Bull. Chem. Soc. Jpn., 70, 767—770 (1997)

pH-Modulated Vectorial Electron Transfer Reactions at a Self-Assembled Monolayer on a Gold Electrode

Naotoshi Nakashima* **and Yonekazu Deguchi**

Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-cho, Nagasaki 852

(Received October 30, 1996)

A self-assembled monolayer of 1-dodecanethiol ($C_{12}SH$) on a gold electrode was prepared by dipping a polished bare electrode into an ethanolic solution of $C_{12}SH$ (1.0 mmol dm^{-3}) for 10 min. The obtained modified electrode blocked the direct electron-transfer reaction of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ with the underlying electrode. However, a pH-dependent redox compound, 4,4′-biphenyldiol (**1**) in solution, was permeable into the monolayer and gave well-defined cyclic voltammograms at both higher and lower pHs. Using this chemical-recognition ability of the modified electrode together with the formal potential shift of **1** according to the Nernst equation, pH-modulated vectorial electron transfer reactions were examined. At pH 3, cyclic voltammograms at the modified electrode in a **1**+$[Fe(CN)_6]^{4-}$ aqueous solution revealed that one-way electron flow from $[Fe(CN)]^{4-}$ to the electrode via **1** (oxidized form) occurred. On the contrary, at higher pHs (pH 9—11), the vectorial electron flow at the electrode in **1**+$[Fe(CN)_6]^{3-}$ solution was reversed. A triggered change ('switching') between the anodic and cathodic vectorial electron transfer reactions by changing the pH was also possible at the $C_{12}SH$-modified electrode in the presence of **1**, $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ in solution. This finding may offer possibilities for the construction of functional molecular devices based on the tuning of rectified electron transfer reactions.

The one-way flow of electrons provides a critical function in biological electron-transfer systems, such as the respiratory electron-transfer chain that is located in the inner membrane of mitochondria.[1] We and others have reported that vectorial electron transfer reactions occur between electrodes and redox compounds in solution via electroactive self-assembled monolayers (SAMs) or redox compounds embedded in SAMs or in Langmuir–Blodgett (LB) lipid bilayers on gold. Creager et al.[2] described mediated electron transfer from 1-methyl-1′-octadecyl-4-4′-bipyridinium dibromide bound to a octadecanethiol monolayer on Au via chemisorption to $[Ru(NH_3)_6]^{3+}$ in solution. One-way electron transfer from an LB monolayer of a flavin to cytochrome *c* in solution was described by Ueyama and Isoda.[3] Uosaki et al.[4] showed the vectorial electron transfer from an assembled monolayer of ferrocenyldodecanethiol on gold to $Fe(ClO_4)_3$ in solution. We reported a rectified transmembrane electron transfer from β-NADH to the electrode via a π-conjugated electroactive compound with the *o*-quinoidal moiety embedded in an octadecanethiol monolayer,[5] as well as a rectified transmembrane electron transfer through LB monolayers of π-conjugated electroactive amphiphiles.[6,7] Buttry and coworkers[8] have examined the kinetics of mediated electron transfer between SAMs of viologen derivatives on gold electrodes and $[Ru(NH_3)_6]^{3+}$ in solution.

Our interest in this field is to design and develop stimuli-responsive vectorial electron transfer systems. Such a study could provide fundamental data for developing a molecular rectifying device based on organized molecular membranes. Recently, Taniguchi reported on the potential-dependent rectified electron transfer at a moldola's blue incorporated decanethiol-modified electrode.[9] We showed that the tuning of the LB lipid bilayer fluidity between the crystalline-to-liquid crystalline phase could regulate a vectorial electron transfer from a flavin with a long alkyl chain embedded in the LB film to hexacyanoferrate(III) in solution.[10] We would now like to report a pH-modulated vectorial electron transfer system using a SAM on gold. Our basic concept is shown in Fig. 1, where compound A is a proton-dependent redox molecule embedded in a SAM (case I) on gold, or is permeable into the SAM (case II) to undergo a direct

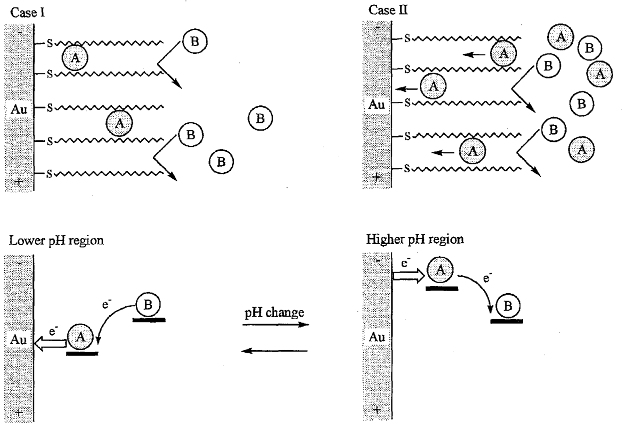


Fig. 1. Schematic representation for molecular recognition at a SAM of an alkanethiol on Au (top) and pH-modulated vectorial electron transfer reactions (bottom). Details see the text.

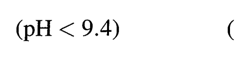
electron transfer reaction with the electrode. Compound B is highly water soluble, and the modified layer acts as a barrier for blocking direct access of B to the electrode. When the formal potential of A is negative compared to B, a vectorial electron transfer reaction from A to B would occur. Through the change in pHs, $E^{\circ\prime}$ of A becomes positive compared to B, and electron flow from B to A is expected. We describe the possibility of case II by choosing 4,4′-biphenyldiol (**1**) as A and $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ as B.

Experimental

4,4′-Biphenyldiol (Tokyo Kasei) and 1-dodecanethiol (Tokyo Kasei) were used as received. Monolayer modified electrodes were prepared using the following procedure. A well-polished gold disk electrode (Bioanalytical Systems, diameter: 1.6 mm) was immersed in 1.0 mM (1 M=1 mol dm^{-3}) 1-dodecanethiol ($C_{12}SH$) in ethanol for 10 min, and then rinsed with ethanol. Cyclic voltammograms (Electrochemical Analyzer BAS-100B, Bioanalytical Systems) at a bare and modified electrode ($C_{12}SH$/Au) were measured in deoxygenated aqueous KCl (0.1 M) at 25°C. The pHs were adjusted with HCl and KOH aqueous solutions. A platinum wire and a saturated calomel electrode were used as the counter and reference electrodes, respectively.

Results and Discussion

SAMs on gold function as physical or chemical molecular recognition interfaces.[11—18] The size, shape, charge, and hydrophobicity (hydrophilicity) of the molecules are important factors for physical recognition. SAMs on gold electrodes can easily block the electrochemical communication of charged inorganic compounds, such as $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$, with the electrodes. On the contrary, organic redox compounds with small sizes are permeable through SAMs, and undergo direct electron transfer reactions with the underlying electrodes. Figure 2 shows typical CVs of **1**, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ at an electrode prepared by the 10-min dipping of an electrode in a $C_{12}SH$ ethanolic solution. At both pHs, well-defined cyclic voltammograms of **1** are evident, indicating that **1** is permeable through the monolayer to the electrode surface to undergo direct electron transfer with the electrode. However, at the measured pH range (pH 3—11), the SAM acted as a barrier for the electrochemistry of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ with the electrode. The pH dependence of the formal potentials of **1** in solution at a bare electrode and the 10 min-dipping prepared electrode were measured, where **1** (50 μM) existed as a monomeric form (from UV-visible absorption spectra; data not shown). For both electrodes, at lower pHs, the formal potentials changed with pH with a slope of −60 mV/pH and at $9.4\pm0.1 < \mathrm{pH} < 10.3\pm0.1$, the $E^{\circ\prime}$ values varied with pH by −30mV/pH. At pHs higher than 10.3 $E^{\circ\prime}$ was pH-independent. These results indicate that pK_{a1} and pK_{a2} of **1** are 9.4±0.1 and 10.3±0.1, respectively. Thus, the redox reaction of **1** is given as:



(pH < 9.4) (1)

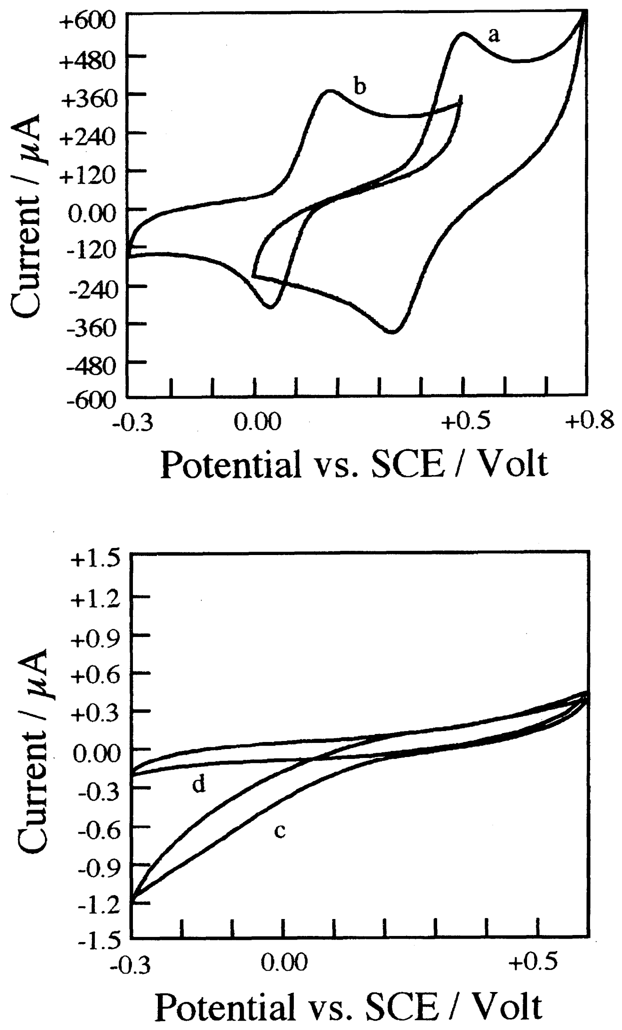
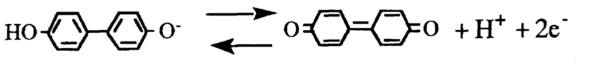
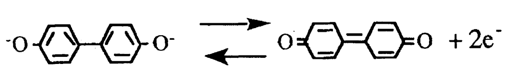


Fig. 2. Cyclic voltammograms at a 10 min-dipped $C_{12}SH$/Au electrode in the presence of **1** (50 μM) at pH 4.0 (a) and pH 10.0 (b) and in the presence of 2 mM $K_3[Fe(CN)_6]$ (c) or 2 mM $K_4[Fe(CN)_6]$ (d). Electrolyte concentration: KCl=0.1 M.



(9.4 < pH < 10.3) (2)



(10.3 < pH) (3)

The formal potentials of **1** at pH 3.0 and pH 9.0 are 493.5 and 130 mV vs. SCE, respectively, and $E^{\circ\prime}$ (167.5mV vs. SCE) of $[Fe(CN)_6]^{3-/4-}$ lies in between these values. The obtained results seem to satisfy the requirements for pH-modulated vectorial electron transfer reactions.

The surface coverage of $C_{12}SH$ should be important for chemical recognition based on electrochemistry. To ascertain this, we examined the electrode-dipping time dependence, and found that modified electrodes prepared by long dipping (>1 h) in an ethanolic solution of $C_{12}SH$ (1.0 mM) resulted in no electrochemical communication of **1** with the electrodes and, therefore, were not suitable for the present study. Hence, the 10 min-dipped SAM electrodes were used for the following experiments.

Figure 3 shows the influence of $K_4[Fe(CN)_6]$ addition for CVs at pH 4.0 at the $C_{12}SH$/Au electrode in the presence of **1**, where the reaction of $[Fe(CN)_6]^{4-}$ and **1** (oxidized form) is downhill by 266 mV. It is evident that the added $[Fe(CN)_6]^{4-}$ induces an increase in the anodic current, demonstrating one-way electron transfer from $[Fe(CN)_6]^{4-}$ to **1** (oxidized form), and then from biphenyldiol to the electrode.

On the contrary, at pH 10.0, where the reaction of **1** (reduced form) and $[Fe(CN)_6]^{3-}$ was downhill by 69 mV, one-way electron flow was found to be reversed (from 'anodic vectorial electron transfer' to 'cathodic'). Typical data are shown in Fig. 4 where the observed decrease and increase in the anodic and cathodic currents, respectively, via the addition of $[Fe(CN)_6]^{3-}$ should be ascribable to a recycled reduction of **1** (oxidized form) with the electrode couple via the oxidation of **1** (reduced form) with $[Fe(CN)_6]^{3-}$.

A triggered change ('switching') between the anodic and cathodic vectorial electron transfer reactions is revealed in Fig. 5, where $[Fe(CN)_6]^{3-}$, $[Fe(CN)]^{4-}$, and **1** coexist in solution. Note that just by changing the pH, one-way electron flow is reversed. Similar results were obtained for the pH change between pH 3.0 and 11.0. A schematic illustration for the pH-modulated vectorial electron transfer reactions is shown in Fig. 6.

In conclusion, pH-modulated vectorial electron transfer reactions between the underlying electrode and $[Fe(CN)_6]^{3-}$

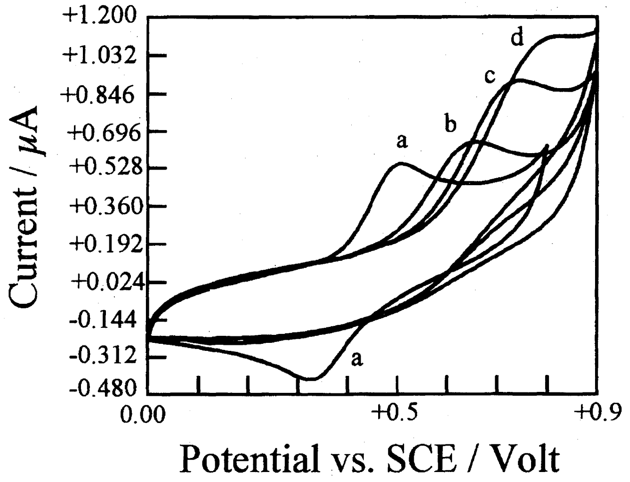


Fig. 3. Influence of $K_4[Fe(CN)_6]$ addition on cyclic voltammograms at a 10 min-dipped $C_{12}SH$/Au electrode in pH 4.0 aqueous solution containing 50 μM **1**, $K_4[Fe(CN)_6]$ and 0.1 M KCl. Concentration of $K_4[Fe(CN)_6]$ are: 0 mM (a), 0.1 mM (b), 0.2 mM (c), and 0.3 mM (d). Sweep rate: 50 mV s^{-1}. Temperature:25°C.

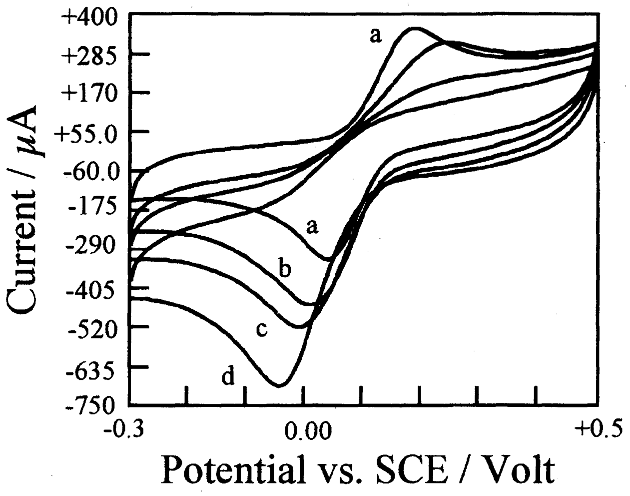


Fig. 4. Influence of $K_3[Fe(CN)_6]$ addition on cyclic voltammograms at a 10 min-dipped $C_{12}SH$/Au electrode in pH 10.0 aqueous solution containing 50 μM **1**, $K_3[Fe(CN)_6]$ and 0.1 M KCl. Concentration of $K_3[Fe(CN)_6]$ are: 0 mM (a), 0.1 mM (b), 0.2 mM (c), and 0.3 mM (d). Sweep rate: 50 mV s^{-1}. Temperature:25°C.

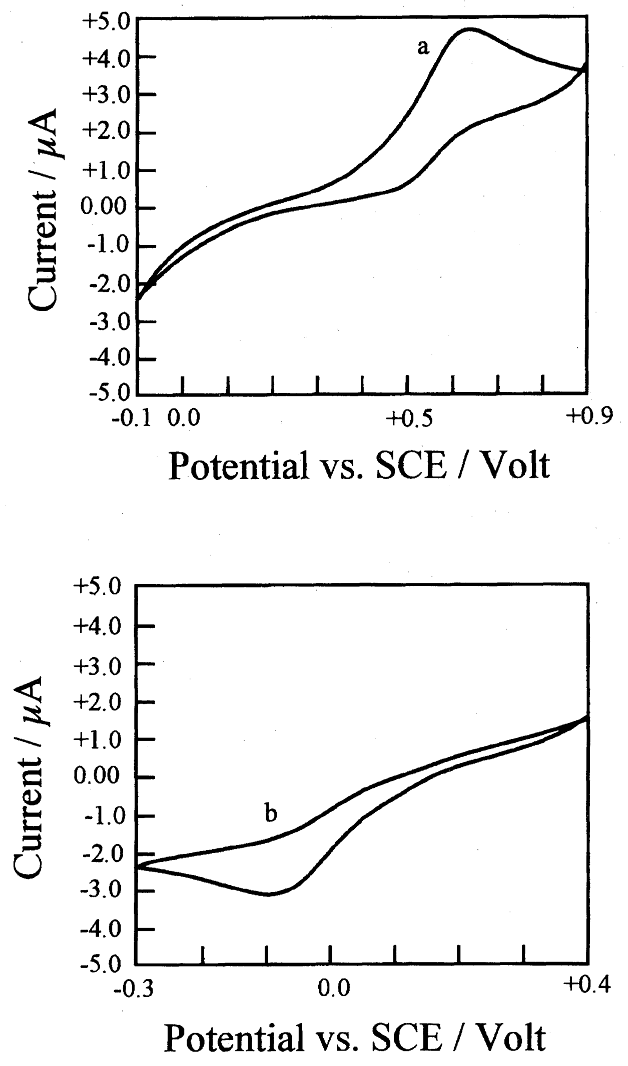


Fig. 5. Cyclic voltammograms at a 10 min-dipped $C_{12}SH$/Au electrode in the presence of 50 μM **1**, 2 mM $K_3[Fe(CN)_6]$ and 2 mM $K_4[Fe(CN)_6]$ in pH 3.0 (a) and pH 9.2 (b) aqueous solution (KCl: 0.1 M). Sweep rate: 50 mV s^{-1}. Temperature:25°C.

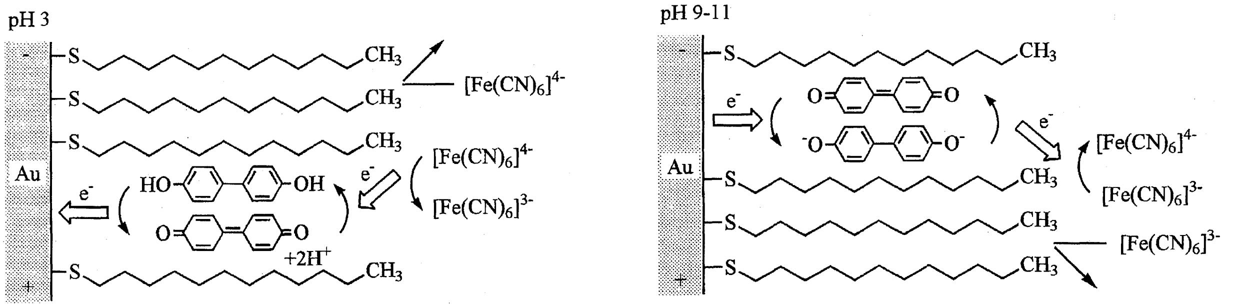


Fig. 6. Schematic illustration for the pH-modulated vectorial electron transfer reactions.

or $[Fe(CN)_6]^{4-}$ via **1** (oxidized or reduced form) at a self-assembled monolayer of $C_{12}SH$ were demonstrated for the first time. This finding may offer possibilities for the construction of functional molecular devices based on the tuning of rectified electron-transfer reactions.

The work was supported, in part, by a Grant-in-Aid for Science Research from the Ministry of Education, Science, Sports and Culture.

References

1) Y. Hatefi, *Annu. Rev. Biochem.*, **54**, 1015 (1985).

2) S. E. Creager, D. M. Collard, and M. A. Fox, *Langmuir*, **6**, 1617 (1990).

3) S. Ueyama and S. Isoda, *J. Electroanal. Chem.*, **310**, 281 (1991).

4) K. Uosaki, Y. Sato, and H. Kita, *Electrochem. Acta*, **36**, 1799 (1991).

5) M. Kunitake, K. Akiyoshi, K. Kawatana, N. Nakashima, and O. Manabe, *J. Electroanal. Chem.*, **292**, 277 (1990).

6) M. Kunitake, K. Nasu, O. Manabe, and N. Nakashima, *Bull. Chem. Soc. Jpn.*, **67**, 375 (1994).

7) M. Kunitake, K. Nasu, Y. Narikiyo, O. Manabe, and N. Nakashima, *Bull. Chem. Soc. Jpn.*, **68**, 2497 (1995).

8) Personal communication.

9) I. Taniguchi, T. Shimoota, M. Tominaga, and K. Nishiyama, *Microchem. J.*, **49**, 340 (1994).

10) N. Nakashima and K. Masuyama, "Redox Mechanisms and Interfacial Properties of Molecules of Biological Importance," ed by F. A. Schultz and I. Taniguchi, The Electrochemical Soc., Pennington, NT (1993), p. 280.

11) K. Odashima, M. Sugawara, and Y. Umezawa, *Trends Anal. Chem.*, **10**, 207 (1991).

12) S. Steinberg and I. Rubinstein, *Langmuir*, **8**, 1183 (1992).

13) R. Bilewicz and M. Majda, *J. Am. Chem. Soc.*, **113**, 5464 (1991).

14) K. D. Schierbaum, T. Weiss, E. U. T. van Velzen, J. F. J. Engbersen, D. N. Reinhoudt, and W. Göpel, *Science*, **265**, 232 (1994).

15) R. M. Crooks, O. Chailapakul, C. B. Ross, L. Sun, and J. K. Schoer, "Interfacial Design and Chemical Sensing," ACS Symp. Ser. 561, ed by T. E. Mallouk and D. J. Harrison, Am. Chem. Soc., Washington, D. C. (1994), p. 104.

16) N. Nakashima, T. Taguchi, Y. Takada, K. Fujio, M. Kunitake, and O. Manabe, *J. Chem. Soc., Chem. Commun.*, **1991**, 232.

17) N. Nakashima and T. Taguchi, "Interfacial Design and Chemical Sensing," ACS Smp. Ser. 561, ed by T. E. Mallouk, and D. J. Harrison, Am. Chem. Soc., Washington, D. C. (1994), p. 145.

18) N. Nakashima, and T. Taguchi, *Colloids Surfaces A: Physicochem. Eng. Aspects*, **103**, 159 (1995).