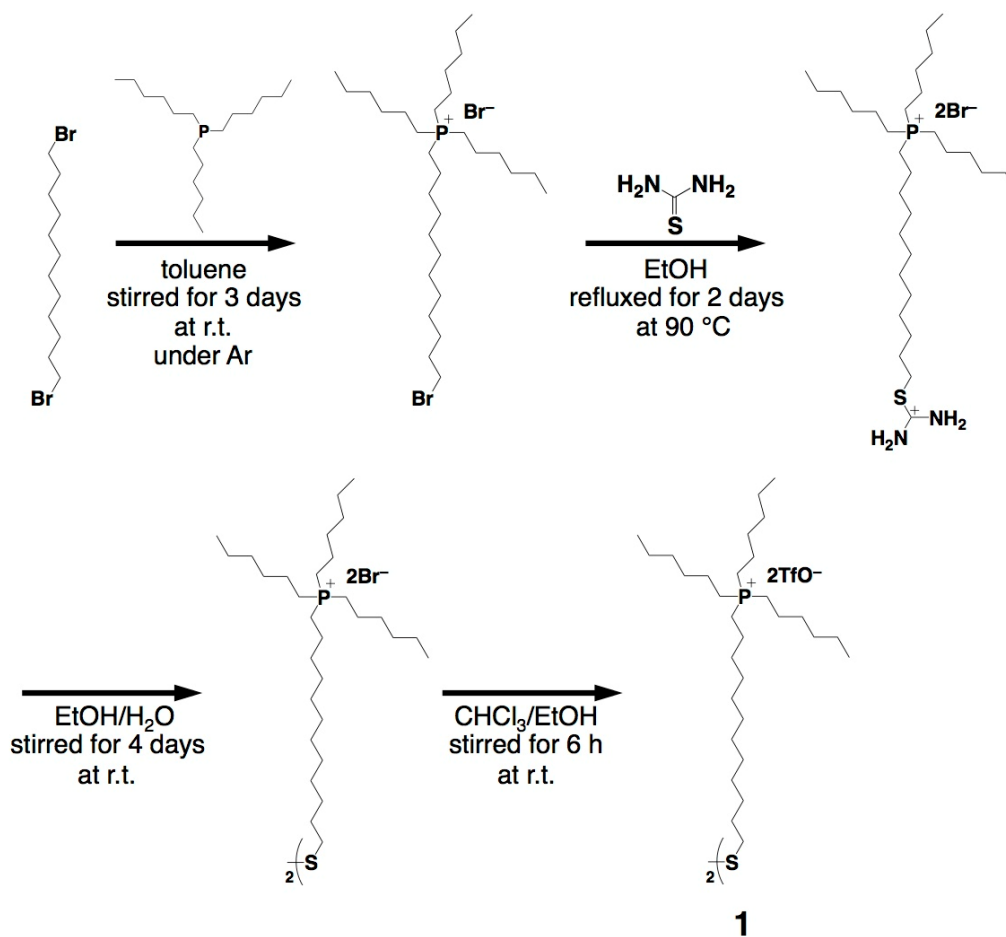
12-Thiuroniumdodecyl(trihexyl)phosphonium dibromide. Thiourea (4.05 mmol) and 12-bromododecyl(trihexyl)phosphonium bromide (3.30 mmol) was dissolved in EtOH (50 mL) and refluxed for 2 days at 90 °C. The resultant solution was evaporated completely. The residue was dissolved in CHCl₃ (200 mL) and washed with H₂O (100 mL x 3) and brine (100 mL). After drying over anhydrous MgSO₄, a viscous pale yellow liquid was obtained by evaporation. This liquid was purified by silica gel column chromatography (eluent: CHCl₃/MeOH (9/1v/v)). After evaporation to dryness, a viscous yellow liquid was obtained. Yield 33.0%. ¹H-NMR (300 MHz, CDCl₃, vs. TMS): δ 0.90 (m, 9H, -CH₃), 1.25-1.84 (m, 44H, -CH₂-), 2.31-2.58 (m, 8H, -P⁺CH₂-), 3.39 (t, 2H, BrCH₂-), 9.00 (br, 4H, -C⁺NH₂). FT-IR (ATR (Ge), cm⁻¹): 2956, 2923, 2853 (ν_{C-H} of the methylene group and the methyl group), 1652 (δ_{N-H} of the amino group), 1458 (δ_{C-H} of the methylene group), 743 (ν_{C-S}). ESI TOF-MS (positive mode): m/z = 529.7 [M - H - 2Br]⁺, 265.3 [M - 2Br]²⁺.

Bis[12-(trihexylphosphonium)dodecyl]disulphane dibromide. 12-Thiuroniumdodecyl-(trihexyl)phosphonium dibromide (1.03 mmol) was dissolved in EtOH (30 mL). An aqueous solution (10 mL) of NaOH (2.20 mmol) was added to this solution. The resultant solution was stirred for 4 days at room temperature. After evaporation, the residue was dissolved in CHCl₃ (80 mL) and washed with H₂O (50 mL x 3) and brine (50 mL). After drying over anhydrous MgSO₄, the solution was evaporated completely. The resulting yellow viscous liquid was purified by silica gel chromatography (eluent: AcOEt/MeOH 9/1(v/v) (1st) and CHCl₃/MeOH (9/1(v/v) (2nd)). After evaporation to dryness, a yellow viscous liquid was obtained. Yield 76.5%. ¹H-NMR (300 MHz, CDCl₃, vs. TMS): δ 0.90 (m, 18H, -CH₃), 1.25-1.71 (m, 88H, -CH₂-), 2.45 (m, 16H, -P⁺CH₂-), 2.68 (t, 4H, -SCH₂-). FT-IR (ATR (Ge), cm⁻¹): 2955, 2926, 2856 (ν_{C-H} of the methylene group and the methyl group), 1465 (δ_{C-H} of the methylene group), 748 (ν_{C-S}). ESI TOF-MS (positive mode): m/z = 1054.0 [M - Br]⁺, 486.5 [M - 2Br]²⁺.

Bis[12-(trihexylphosphonium)dodecyl]disulfane bis(trifluoromethanesulfonate)
1. Bis[12-(trihexylphosphonium)dodecyl]disulphane dibromide (0.394 mmol) was dissolved in CHCl₃ (25 mL). A EtOH solution (15 mL) of NaTfO (0.860 mmol) was added to the solution. The resultant mixture was stirred at room temperature until the TLC spot of starting material disappeared (eluent: CHCl₃/MeOH = 4/1, R_F = 0.7). After removal of the white precipitate (NaBr), the solution was evaporated completely. The

residue was dissolved in CHCl_3 (100 mL) and washed with H_2O (100 mL x 3). After drying over anhydrous MgSO_4 , the solution was evaporated completely. A pale yellow viscous liquid was obtained. Yield 82 %. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , vs. TMS): δ 0.90 (m, 18H, $-\text{CH}_3$), 1.25-1.69 (m, 88H, $-\text{CH}_2-$), 2.20 (m, 16H, $-\text{P}^+\text{CH}_2-$), 2.69 (t, 4H, $-\text{SCH}_2-$). FT-IR (ATR (Ge), cm^{-1}): 2957, 2927, 2855 ($\nu_{\text{C-H}}$ of the methylene group and the methyl group), 1465 ($\delta_{\text{C-H}}$ of the methylene group), 1260 ($\nu_{\text{C-F}}$ of TfO^-), 1153 sulfonate ($\nu_{\text{SO}_3^-}$ of TfO^-), 1030 ($\nu_{\text{S=O}}$ of TfO^-), 748 ($\nu_{\text{C-S}}$). ESI TOF-MS (positive mode): $m/z = 1121.7 [\text{M} - \text{TfO}^-]^+$, $486.3 [\text{M} - 2 \text{TfO}^-]^{2+}$.

Preparation of 1/Au. Au film with a thickness of 1,000 Å was deposited onto a cleaved mica substrate (14 × 14 mm) at 1.0 Å s^{-1} 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 and the Au film was allowed to stand for a few days. After removal of excess **1** by washing with EtOH and CHCl_3 , **1/Au** was obtained.



Scheme S1 Synthetic scheme for preparation of the ionic liquid containing the disulphide group, **1**.

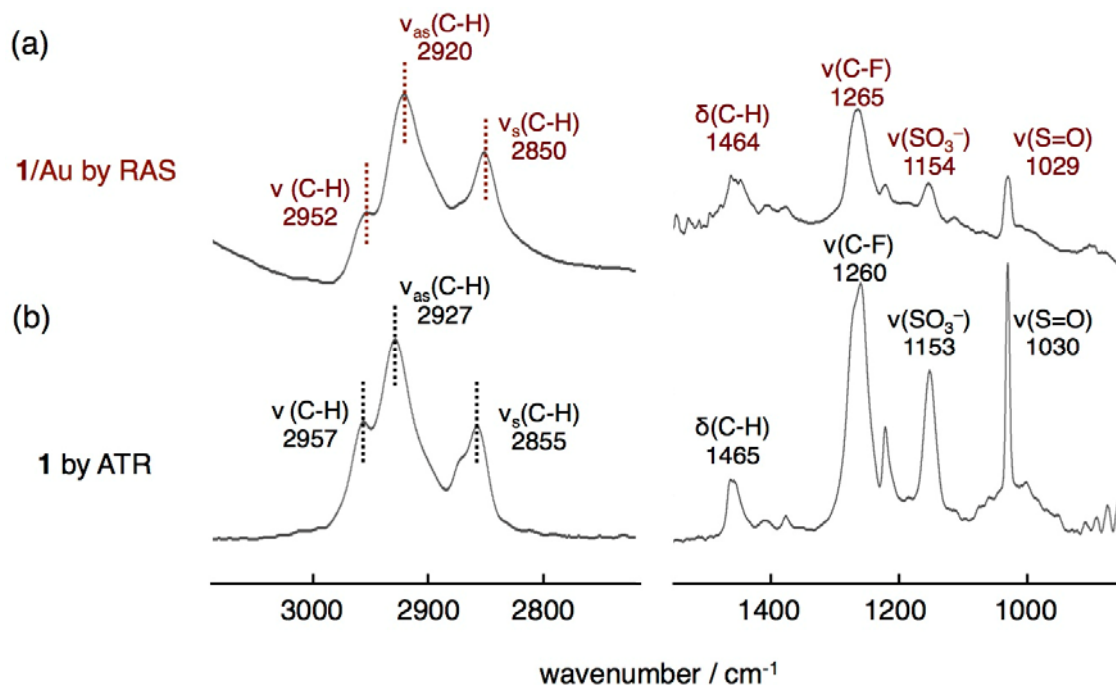


Fig. S1 FT-IR spectra of (a) **1/Au** (IR-RAS method) and (b) **1** (ATR method). (Left) C-H stretching vibration region. (Right) C-H deformation and counter anion regions of TfO^- .

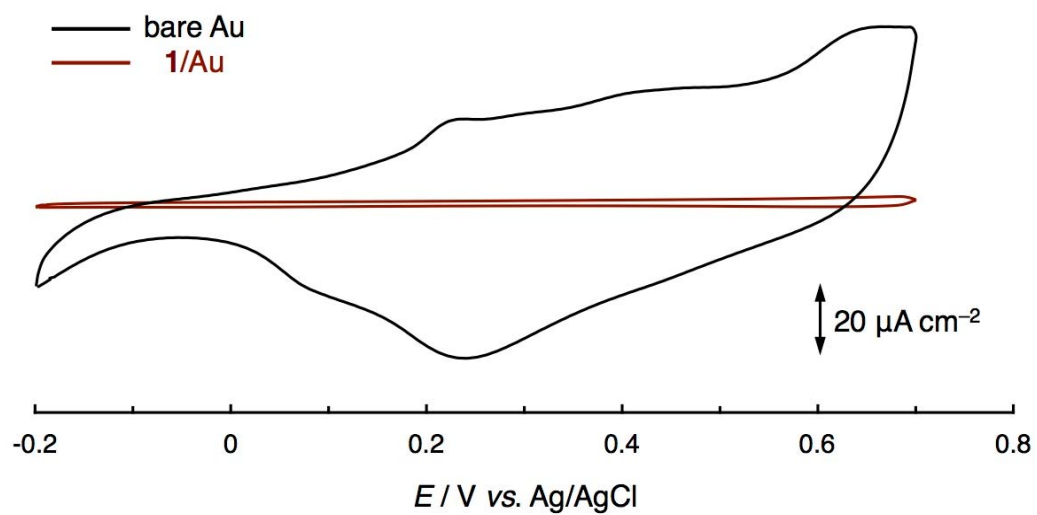


Fig. S2 Cyclic voltammograms of the bare Au electrode (black line) and 1/Au (red line) in 0.1 M $NaClO_4$ aq.

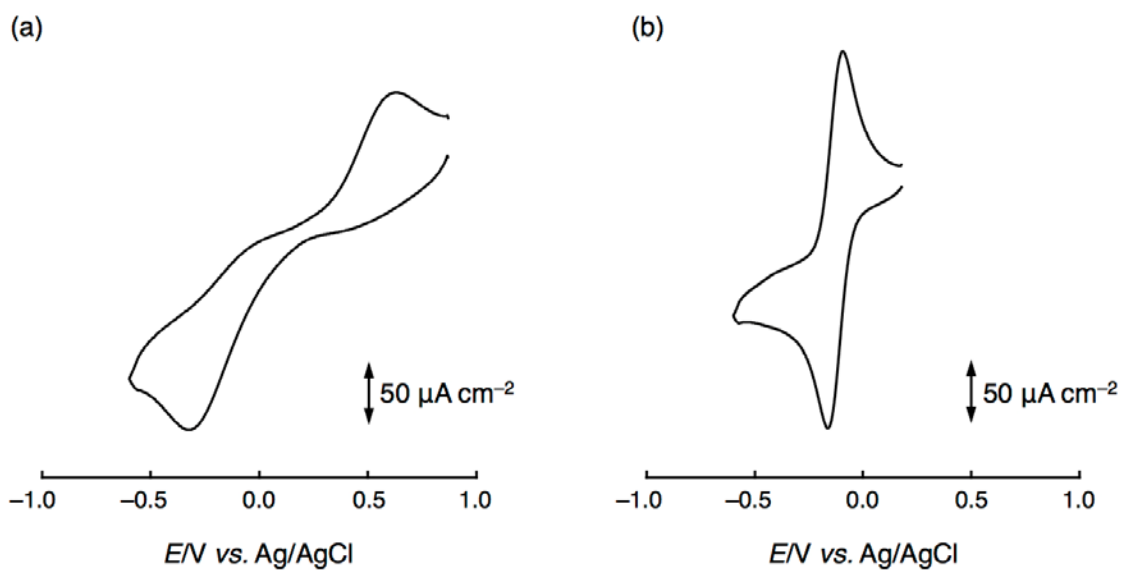


Fig. S3 Cyclic voltammogram of 1/Au in 0.1 M NaClO₄ (scan rate = 0.1 V s⁻¹) containing 0.5 mM (a) [Fe(CN)₆]³⁻ and (b) [Ru^{II}(NH₃)₆]²⁺.

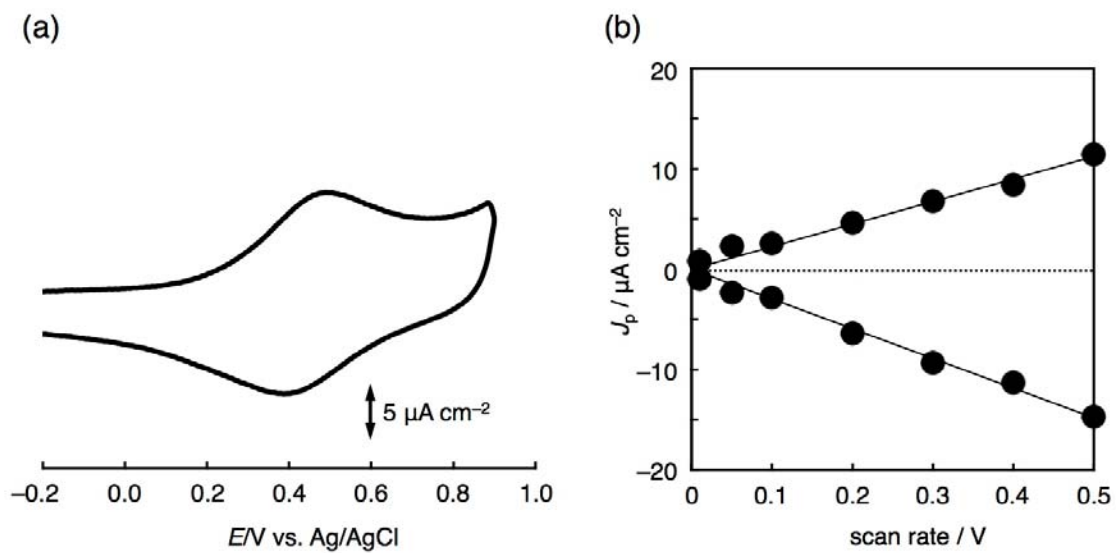


Fig. S4 (a) Cyclic voltammogram of **Fe@1/Au** in 0.1 M NaClO_4 (scan rate = 0.1 V s^{-1}).
(b) The linear relationship between scan rates and peak current densities of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ / $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$.

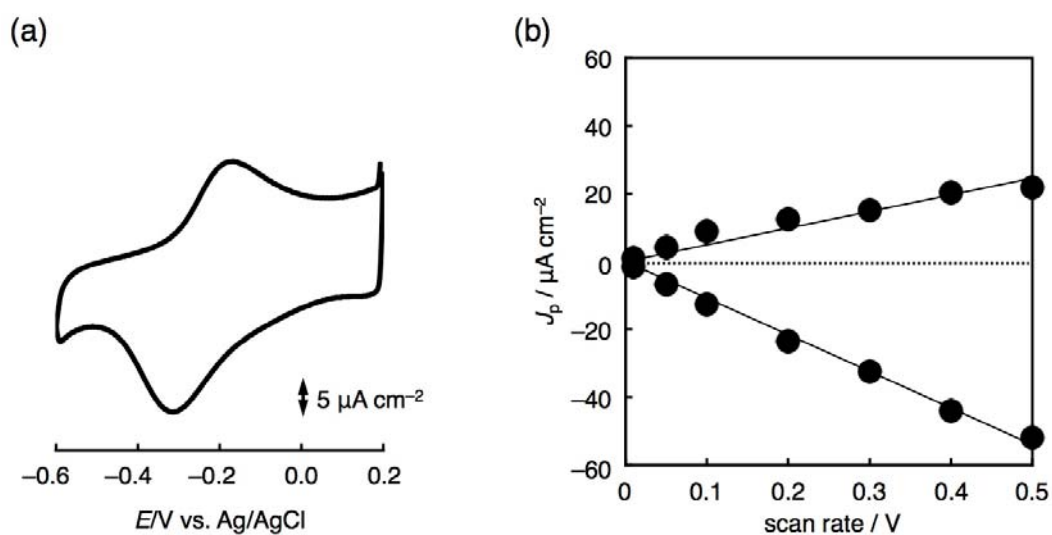


Fig. S5 (a) Cyclic voltammogram of **Ru@1/Au** in 0.1 M NaClO_4 (scan rate = 0.1 V s^{-1}).
(b) The linear relationship between scan rates and peak current densities of $[\text{Ru}^{\text{II}}(\text{NH}_3)_6]^{2+}/[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}$.