

**Supporting Information**

Electrochemical reduction of CO<sub>2</sub> to ethylene glycol on imidazolium ion-terminated self-assembly monolayer-modified Au electrodes in an aqueous solution

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## **Synthetic Methods and Analysis Data:**

### **1-(2-mercaptoethyl)-3-methylimidazolium bromide (IL-2)**

### **1-(6-mercaptohexyl)-3-methylimidazolium bromide (IL-6)**

### **1-(8-mercaptooctyl)-3-methylimidazolium bromide (IL-8)**

### **1-(12-mercaptododecyl)-3-methylimidazolium bromide (IL-12)**

## **General Methods.**

1-methylimidazole was reacted with dibromoalkane (methylene units = 2, 6, 8 and 12) in chloroform followed by substitution with potassium thioacetate in tetrahydrofuran and then saponification with NaOH aqueous solution and acidification with HBr aqueous solution. All reagents were used as received. 1-methylimidazole, potassium thioacetate (KSCOCH<sub>3</sub>), NaOH, HBr aqueous solution, chloroform, hexane, tetrahydrofuran, methanol and ethanol were obtained from Wako Pure Chemicals. 1,2-dibromoethane, 1,6-dibromohexane, 1,8-dibromooctane and 1,12-dibromododecane were obtained from Tokyo Chemical Industry. <sup>1</sup>H NMR spectra were obtained on a JEOL 270 MHz calibrated against the tetramethylsilane (TMS) standard.

## **Synthesis of 1-(2-mercaptoethyl)-3-methylimidazolium bromide (IL-2)**

A solution of 1-methylimidazole (3.60 g, 44.3 mmol) in chloroform (40 mL) was added to a solution of 1,2-dibromoethane (100 g, 532 mmol) at room temperature. The mixture was stirred at 35 °C for 24 h. The unreacted reagents were removed with hexane (100 mL x2). The obtained solution, 1-(2-bromoethyl)-3-methylimidazolium bromide, was purified by silica column chromatography (methanol / chloroform = 1 / 5).

Potassium thioacetate (1.52 g, 13.3 mmol) was added to a solution of 1-(2-bromoethyl)-3-methylimidazolium bromide (3.60 g, 13.3 mmol) in dry tetrahydrofuran (15 mL) at room temperature. The mixture was refluxed for 12 h. After cooling to room temperature, the unsolved precipitate was filtered off, and the filtrate was evaporated to remove tetrahydrofuran. The obtained solution, 1-(2-(S-acetyl)mercaptoethyl)-3-methylimidazolium bromide, was purified by silica column chromatography (methanol / chloroform = 1 / 5).

A solution of NaOH (0.528 g, 13.2 mmol) in H<sub>2</sub>O (10 mL) was added to a solution of 1-(2-(S-acetyl)mercaptoethyl)-3-methylimidazolium (1.40 g, 5.3 mmol) in ethanol (30 mL) at 0 °C. The mixture was stirred at the same temperature, and then acidified with 2N HBr until pH = 2. The resulting powder, 1-(2-mercaptoethyl)-3-methylimidazolium bromide, was dried with MgSO<sub>4</sub>, evaporated to remove solvents. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 2.85-3.01 (m, 3H), 3.89 (s, 3H), 4.37 (t, *J* = 6.26 Hz, 2H), 7.77 (s, 1H), 7.84 (s, 1H), 9.31 (s, 1H)

## **Synthesis of 1-(6-mercaptohexyl)-3-methylimidazolium bromide (IL-6)**

A solution of 1-methylimidazole (2.69 g, 32.7 mmol) in chloroform (40 mL) was added to a solution of 1,6-dibromohexane (25.0 g, 102 mmol) at room temperature. The mixture was stirred at 65 °C for 12 h. The unreacted reagents were removed with hexane (100 mL x2). The obtained solution, 1-(6-bromohexyl)-3-methylimidazolium bromide, was purified by silica column chromatography (methanol / chloroform = 1 / 5).

Potassium thioacetate (1.09 g, 9.52 mmol) was added to a solution of 1-(6-bromohexyl)-3-methylimidazolium bromide (3.10 g, 9.52 mmol) in dry tetrahydrofuran (15 mL) at room temperature. The mixture was refluxed for 12 h. After cooling to room temperature, the unsolved precipitate was filtered off, and the filtrate was evaporated to remove tetrahydrofuran. The obtained solution, 1-(6-(S-acetyl)mercaptohexyl)-3-methylimidazolium bromide, was purified by silica column chromatography (methanol / chloroform = 1 / 5).

A solution of NaOH (0.368 g, 9.2 mmol) in H<sub>2</sub>O (10 mL) was added to a solution of 1-(6-(S-acetyl)mercaptohexyl)-3-methylimidazolium (1.48 g, 4.6 mmol) in ethanol (30 mL) at 0 °C. The mixture was stirred at the same temperature, and then acidified with 2N HBr until pH = 2. The resulting solution, 1-(6-mercaptohexyl)-3-methylimidazolium bromide, was dried with MgSO<sub>4</sub>, evaporated to remove solvents. <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 1.35-1.64 (m, 7H), 1.90 (m, 2H), 2.50 (t, *J* = 7.09 Hz, 2H), 3.93 (s, 3H), 4.23 (t, *J* = 7.25 Hz, 2H), 7.58 (s, 1H), 7.65 (s, 1H), 8.98 (s, 1H)

#### **Synthesis of 1-(8-mercaptooctyl)-3-methylimidazolium bromide (IL-8)**

A solution of 1-methylimidazole (2.50 g, 30.6 mmol) in chloroform (40 mL) was added to a solution of 1,8-dibromooctane (25.0 g, 91.9 mmol) at room temperature. The mixture was stirred at 65 °C for 12 h. The unreacted reagents were removed with hexane (100 mL x2). The obtained solution, 1-(8-bromooctyl)-3-methylimidazolium bromide, was purified by silica column chromatography (methanol / chloroform = 1 / 5).

Potassium thioacetate (1.40 g, 12.3 mmol) was added to a solution of 1-(8-bromooctyl)-3-methylimidazolium bromide (4.34 g, 12.3 mmol) in dry tetrahydrofuran (15 mL) at room temperature. The mixture was refluxed for 12 h. After cooling to room temperature, the unsolved precipitate was filtered off, and the filtrate was evaporated to remove tetrahydrofuran. The obtained solution, 1-(8-(S-acetyl)mercaptooctyl)-3-methylimidazolium bromide, was purified by silica column chromatography (methanol / chloroform = 1 / 5).

A solution of NaOH (0.324 g, 8.10 mmol) in H<sub>2</sub>O (10 mL) was added to a solution of 1-(8-(S-acetyl)mercaptooctyl)-3-methylimidazolium (1.13g, 3.2 mmol) in ethanol (30 mL) at 0 °C. The mixture was stirred at the same temperature, and then acidified with 2N HBr until pH = 2. The resulting solution, 1-(8-mercaptooctyl)-3-methylimidazolium bromide, was extracted with CHCl<sub>3</sub>, and dried with MgSO<sub>4</sub>, evaporated to remove solvents. <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 1.36-1.61 (m, 10H), 1.86 (m, 3H), 2.48 (t, *J* = 7.09 Hz, 2H), 3.92 (s, 3H), 4.20 (t, *J* = 7.25 Hz, 2H), 7.57 (s, 1H), 7.64 (s,

1H), 8.93 (s, 1H)

### **Synthesis of 1-(12-mercaptododecyl)-3-methylimidazolium bromide (IL-12)**

A solution of 1-methylimidazole (2.00 g, 24.4 mmol) in chloroform (40 mL) was added to a solution of 1,12-dibromododecane (25.0 g, 76.2 mmol) at room temperature. The mixture was stirred at 65 °C for 12 h. The unreacted reagents were removed with hexane (100 mL x2). The obtained solution, 1-(12-bromododecyl)-3-methylimidazolium bromide, was purified by silica column chromatography (methanol / chloroform = 1 / 5).

Potassium thioacetate (1.04 g, 9.09 mmol) was added to a solution of 1-(12-bromododecyl)-3-methylimidazolium bromide (3.70 g, 9.09 mmol) in dry tetrahydrofuran (15 mL) at room temperature. The mixture was refluxed for 8 h. After cooling to room temperature, the unsolved precipitate was filtered off, and the filtrate was evaporated to remove tetrahydrofuran. The obtained solution, 1-(12-(S-acetyl)mercaptododecyl)-3-methylimidazolium bromide, was purified by silica column chromatography (methanol / chloroform = 1 / 5).

A solution of NaOH (0.368 g, 9.20 mmol) in H<sub>2</sub>O (10 mL) was added to a solution of 1-(12-(S-acetyl)mercaptododecyl)-3-methylimidazolium (1.49 g, 3.68 mmol) in ethanol (30 mL) at 0 °C. The mixture was stirred at the same temperature, and then acidified with 2N HBr until pH = 2. The resulting powder, 1-(12-mercaptododecyl)-3-methylimidazolium bromide, was extracted with CHCl<sub>3</sub>, and dried with MgSO<sub>4</sub>, evaporated to remove solvents. <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 1.30-1.63 (m, 19H), 1.88 (m, 2H), 2.48 (t, *J* = 7.09 Hz, 2H), 3.92 (s, 3H), 4.20 (t, *J* = 7.42 Hz), 7.57 (s, 1H), 7.64 (s, 1H), 8.93 (s, 1H)

### **The electrochemical cleaning by cyclic voltammetry (CV)**

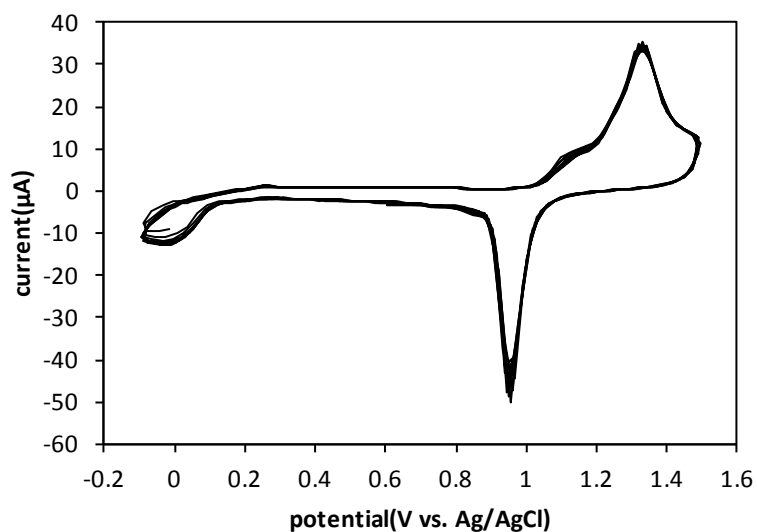
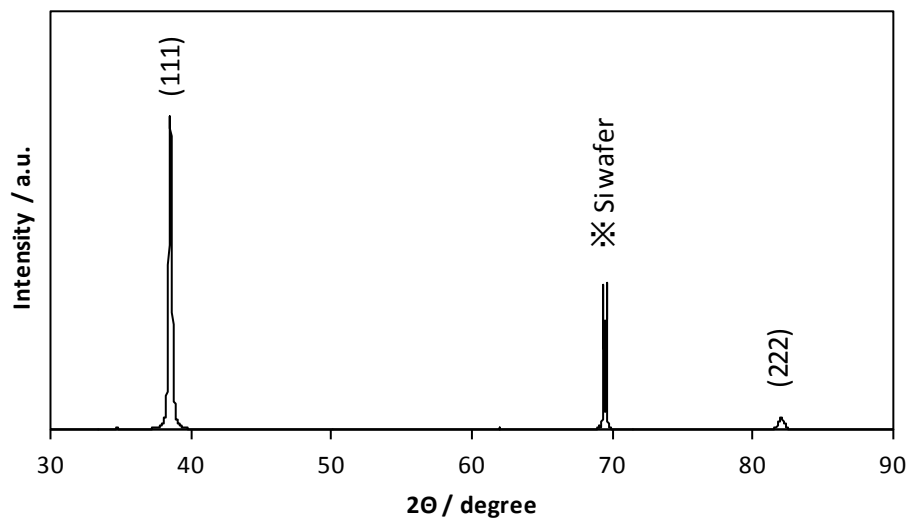


Figure S1. Cyclic voltammogram of cleaned gold electrode. The experiment was carried out with 1 M  $\text{H}_2\text{SO}_4$  at a scan rate of  $50 \text{ mVs}^{-1}$  for 10 min.

### **Investigation of an Au electrode surface after the electrochemical cleaning**

X-ray diffraction (XRD) patterns were collected at room temperature using a Rigaku SmartLab diffractometer. Atomic Force Microscope (AFM) images were collected using a Dimension Icon (Bruker AXS). The scan size was  $3 \times 3 \mu\text{m}^2$ , and the scan rate was 1.0 Hz. The roughness of the surface was defined as the roughness of root mean square (Rms). The electrochemical cleaning continuously oxidized and reduced an Au electrode surface. The roughness increased with adoption of wide oxidation - reduction potential or cleaning for a long time. The crystal of Au electrode had a face-centered structure (fcc) and there was no change after the electrochemical cleaning.

(a)



(b)

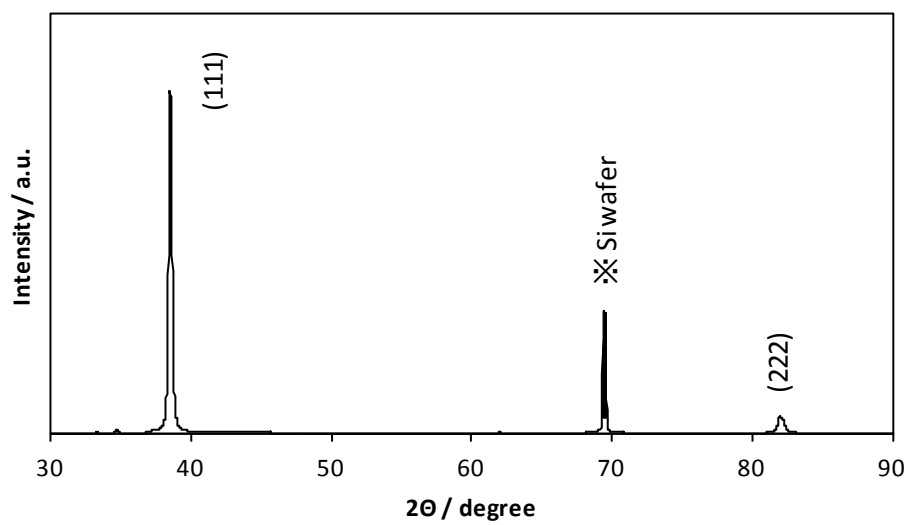
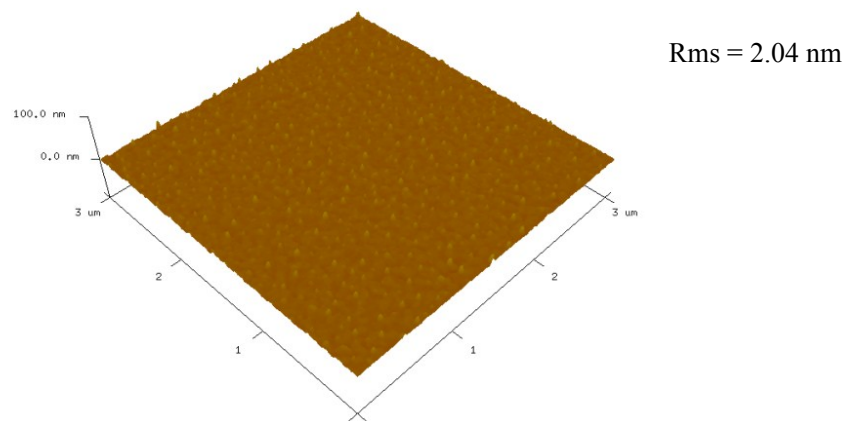


Figure S2. X-ray diffraction (XRD) patterns (a) before the electrochemical cleaning, (b) after the electrochemical cleaning

(a)



(b)

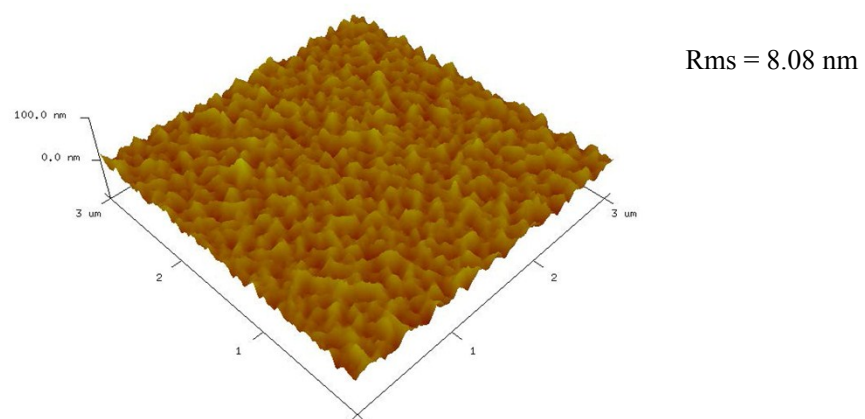


Figure S3. Atomic force microscope (AFM) images (a) before the electrochemical cleaning, (b) after the electrochemical cleaning

## Investigation of a SAM-modified Au electrode surface

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the samples were recorded using a JASCO FT/IR-6700 spectrometer equipped with an MCT (MCT\_M) detector with a resolution of  $4\text{ cm}^{-1}$ . The incidence angle of the Ge-ATR unit was 65 degrees. An accumulation of 128 scans was used for collecting the spectra. A bare gold mirror plate was used as a reference. A SAM-modified gold electrode was placed in the cell and pretreated by  $\text{N}_2$  flow in order to remove water and carbonate in the catalyst. FTIR showed  $\text{CH}_2$  stretching bands at  $2924$  and  $2854\text{ cm}^{-1}$ , characteristic of between a well-ordered and a disordered film.<sup>19</sup>

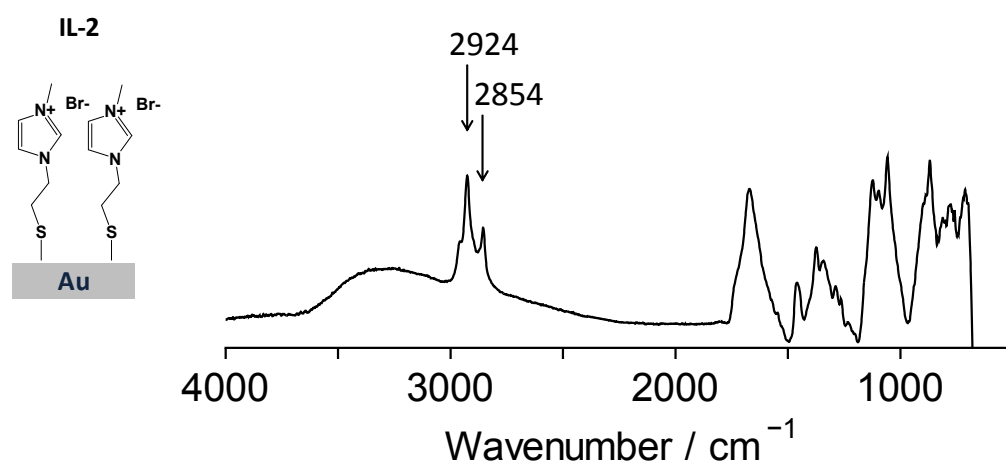


Figure S4. Surface ATR-FTIR spectrum of SAM (IL-2)-modified gold electrode

## Reference

19 R. G. Snyder, H. L. Strauss, and C. A. Elliger, *J. Phys. Chem.*, 1982, **86**, 5145-5150.



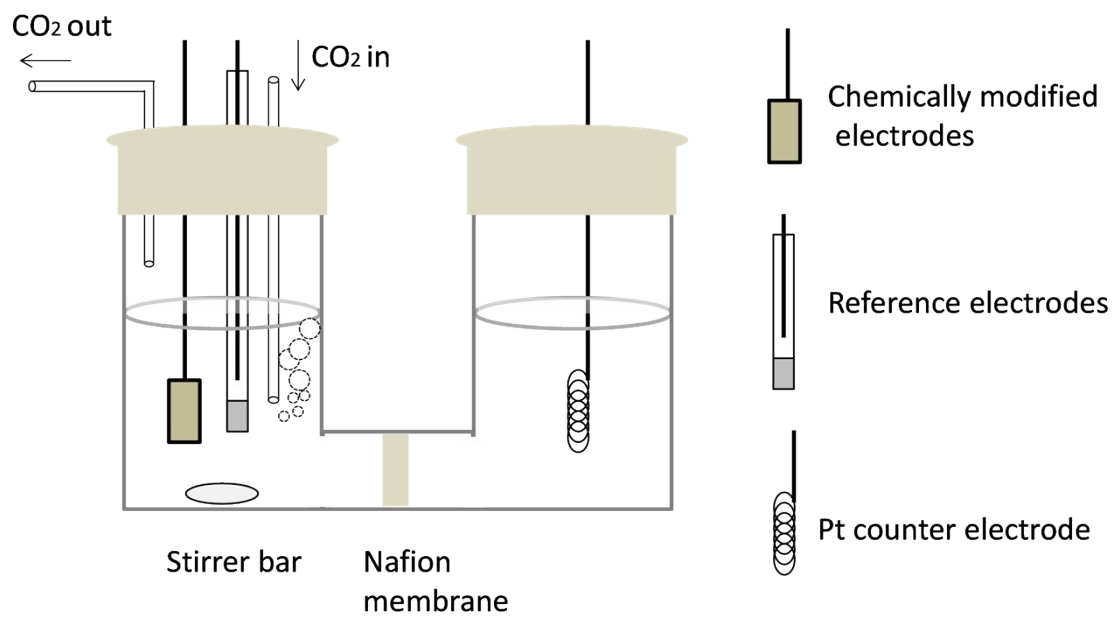


Figure S5. Schematic illustration of the two-compartment electrochemical cell employed for CO<sub>2</sub> electrolysis experiments. Each compartment contained NaHCO<sub>3</sub> aqueous solution saturated with CO<sub>2</sub>.

### Cyclic voltammogram of the IL-based SAMs-modified Au electrodes

The cyclic voltammograms compare the distance dependence of electron transfer through the different length IL-based SAMs on Au electrodes and the bare Au electrode. As the number of methylene units in the alkyl chain on the SAM-modified Au electrodes increased, the redox behavior was blocked and the ability of the SAM to passivate the Au electrode also increased. ILs-based SAMs acted as insulating layers for the positively charged redox molecule,  $\text{Ru}(\text{NH}_3)_6^{3+}$ , and realized high resistance to electron transfer through this layer. The blocking of faradaic electrochemistry is the evidence of the coverage of ILs-based SAMs on Au electrodes.<sup>20</sup>

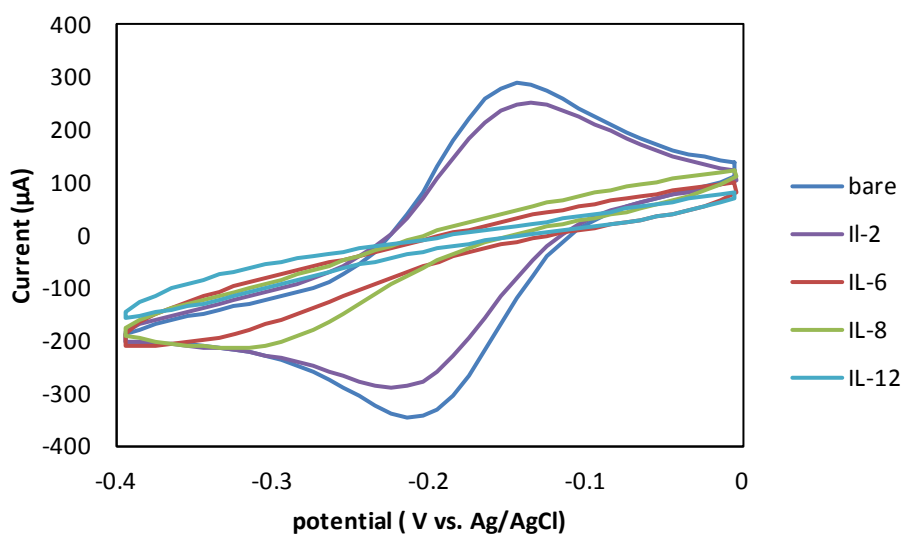
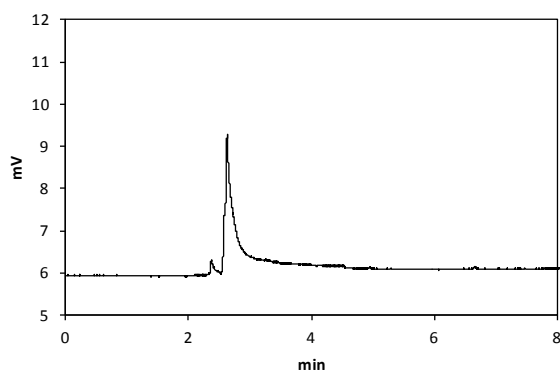


Figure S6. Cyclic voltammogram of the different length IL-based SAMs on Au electrodes and the bare Au electrode. All experiments were carried out in 0.1 M  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  dissolved in 0.5 M KCl, between the potential range of -400 to 0 mV, at a scan rate of  $100 \text{ mV s}^{-1}$  and were referenced relative to Ag / AgCl.

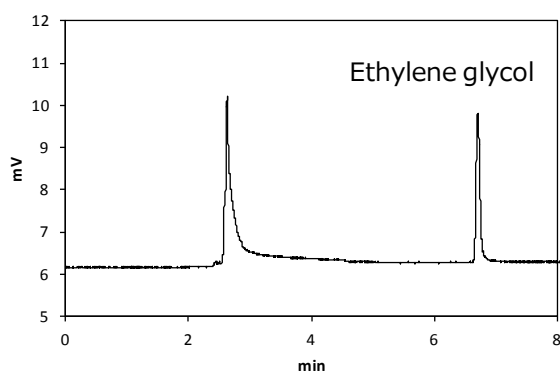
#### Reference

20 Y. Shen, J. Wang, U. Kuhlmann, P. Hildebrandt, K. Ariga, H. Möhwald, D. G. Kurth D, and T. Nakanishi, *Chem. Eur. J.* 2009, **15**, 2763-2767

(a)



(b)



(c)

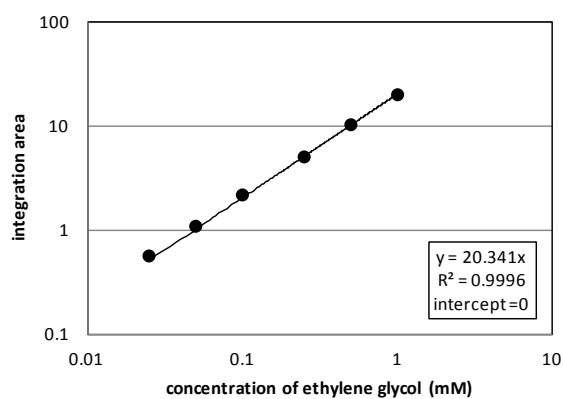


Figure S7. Gas chromatogram of the electrolyte solution in the cathodic compartment with IL-2-modified Au electrodes at -0.58 V for RHE in the CO<sub>2</sub>-purged NaHCO<sub>3</sub> aqueous solution. (a) Before reduction. (b) After 8 hour reduction. (c) GC calibration curve.

Ethylene glycol was analyzed on a JEOL 270 MHz spectrometer. A 0.5 mL aliquot of the electrolyte was mixed with 0.1 mL D<sub>2</sub>O and 1.67 ppm (m/m) dimethyl sulfoxide (DMSO, Wako

Pure Chemicals, 99.99%) was added as an internal standard for calibration. The 1D  $^1\text{H}$  spectrum was obtained with water suppression using a presaturation method. <sup>13</sup>

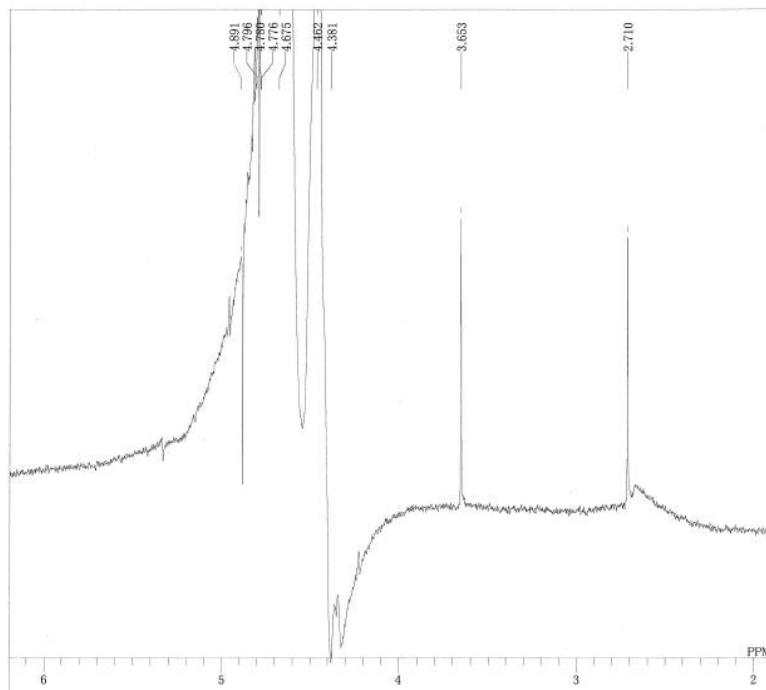


Figure S8.  $^1\text{H}$  spectrum of the electrolyte solution in the cathodic compartment with IL-2-modified Au electrodes at -0.58 V for RHE after 8 hour reduction in the  $\text{CO}_2$ -purged  $\text{NaHCO}_3$  aqueous solution.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  2.710 (s, DMSO), 3.653 (s, ethylene glycol)

### Cyclic voltammogram of the IL-2-based SAMs-modified Au electrodes after electrolysis

The cyclic voltammograms compare the redox behavior of ruthenium hexamine on IL-2-modified Au electrodes after CO<sub>2</sub> reduction. The redox behavior was blocked and the ability of the SAM to passivate the Au electrode also increased after electrolysis for 5 h and 7 h. The faradaic efficiency of ethylene glycol increased with time, attaining a maximum of 87%, and equilibrium values were reached after 5 hours (Figure 5(c)). It is possible that the SAM changes to a more packed and well-ordered structure as a result of the applied potential for electrolysis and is highly resistant to electron transfer between the Au electrode and the redox molecule. Thus, it is speculated that the faradaic efficiency increase obtained by the advantageous SAM structure produces ethylene glycol as the electrolysis time increases.

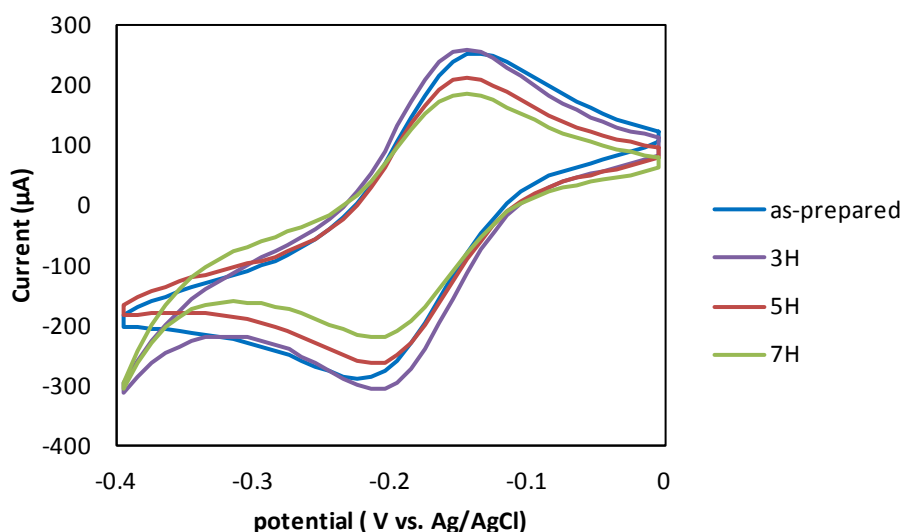


Figure S9. Cyclic voltammograms of the IL-2-modified Au electrodes after CO<sub>2</sub> reduction. All experiments were carried out in 0.1 M [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> dissolved in 0.5 M KCl, between the potential range of -400 to 0 mV, at a scan rate of 100 mV s<sup>-1</sup> and were referenced relative to Ag / AgCl.

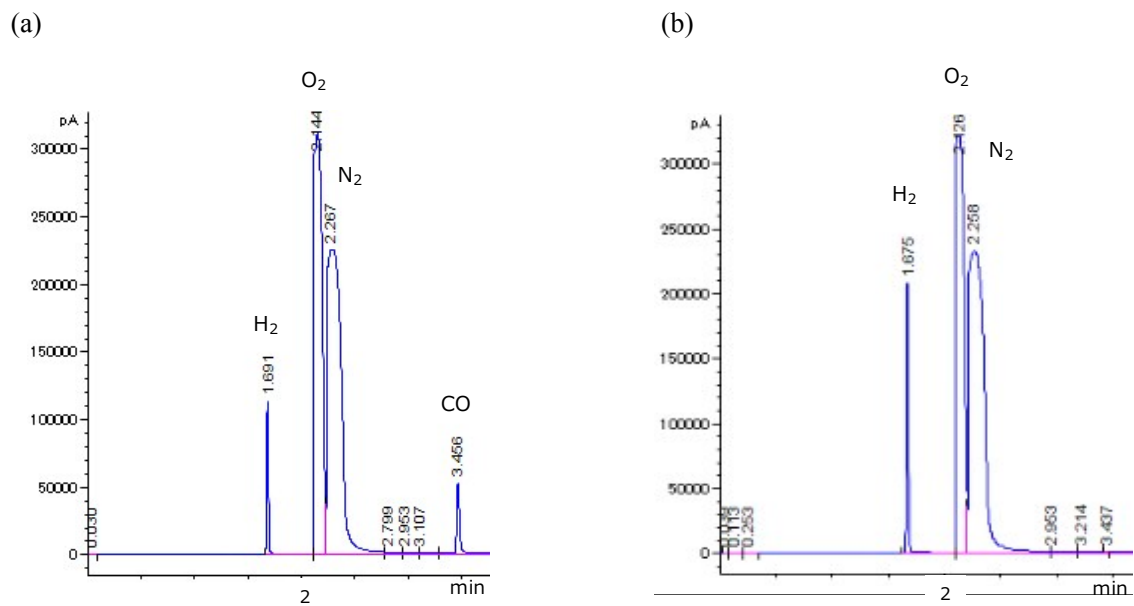


Figure S10. Gas chromatogram of the outlet gas from the cathodic compartment with (a) bare and (b) IL-2-modified Au electrodes at -0.58 V for RHE in the CO<sub>2</sub>-purged NaHCO<sub>3</sub> aqueous solution.