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Electrochemical Properties of Tetrathiafulvalenyl-thiol, disulfide, thioacetate, and sulfide, and Their Self-Assembled Monolayers on Gold Surfaces

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Abstract

Tetrathiafulvalenyl-thiol (**1**), disulfide (**2**), thioacetate (**3**), and sulfide (**4**) have been prepared. The redox behaviors of the tetrathiafulvalene derivatives (**1-3**) depended on the nature of an electrolyte and a solvent used. Though a difference of electrochemical behavior between **1** and **2** was found in the cyclic voltammograms, the self-assembled monolayers (SAMs) from **1** and **2** showed the similar redox behaviors, while, **4** did not form SAM on a gold (Au) electrode.

Key-words : Self-assembled monolayer (SAM), Electrochemistry, Tetrathiafulvalene derivatives

1. Introduction

Organosulfur compounds such as alkanethiols and dialkyl disulfides form their self-assembled monolayers (SAMs) on gold surface. The investigation of SAMs has attracted enormous interest in the past years due to the potential applications of those interfaces to important technologies, such as adhesion, chemical sensing, and microdevice patterning¹⁻⁴. In particular the self assembly of alkanethiols on gold surfaces has been extensively studied, which allowed a better understanding of the structural orga-

nization and the properties of these layers. SAMs containing redox-active molecules provide an opportunity for us to study redox processes within a well-defined chemical environment. To date, the majority of studies has been carried out on *n*-alkanethiols possessing redox-active headgroup such as ferrocene.

We are interested in the synthesis and surface electrochemical properties of a new class of molecule with a tetrathiafulvalene (TTF) headgroup which undergoes reversible two-electron oxidation⁵. TTF derivatives are still regarded as the best precursor for superconducting organic metals⁶. In this paper, we describe the synthesis and the electrochemical properties of tetrathiafulvalenyl-thiol (**1**), disulfide (**2**), thioacetate (**3**), and sulfide (**4**), and the corresponding SAMs on gold (Au) surface. Although alkanethiol-derived monolayers self-assembled on Au surface are particularly well behaved, the comparison on the electrochemical behaviors of the SAMs formed from alkanethiol, dialkyl disulfide, and dialkyl sulfide containing the same redox-active headgroup has received much less attention.

2. Experimental

2.1 Synthesis of 3

To a solution of TTF (300 mg, 1.5 mmol) in anhydrous THF (18 ml), lithium diisopropylamine (LDA ; 1.6 mmol) was added at -78°C under an Ar atmosphere. Then elemental sulfur (65 mg, 2.0 mmol) was

Structural Formula 1

1 : X = SH

3 : X = SCOCH_3

4 : X = SCH_3

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added to this mixture. After being kept at -78°C for 2 h, 3-iodopropyl thioacetate (370 mg, 1.5 mmol) was added to the mixture; the reaction mixture was stirred at room temperature for 24 h and treated with 1 M HCl. After evaporation of the solvent, the residue was purified by preparative liquid chromatography (Japan Analytical Co, Model LC-908) to give 4-(3-thioacetoxypentylthio)-tetrathiafulvalene (**3**). **3**: FT-IR 1686 cm^{-1} (C=O); ^1H NMR (CDCl_3) δ 1.91 (q, 2H, $J=7.5\text{ Hz}$, CH_2), 2.34 (s, 3H, CH_3), 2.79 (t, 2H, $J=7.5\text{ Hz}$, SCH_2), 2.97 (t, 2H, $J=7.5\text{ Hz}$, COSCH_2), 6.32 (s, 2H, C=CH), 6.39 (s, 1H, C=CH); ^{13}C NMR (CDCl_3) δ 27.4, 29.2, 30.6, 34.4, 109.4, 112.8, 118.9, 119.0, 123.2, 126.4, 195.5. MS, m/z 352 (M^+).

2.2 Synthesis of 2

To a stirred solution of **3** (150 mg, 0.4 mmol) in anhydrous THF (18 ml), NaBH_4 (19 mg, 0.5 mmol) was added at -78°C under an Ar atmosphere. The mixture was stirred at -78°C for 3 h and then at room temperature for 24 h. After the general work-up, the product was purified by the preparative liquid chromatography to give 4-(3-mercaptopentylthio)-tetrathiafulvalene (**1**) and bis[4-(3-thiopentylthio)-tetrathiafulvalene] (**2**). **2** was formed from the oxidation of **1** during the work-up. **1**: FT-IR 2557 cm^{-1} (SH); ^1H NMR (CDCl_3) δ 1.37 (t, 1H, $J=8.0\text{ Hz}$, SH), 1.93 (q, 2H, $J=7.0\text{ Hz}$, CH_2), 2.65 (dt, 2H, $J=8.0, 7.0\text{ Hz}$, CH_2SH), 2.87 (t, 2H, $J=7.0\text{ Hz}$, SCH_2), 6.32 (s, 2H, C=CH), 6.37 (s, 1H, C=CH); ^{13}C NMR (CDCl_3) δ 22.9, 33.2, 34.0, 109.4, 112.9, 118.9, 119.0, 122.9, 126.6. MS, m/z 310 (M^+). **2**: ^1H NMR (CDCl_3) δ 2.03 (q, 2H, $J=7.5\text{ Hz}$, CH_2), 2.78 (t, 2H, $J=7.5\text{ Hz}$, CH_2SS), 2.85 (t, 2H, $J=7.5\text{ Hz}$, SCH_2), 6.32 (s, 2H, C=CH), 6.39 (s, 1H, C=CH). MS, m/z 618 (M^+).

2.3 Synthesis of 4

3-Iodopentyl methyl sulfide was prepared according to the reported method⁷⁾.

To a solution of TTF (300 mg, 1.5 mmol) in anhydrous THF (18 ml), LDA (1.6 mmol) was added at -78°C under an Ar atmosphere. Then elemental sulfur (65 mg, 2.0 mmol) was added to this mixture. After being kept at -78°C for 2 h, 3-iodopentyl methyl sulfide (324 mg, 1.5 mmol) was added to the mixture; the reaction mixture was stirred at room temperature for 24 h and treated with 1 M HCl. After evaporation of the solvent, the residue was purified by the preparative liquid chromatography to give 4-(3-thiomethylpentylthio)-tetrathiafulvalene (**4**). **4**:

^1H NMR (CDCl_3) δ 1.92 (q, 2H, $J=7.0\text{ Hz}$, CH_2), 2.10 (s, 3H, CH_3), 2.60 (t, 2H, $J=7.0\text{ Hz}$, CH_2SCH_3), 2.86 (t, 2H, $J=7.0\text{ Hz}$, SCH_2), 6.32 (brs, 3H, C=CH); ^{13}C NMR (CDCl_3) δ 15.4, 28.5, 32.5, 34.4, 118.9, 119.0, 122.6, 126.8. MS, m/z 324 (M^+).

2.4 Electrodes and instrumentation

All the electrochemical experiments were performed at room temperature using a BAS Instrument model 100B/W electrochemical workstation. Platinum wire was used as the counter electrode and glassy carbon (GC, 3.0-mm diameter) or Au (1.6-mm diameter) was used as the working electrode in a one-compartment cell. Potentials were relative to the system Ag/0.1 M AgNO_3 in acetonitrile or Ag/AgCl in H_2O . Bu_4NClO_4 and Bu_4NPF_6 (both Fluka, electrochemical grade), HClO_4 (Wako), and CH_3CN and CH_2Cl_2 (both Wako, anhydrous) were used for the preparation of the electrolyte solutions.

3. Results and Discussion

3.1 Electrochemical property of tetrathiafulvalene derivatives

The electrochemical properties of **1** and **2** in $\text{CH}_2\text{Cl}_2 + 0.1\text{ M Bu}_4\text{NPF}_6$ were studied by cyclic voltammetry (CV). The cyclic voltammogram of **1** showed the oxidation potentials at $E_p = +0.29$ and $+0.75\text{ V}$ (vs Ag/0.1 M AgNO_3) [Figure 1(a)], while the cyclic voltammogram of **2** showed the two quasi-reversible redox peaks at $E_p = +0.27$ and $+0.66\text{ V}$ (vs Ag/0.1 M AgNO_3) [Figure 1(b)]. The second oxidation potential of **2** was lower than that of **1**. This result suggests that the cationic species generated on the TTF units may be affected by electronic factor. Therefore, we have studied the effect of the counter anion of electrolyte and the solvent effect. In this study, **3** was used instead of **1**, since the oxidation of **1** may occur during CV measurements.

The effect of the counter anion of electrolyte for the redox behaviors of **2** and **3** was investigated by CV. **3** having single TTF unit in 0.1 M $\text{Bu}_4\text{NPF}_6 + \text{CH}_2\text{Cl}_2$ showed that the two quasi-reversible redox peaks appeared at $E_p = +0.30$ and $+0.77\text{ V}$ (vs Ag/0.1 M AgNO_3) (Figure 2). The oxidation potential for the $\text{TTF}^+/\text{TTF}^{2+}$ redox couple of **3** was found to depend on electrolyte, that is, the second oxidation potential in 0.1 M $\text{Bu}_4\text{NClO}_4 + \text{CH}_2\text{Cl}_2$ was lower than that in 0.1 M $\text{Bu}_4\text{NPF}_6 + \text{CH}_2\text{Cl}_2$ (Figure 2). This negative shift may be explained by the stabilization of the generated cationic species of the TTF unit by ClO_4^- , since it has been reported that the ion-pairing

Fig. 1 Cyclic voltammogram of (a) **1** (1 mM) or (b) **2** (0.5 mM) on a GC electrode in 0.1 M $\text{Bu}_4\text{NPF}_6 + \text{CH}_2\text{Cl}_2$; scan rate 100 mV s^{-1} .

Fig. 2 Cyclic voltammograms of **3** (1 mM) on a GC electrode in 0.1 M $\text{Bu}_4\text{NPF}_6 + \text{CH}_2\text{Cl}_2$ (solid line) and in 0.1 M $\text{Bu}_4\text{NClO}_4 + \text{CH}_2\text{Cl}_2$ (dotted line); scan rate 50 mV s^{-1} .

constant for ClO_4^- with cationic species is larger than that for PF_6^- with cationic species⁸⁾. Interestingly, the redox behaviors of **2** depend markedly on the nature of the counter anion, that is, the $\text{TTF}^+/\text{TTF}^{2+}$ redox couple of **2** in ClO_4^- shows the remarkable negative shift (**Figure 3**). However, these effects of the counter-anion of electrolyte were not observed when CH_3CN as a polar solvent was used instead of CH_2Cl_2 (**Figures 4 and 5**). In the case of CH_3CN as a solvent,

Fig. 3 Cyclic voltammograms of **2** (0.5 mM) on a GC electrode in 0.1 M $\text{Bu}_4\text{NPF}_6 + \text{CH}_2\text{Cl}_2$ (solid line) and in 0.1 M $\text{Bu}_4\text{NClO}_4 + \text{CH}_2\text{Cl}_2$ (dotted line); scan rate 50 mV s^{-1} .

Fig. 4 Cyclic voltammograms of **2** (0.5 mM) on a GC electrode in 0.1 M $\text{Bu}_4\text{NPF}_6 + \text{CH}_3\text{CN}$ (solid line) and in 0.1 M $\text{Bu}_4\text{NClO}_4 + \text{CH}_3\text{CN}$ (dotted line); scan rate 50 mV s^{-1} .

the two reversible redox peaks appeared at the following potentials ($E_{1/2}$ vs $\text{Ag}/0.1 \text{ M AgNO}_3$), **2**: +0.15 and +0.51 V in $\text{CH}_3\text{CN} + 0.1 \text{ M Bu}_4\text{NPF}_6$, +0.13 and +0.48 V in $\text{CH}_3\text{CN} + 0.1 \text{ M Bu}_4\text{NClO}_4$ (**Figure 4**); **3**: +0.14 and +0.49 V in $\text{CH}_3\text{CN} + 0.1 \text{ M Bu}_4\text{NPF}_6$, +0.14 and +0.48 V in $\text{CH}_3\text{CN} + 0.1 \text{ M Bu}_4\text{NClO}_4$ (**Figure 5**). These findings indicate that the redox behaviors of the TTF derivatives (**1-3**) were affected by the solvent and the counter anion of electrolyte. Although a number of studies for electrochemistry of TTF derivatives have been reported, much less is known about the effect of solvent and of electrolyte on the redox behaviors of TTF derivatives.

Fig. 5 Cyclic voltammograms of **3** (1 mM) on a GC electrode in 0.1 M $\text{Bu}_4\text{NPF}_6 + \text{CH}_3\text{CN}$ (solid line) and in 0.1 M $\text{Bu}_4\text{NClO}_4 + \text{CH}_3\text{CN}$ (dotted line); scan rate 50 mV s^{-1} .

3.2 Self-assembled monolayers (SAMs)

The difference in the redox behaviors between **1** and **2** is described in the above section. Interestingly, however, the similar redox behaviors were found in the SAMs formed from **1** and **2**. SAMs of **1** were formed by the soaking of Au electrode in a CH_2Cl_2 solution of **1** (1 mM). After soaking for 24 h at 40°C , the sample was removed and rinsed, then used for electrochemical studies in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M Bu}_4\text{NPF}_6$. The cyclic voltammogram for the SAMs of **1** adsorbed on Au electrode in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M Bu}_4\text{NPF}_6$ exhibited two reversible redox waves corresponding to the $\text{TTF}/\text{TTF}^+/\text{TTF}^{2+}$ system at $E_{1/2} = +0.21$ and $+0.62 \text{ V}$ (vs $\text{Ag}/0.1 \text{ M AgNO}_3$) [Figure 6(a)]. Similarly, the immersion of a Au electrode in a CH_2Cl_2 solution of **2** (0.5 mM) at room temperature for 24 h led to the monolayer of **2**; the cyclic voltammogram of the SAMs of **2** showed two reversible redox waves at $E_{1/2} = +0.22$ and $+0.63 \text{ V}$ (vs $\text{Ag}/0.1 \text{ M AgNO}_3$) [Figure 6(b)]. These findings indicate no difference in the oxidation potentials and the redox behaviors between **1-SAM** and **2-SAM**. The thiol-monolayer-modified Au electrode allowed to stand at 0 V in CH_2Cl_2 or CH_3CN showed no diminution of the anodic peak current response over more than several weeks, showing that the molecular film is not readily stripped by nonaqueous solvents. Scanning repetition through the oxidation wave, however, leads to some loss of electroactivity (Figure 7).

Meanwhile, the cyclic voltammogram of **4** in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M Bu}_4\text{NPF}_6$ showed two quasi-reversible redox waves at $E_p = +0.29$ and $+0.78 \text{ V}$ (vs $\text{Ag}/0.1$

Fig. 6 Cyclic voltammogram of (a) **1-SAM** and (b) **2-SAM** modified Au electrode in 0.1 M $\text{Bu}_4\text{NPF}_6 + \text{CH}_2\text{Cl}_2$; scan rate 100 mV s^{-1} .

Fig. 7 Multiple-CV scans (100 mV s^{-1}) of **1-SAM** adsorbed onto the Au electrode in 0.1 M $\text{Bu}_4\text{NPF}_6 + \text{CH}_2\text{Cl}_2$.

M AgNO_3). None of the SAM from **4** was formed by the soaking of Au electrode in a CH_2Cl_2 solution of **4**. This result suggests that the chemisorption of the sulfenyl group of **4** onto the Au surface is extremely weak; therefore the monolayer was not formed in this case. Literature precedent for attachment of sulfides bearing redox-active headgroup to Au surface is limited⁴⁹.

In conclusion, the redox behaviors of **2** and **3** depended on the nature of the counter anion of electrolyte and of the solvent. The immersion of the Au

electrode in a solution of **1** or **2** led to the corresponding SAMs, which indicated the same redox behaviors. SAM was not formed from **4**.

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テトラチアフルバレンニル-チオール, ジスルフィド,
チオアセテートとスルフィドの電気化学的性質および
金表面上における自己集合単分子膜

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要 旨

テトラチアフルバレンニル-チオール (**1**), ジスルフィド (**2**), チオアセテート (**3**) およびスルフィド (**4**) を合成した。テトラチアフルバレンニル誘導体 (**1-3**) の電気化学的挙動は、電解質および溶媒の性質に依存する。**1** と **2** の電気化学的挙動は異なるが、金表面上に生成する **1** と **2** の自己集合単分子膜 (SAM) の電気化学的性質は類似している。**1** と **2** とは対照的に、**4** の SAM は生成しない。