

## Synthesis and Electrochemical Characterizations of 7-Ferrocenecarboxyloxy-1-heptanethiol on Gold Substrates

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### Abstract

The 7-ferrocenecarboxyloxy-1-heptanethiol ( $\text{FcCO}_2\text{C}_7\text{SH}$ ) is synthesized using ferrocene carboxylic acid, 1,6-hexanedithiol, and NaS, which is confirmed and separated by FT-IR,  $^1\text{H}$  NMR, and column chromatography. The basic redox (interfacial) properties are also studied of the self-assembled monolayers (SAMs) formed with this synthesized compound on polycrystalline gold electrode by Electrochemical Quartz Crystal Microbalance (EQCM). The  $\text{FcCO}_2\text{C}_7\text{SH}$  on gold acts as a barrier for the electron transfer between the gold electrode and  $\text{HClO}_4$  in solutions and as a mediator for the reduction of  $\text{Fe}^{3+}$  in solution. The frequency change (interfacial mass change) on the gold electrode surface is observed during the redox of ferrocenyl groups.

*Keywords:* 7-Ferrocenecarboxyloxy-1-heptanethiol; Self-Assembled Monolayers; EQCM; Peak current; Modified gold electrode.

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### 1. Introduction

Self-assembled monolayers (SAMs) based on alkane thiols ( $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ) represent a versatile means for the modification of surfaces [1-3]. The SAM can be tailored to have a specific thickness or to present, at the SAM/solution interface, a given physical (such as hydrophobicity or hydrophilicity) or chemical property (for example a specific chemical group able to react with or bind to another chemical entity). Supramolecular structures that might undergo redox conversions are relevant to molecular biosensors and other electronic devices of the future [4]. Examples of such systems in this diverse field of research include redox-active self-assembled monolayers (SAMs), redox-modulated recognition sensors, redox-switchable membranes etc. Commonly used organic compounds for SAMs include various derivatives containing a mercapto group. The self-assembly method has been recognized as one of the most attractive approaches to creating well-defined functional molecular layers on solid surfaces [5]. The most widely studied self-assembly system is the chemisorption of sulfur derivatives (i.e. thiols and disulfides)

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on gold [6-12]. Many scientists have been reported the electrochemical characteristics of ferrocenyl-alkanethiol self-assembled monolayers on gold [13-24].

Ferrocene (Fc)-terminated alkanethiols occupy a highly important place in the field of SAM-forming substances because of their potential applications in electrochemical biosensors, heterogeneous catalysis, etc. [25-36]. EQCM has been studied at the gold electrode modified with  $\text{FcCO}_2\text{C}_7\text{SH}$  monolayer in solution containing other redox species  $\text{K}_3\text{Fe}(\text{CN})_6$  to monitor the mass change (frequency in Hz) during the potential cycling. The  $\text{FcCO}_2\text{C}_7\text{SH}$  SAM on gold acts as a mediator for the electron transfer in electrochemical solutions [37]. It has been shown that the redox properties of a Fc group depend both on the length and molecular structure of the chain. For instance, introduction of an ester group with a considerable dipole moment into the chain may perturb the monolayer packing, and the interfacial orientation of the redox-active moiety due to the dipole-dipole interactions [38]. However, as far as we know, Fc-terminated alkylthiols containing an ester group somewhere in the middle of the  $\text{C}_{12}$ - $\text{C}_{13}$  chain have not been synthesized or investigated. Our main attention is to synthesize new SAM-forming 7-ferrocenecarbonyloxy-1-heptanethiol compound and study its electrochemical interfacial properties on polycrystalline gold substrates.

## 2. Experimental

Sodium perchlorate monohydrate (98%), perchloric acid (70%), ferrocene carboxylic acid (97%), 1,6-dibromohexane (96%),  $\text{CH}_3\text{CN}$ , NaS,  $\text{Fe}(\text{ClO}_4)_3$  (98%) and tetrahydrofuran (THF) were purchased from Aldrich Chemical Company, and used without further purification. The voltammetry performed in this study employed a conventional three-electrode cell with a polycrystalline gold working electrode, Pt counter electrode and Ag/AgCl (satd. KCl) as the reference. The commercial potentiostat, an electrochemical quartz crystal microbalance (EQCM, Shin EQCN1000, Korea) was used for all electrochemical investigations. Electrodes were gold on 9 MHz AT-cut quartz crystals, which were usually used for EQCM. The mass sensitivity of 9 MHz quartz crystals is calculated to be  $5.46 \text{ ng cm}^{-2} \text{ Hz}^{-1}$ . The gold used was 99.99% pure and vacuum (ca.  $1 \times 10^{-7}$  Torr) deposited on 5 nm Ti underlayer to form a Au-layer of ca. 100 nm thickness by Thermal and E-beam evaporation system (HVEB 200, Hanvac, Korea).

All electrodes were pretreated and polishing by repeated cycling ( $50 \text{ mVs}^{-1}$ ) of the electrode in 0.1M  $\text{H}_2\text{SO}_4$  between the system's  $\text{O}_2$  and  $\text{H}_2$  evolution potentials, until a reproducible voltammogram with well defined features was obtained. The gold evaporated crystals were cleaned thoroughly by Piranha solution for 10.0 mins (a mixture of 98%  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$  at 2:1 v/v) [Caution! Piranha solution is a very strong oxidizing agent and reacts violently with organic compounds. Freshly prepared piranha solution should be handled with extreme care]. The average roughness factor and surface areas calculated for lab made polycrystalline gold electrode were  $1.2 (\pm 0.10)$  and  $0.26 \text{ cm}^2$ , respectively. To prepare the electrochemical and electrolyte solutions for electrochemical observation, deionize water (resistivity,  $>18.2 \text{ M}\Omega\cdot\text{cm}$ ) is used. The 7-

ferrocenecarboxyloxy-1-heptanethiol ( $\text{FcCO}_2(\text{CH}_2)_7\text{SH}$ ) is synthesized according to reactions (scheme-1) using ferrocene carboxylic acid (97%) and 1,6-dibromohexane (98%). The cleaned gold polycrystalline electrode was modified by dip-treatment in an ethanol solution containing  $\text{FcCO}_2\text{C}_7\text{SH}$  at 24.0 hours. After modification of the substrates, it was rinsed thoroughly with pure ethanol and then dried with stream of  $\text{N}_2$ . The  $\text{FcCO}_2\text{C}_7\text{SH}$  monolayer modified crystal was monitored with EQCM. IR spectra ( $4000\text{--}200\text{ cm}^{-1}$ ) were recorded by a FT-IR spectrometer (AVATAR 330, Thermo Nicolet, USA) as a KBr disc. The  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  (ppm) on the 400 MHz NMR Instrument (Japan).

#### ***Synthesis procedure of compound $\text{FcCOO}(\text{CH}_2)_7\text{SH}$ (Scheme-1)***

(1) Ferrocene carboxylic acid (500 mg, 2.17 mmol), 1,7 Dibromoheptane (700 mg, 2.71 mmol) and NaOH (80 mg, 2.20 mmol) in dried  $\text{CH}_3\text{CN}$  (20.0 ml) were reacted (stirred by magnetic stirring bar) in oil bath (ca.  $40.0\text{ }^\circ\text{C}$ ) under argon atmosphere to produce compound A [ $\text{FcCO}_2(\text{CH}_2)_7\text{Br}$ ]. Reacted solvents were removed using rotary vacuum evaporator. The residue was purified and separated by column chromatography.

$^1\text{H}$  NMR data for compound A: Yield 62%,  $^1\text{H}$  NMR  $\delta$  (ppm),  $\text{CDCl}_3$ : 1.80-1.85 (14H, m), 3.40 (2H, t,  $J=8\text{Hz}$ ), 4.12-4.22 (7H, m), 4.39 (2H, s), 4.80 (2H, s).

(2) To make solution with compound A (300 mg, 0.73 mmol) and NaSH (200mg, 0.36 mmol) in dried THF (30ml) was stirred by magnetic stirring bar in oil bath (ca.  $40.0\text{ }^\circ\text{C}$ ) for 24 hours under argon atmospheres. The reaction solvent was removed and residue was dissolved in diethyl ether (30.0 ml) and water (10.0 ml). Ether layer was selected and dried with anhydrous  $\text{MgSO}_4$ . Ether layer was removed with the rotary vacuum evaporator. The residue was purified and separated with column chromatography.

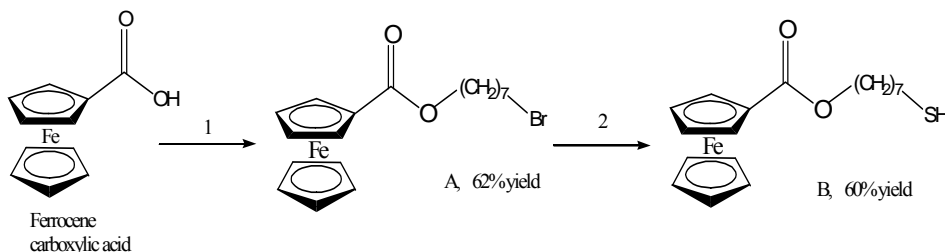
$^1\text{H}$  NMR data for final product B: Yellow powder, yield 0.424 g, 60%,  $^1\text{H}$  NMR  $\delta$  (ppm),  $\text{CDCl}_3$ : 1.42-1.72 (14H, m), 1.56(1H, s), 2.68 (2H, t,  $J=8\text{Hz}$ ), 4.20-4.22 (7H, m), 4.39 (2H, s), 4.80 (2H, s).

The final product (B,  $\text{FcCO}_2\text{C}_7\text{SH}$ ) is detected in the FT-IR spectrum by a  $-\text{CO}-$  (ester) stretching mode at  $1702\text{ cm}^{-1}$ , C-H stretching (pentene) at  $3020\text{ cm}^{-1}$ ,  $-\text{SH}$  (mercaptans) at  $2550\text{ cm}^{-1}$  alkane chain ( $-\text{CH}_2-$ ) C-H stretching at  $2852\text{ cm}^{-1}$  and bending at  $1456\text{ cm}^{-1}$ .

### **3. Results and Discussion**

Investigations of the chemical modification of metal and semiconductor electrode surfaces by adsorption of functional molecules have been carried out by synthesized ferrocene alkane thiol. Considering the foregoing, we synthesized the 7-ferrocenecarboxyloxy-1-heptanethiol [ $\text{FcCOO}(\text{CH}_2)_7\text{SH}$ , shortly  $\text{FcCO}_2\text{C}_7\text{SH}$ ] compound. The synthetic steps are presented in Scheme 1. In step-1, ferrocene carboxylic acid (97%) reacted with 1,7 dibromoheptane in presence of  $\text{CH}_3\text{CN}$ , NaOH under  $40.0\text{ }^\circ\text{C}$  (in argon environment) for 24 hours to produce product A (62% yield). Finally, the Fe-terminated with thiol derivatized compound B is obtained using NaS, THF in ca.  $40.0\text{ }^\circ\text{C}$  (in argon

environment) for 24 hours. We succeeded in obtaining compound product B [ $\text{FcCO}_2(\text{CH}_2)_7\text{SH}$ ] in 60% yields.



Scheme 1. Reagents and conditions: (1) Dibromoheptane, NaOH,  $\text{CH}_3\text{CN}$ , 40.0 °C, 24 hours, argon environment, 87% yield (2) NaSH, THF, 40.0 °C, 24 hours, argon environment, 42% yield.

Following the synthesis, basic self-assembling and electrochemical features of the monolayers formed by compound B ( $\text{FcCO}_2\text{C}_7\text{SH}$ ) on gold were studied by cyclic voltammetry (CV). For electrochemical experiments, monolayers were obtained via self-assembly of the compounds for 24 h from 2.0 mM ethanolic solutions on a pre-treated polycrystalline Au surface. In anaerobic 1.0 M  $\text{NaClO}_4$  at 25.0 °C, the CV curves of the SAMs exhibited clearly expressed oxidation–reduction peaks of the  $\text{Fc}^+/\text{Fc}^\circ$  couple as shown in Fig. 1. This curve served to determine the formal redox potentials  $E^\circ$  (+0.634V) and surface concentrations (surface coverage,  $\Gamma=2.67\times 10^{-10}$  mole  $\text{cm}^{-2}$ ) of compound  $\text{FcCO}_2\text{C}_7\text{SH}$  in the monolayers on gold substrates.

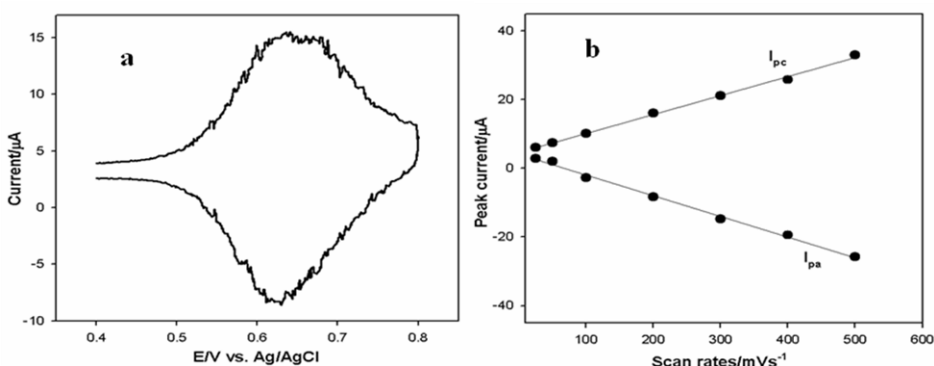


Fig. 1. (a) Cyclic voltammetric curves of the gold working electrode modified by compound recorded in 1.0 M  $\text{NaClO}_4$  solution at 25 °C and a scan rate of 20 mV/s. (b) Anodic ( $I_{pa}$ ) and cathodic peak ( $I_{pc}$ ) current showing the dependence on the scan rates.

In an effort to study a well-known degradation of the Fc-terminated monolayers in aqueous media [39], a decrease of the electrochemically determined  $\Gamma$  after a particular

time of  $E$  cycling over the  $E$  scan range from  $E^{\circ'}$  (+300 mV) to  $E^{\circ'}$  (+1000 mV) was taken to be a measure of the monolayer stability. The later results indicate the exceptional stability of the SAMs of  $\text{FcCO}_2\text{C}_7\text{SH}$  in the  $\text{NaClO}_4$  solution. Another interfacial feature of the monolayers  $\text{FcCO}_2\text{C}_7\text{SH}$  was derived from the electrochemical experiments performed at relatively low scan rates. The slope of the CV anodic ( $I_{\text{pa}}$ ) and cathodic ( $I_{\text{pc}}$ ) peak currents versus scan rates reflects the interaction between attached molecules in Fig. 1(b). From these slopes the interaction parameters were calculated [40, 41]. For compound,  $\text{FcCO}_2\text{C}_7\text{SH}$  the obtained interaction parameters were of opposite signs,  $-0.371 \times 10^{10}$  and  $0.377 \times 10^{10}$   $\text{cm}^2/\text{mol}$ , respectively, indicating repulsion between the Fc-centre in the monolayer of  $\text{FcCO}_2\text{C}_7\text{SH}$ . It might be speculated that, in the case of this compound, the presence of a C=O group close to the Fc ring prevents the effective neutralization of  $\text{Fc}^+$  by counter ions, resulting in repulsion between attached molecules.

EQCM response of the  $\text{FcCO}_2\text{C}_7\text{SH}$ -modified gold electrode in  $\text{Fe}^{3+} + \text{HClO}_4$  solution is studied at room conditions. Fig. 2(a) shows CVs of the  $\text{FcCO}_2\text{C}_7\text{SH}$ -modified gold electrode and an unmodified gold electrode in 1.0 M  $\text{HClO}_4$  solution containing 1.0 mM  $\text{Fe}(\text{ClO}_4)_3$  with a sweep rate of  $50 \text{ mV s}^{-1}$ . Reversible redox peaks were observed in 1.0 mM  $\text{Fe}(\text{ClO}_4)_3 + 1.0 \text{ M HClO}_4$  solution at the unmodified gold electrode around +650 mV. At the modified gold electrode, however, these high current peaks were not observed, showing that the direct electron transfer between  $\text{Fe}^{3+}$  and the gold electrode surface was blocked by the  $\text{FcCO}_2\text{C}_7\text{SH}$  monolayer. In addition to a pair of peaks around +590 mV, a relatively large cathodic current peak was observed around +500 mV. This peak current increased linearly with the concentration of  $\text{Fe}^{3+}$  in solution, and became larger at a slower sweep rate. The peak potential was not affected by the sweep rate. The compact surface monolayer inhibits the direct electron transfer between the electrode and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in solution, and that the surface  $\text{FcCO}_2\text{C}_7\text{SH}$  monolayer acts as a mediator for the electron transfer from the electrode to  $\text{Fe}^{3+}$  in solution [19].

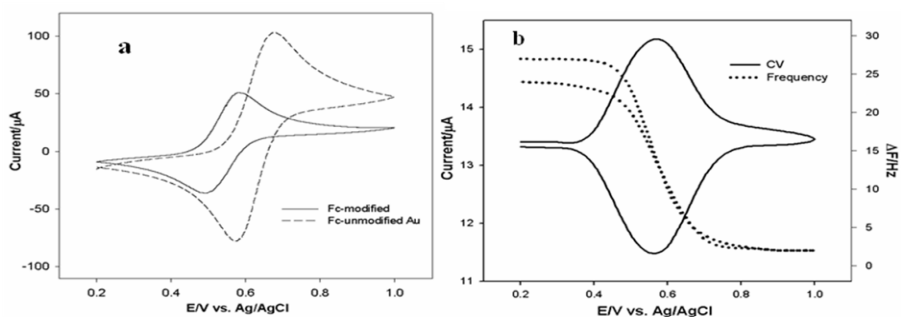
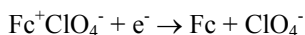


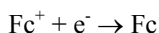
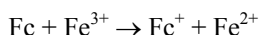
Fig. 2. (a) Cyclic voltammograms of a gold electrode modified and unmodified with  $\text{FcCO}_2\text{C}_7\text{SH}$  molecule in 1.0M  $\text{HClO}_4$  and 1.0 mM  $\text{Fe}(\text{ClO}_4)_3$ . Sweep rate  $50 \text{ mV s}^{-1}$ . (b) EQCM (CV and frequency change) of the  $\text{FcCO}_2\text{C}_7\text{SH}$  modified gold electrode recorded simultaneously with potential cycling.

Fig. 2 shows the frequency change recorded simultaneously with the measurement of the CV at the modified electrode. It is measured that the frequency change is due to the redox

reaction of the ferrocene moiety. Since the total frequency change was larger than that in HClO<sub>4</sub> solution without Fe<sup>3+</sup>, the actual frequency value in Fe<sup>3+</sup>-containing solution may not be the same as that obtained in Fe<sup>3+</sup>-free solution. Fig. 2(b) shows the potential dependence of the calculated current. This is very similar to the CV obtained in 1.0 M HClO<sub>4</sub> solution without Fe<sup>3+</sup>, although one must note that the absolute value of the current may not be accurate because of the ambiguity of electrode surface. Thus, this treatment enables one to separate the current due to the redox of ferrocene moieties from the measured current. These results show clearly that the redox of the ferrocene moiety occurs as if there is no Fe<sup>3+</sup> in solution and the mediation reaction proceeds without ion pair formation. Thus, around +570 mV, reduction of the ferricenium cation takes place as:



and ClO<sub>4</sub><sup>-</sup> desorbs from the monolayer. Then ferrocene reduces Fe<sup>3+</sup> in solution and ferrocene is converted to ferricenium cation which accepts an electron from the electrode as soon as it is formed:



The rate of mediation process is limited by the diffusion of Fe<sup>3+</sup>. In contrast, the total frequency change, ca. 25.0 Hz, was larger than that observed in solution without Fe<sup>3+</sup> cation. One possible reason why the frequency change was larger in solution containing Fe<sup>3+</sup> cation is that the Fe<sup>3+</sup> cation is adsorbed on and desorbed from the modified surface during the redox of the ferrocene moiety. When the ion pairs (Fc<sup>+</sup>ClO<sub>4</sub><sup>-</sup>) were formed on the modified surface in the oxidation process, Fe<sup>3+</sup> cations in electrolyte solution may approach and adsorb on the ClO<sub>4</sub><sup>-</sup> sites of ion pairs (Fc<sup>+</sup>ClO<sub>4</sub><sup>-</sup>). Thus, the weight increase and, therefore, the frequency decrease are much more than those in HClO<sub>4</sub> solution without Fe<sup>3+</sup>. Since both the ClO<sub>4</sub><sup>-</sup> anion and the Fe<sup>3+</sup> cation are removed from the monolayer in the reduction process, a larger frequency change should be observed. After the measurement in Fe<sup>3+</sup>+HClO<sub>4</sub> solution, the total frequency change of this electrode returns to the initial value obtained in HClO<sub>4</sub> solution without Fe<sup>3+</sup> cation.

#### 4. Conclusions

FcCO<sub>2</sub>C<sub>7</sub>SH is synthesized and studied self-assembled monolayer on gold surface. Electrochemical current responses were complicated because the observed currents were due to the redox of both the ferrocenyl group immobilized on gold and others in electrolyte solutions. The interfacial electrochemical change on the gold electrode surface observed during the redox of ferrocenyl groups. In presence of carbonyl group in FcCO<sub>2</sub>C<sub>7</sub>SH compound, the Fc ring neutralized of its Fc<sup>+</sup> by counter ions. We have carried out the EQCM study at the gold electrode modified with FcCO<sub>2</sub>C<sub>7</sub>SH monolayer

in solution containing other redox species ( $\text{Fe}(\text{CN})_6^{4-/3-}$  or  $\text{Fe}^{2+/3+}$ ) to monitor the mass transport during the potential cycling. It was found that the mass transport occurred by the adsorption and desorption of  $\text{ClO}_4$  anion on the electrode surface as a result of oxidation and reduction respectively of the Fc group. Although the CVs observed in the solution containing  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}^{3+}$  are complicated, it is possible to separate the current component due to the redox reaction of Fc groups from that of others by the comparison of the measured CV and the CV calculated from the frequency change.

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