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Transmembrane Rectified Electron Transfer through π-Conjugated Electroactive Langmuir–Blodgett Monolayers on Gold Electrodes

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Novel amphiphiles with π-conjugated electroactive groups, 1-methyl-4-[2-[4-[2-(4-pyridyl)vinyl]phenyl]vinyl]pyridinium perchlorate (**1**), and 1-methyl-4-[2-[4-[2-(4-quinolyl)vinyl]phenyl]vinyl]quinolinium perchlorate (**2**), were designed and synthesized. Both compounds formed expanded monolayers at air–water interfaces. The monolayers transferred on gold disk electrodes at 25 $\mathrm{mN\,m^{-1}}$ by the Langmuir–Blodgett technique (horizontal lifting method) show one electron reduction/oxidation couple: $E_{\mathrm{pa}}=-0.86$ V, $E_{\mathrm{pc}}=-1.08$ V vs. SCE for **1**/Au and $E_{\mathrm{pa}}=-0.78$ V, and $E_{\mathrm{pc}}=-0.84$ V vs. SCE for **2**/Au. Rectified transmembrane electron transfer through the LB monolayers of **1** and **2** on gold electrodes to $[\mathrm{Fe(CN)_6}]^{3-}$ in aqueous solutions has been proved by cyclic voltammetry and potential-step chronocoulometry.

The interfacial characteristics of modified electrodes by assembled organic monolayers, especially possessing electroactive moieties, are of considerable current interest, because such systems provide oriented redox reaction sites at electrode surfaces.[1—14)] One of our concerns in this field is to create vectorial electron flow systems at metal electrode surfaces based on the nature of electroactive monolayer membranes.[10—14)] Recently we have reported stepwise and rectified electron transfer from a gold electrode to a substrate in aqueous solution through the thin electroactive film of 1-octadecyl-4-(4-pyridyl) pyridinium perchlorate fabricated onto a gold surface via chemisorption from acetonitrile solution.[14)] The structure of the adsorbed thin film, however, was not clear. Langmuir–Blodgett (LB) technique is one of the best method to create highly oriented and well-organized organic reaction sites on electrodes.

In this article, we first describe the design and synthesis of novel redox compounds **1** and **2**, having π-conjugated electroactive (1-alkyl-)4-pyridinio group and the characterization of their monolayer properties at air/water interfaces (Chart 1). Secondary, rectified electron transfer from the LB monolayers of **1** and **2** formed on gold electrodes to $[\mathrm{Fe(CN)_6}]^{3-}$ in solution was explored in terms of cyclic voltammetry and double-step chronocoulometry. There are already some reports on the electrochemistry of redox-active LB monolayers,[1—3,5,13)] and on one-way electron transfer at monolayer electrode systems.[10—14)] However, no report has been reported on vectorial electron transfer through a *LB monolayer of a π − conjugated electroactive compound.*

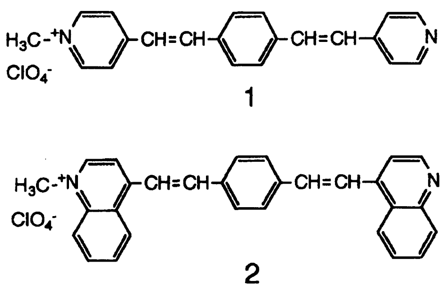

Chart 1.

Experimental

Synthesis. 1-Methyl-4-[2-[4-[2-(4-pyridyl)vinyl]phenyl]vinyl]pyridinium Perchlorate (1). Dimethyl sulfate (180 μl) was added dropwise to chloroform solution (40 ml) of 4,4′-[*p*-phenylenebis(vinylene)]bipyridine (0.5 g) that was prepared by Nethsinghe's method.[15)] Resulted precipitate was filtered and then washed with chloroform. The compound thus obtained was recrystallized twice from $\mathrm{CHCl_3}$. Yield, 0.35 g (48%); mp >300 °C. Ion-exchange from methyl sulfate anion to perchlolate form gave compound **1**. Yield, 0.25 g (89%). Anal. Calcd for $\mathrm{C_{21}H_{19}N_2O_4Cl+1H_2O}$; C, 60.51; H, 5.08; N, 6.72; Cl, 8.50%. Found: C, 59.92; H, 4.90; N, 6.60; Cl, 8.67%.

4,4′-*p*-Phenylenebis(vinylene)bisquinoline. 4-Methylquinoline (2.0 g), terephthalaldehyde (0.9 g) and methanesulfonic acid (1.4 g) were dissolved in *p*-xylene (150 ml) and were refluxed for 22 h in a flask equipped with a Dean–Stark trap.[15)] Cooling to room temperature gave a red precipitate which was collected and then was dissolved in 200 ml KOH aqueous solution (pH >10). Chloroform extraction followed by the solvent evaporation gave 4,4′-[*p*-phenylenebis(vinylene)]bisquinoline which was recrystallized twice from *p*-xylene. Yield, 1.6 g (61%); mp 248—249 °C. Anal. Calcd for $\mathrm{C_{28}H_{20}N_2}$: C, 87.47; H, 5.24; N, 7.29%. Found: C, 87.31; H, 5.55; N, 7.08%.

1-Methyl-4-[2-[4-[2-(4-quinolyl)vinyl]phenyl]vinyl]quinolinium Perchlorate (2). Dimethyl sulfate 50 μl was slowly added to chloroform solution (30 ml) of 4,4′-[*p*-phenylenebis(vinylene)]bisquinoline (0.2 g) with stirring. Resulted precipitate was collected and was washed with chloroform. The methylsulfonic acid salt was recrystallized from $\mathrm{CH_3CN}$. Yield, 0.15 g (57%); mp >300 °C. Compound **2** was prepared by ion-exchange into perchlorate form. Yield, 0.2 g (92%); mp >300 °C. Anal. Calcd for $\mathrm{C_{29}H_{23}N_2O_4Cl+1H_2O}$: C, 67.37; H, 4.87; N, 5.42; Cl, 6.86%. Found: C, 67.52; H, 4.72; N, 5.41; Cl, 6.79%.

Surface Pressure-Area Isotherms. Acetonitrile/benzene (v/v=1/9, Tokyo-Kasei spectroscopic grade)

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was used as a spreading solvent. Surface pressure–area isotherms of the monolayers of **1** and **2** were measured on 0.1 M $\mathrm{KClO_4}$ aqueous solution (1 M=1 mol dm^{-3}) at a compression rate of 0.4 mm s^{-1} by a computer-controlled film balance (USI system, Model FSD-20).

Formation of LB Monolayer Electrodes and Electrochemical Measurements. Deposition of monolayer and in situ electrochemical measurements were conducted with a computer controlled Langmuir trough (trough size, 330 mm×40 mm; are a controller, USI System Co., Ltd., FSD-111) and an electrochemical analyzer (Bioanalytical Systems, Co., Ltd., Model 100B). The trough was placed in a closed box to keep nitrogen atmosphere. Under the conditions of each constant surface area corresponding to the surface pressure of 25 mN m^{-1}, a polished Au disk electrode (Bioanalytical Systems, Co., Ltd. diameter 1.6 mm) was slowly lowered horizontally to the air/water interface and then push it into the subphase in order to transfer the monolayer of **1** or **2** on each electrode (**1**/Au and **2**/Au). The vertical dipping method did not give LB monolayer electrodes with satisfactory surface coverages.

In situ cyclic voltammetry and potential-step chronocoulometry of the modified electrodes were conducted in a subphase solution with the electrochemical analyzer. A saturated calomel electrode and a Pt wire were used as the reference and the counter electrode, respectively.

Results and Discussion

Formation of Monolayers. Figure 1 shows surface pressure–area isotherms of **1** and **2**. Both monolayers show typical expanded phase. Limited molecular occupied areas of **1** and **2** monolayers are 0.27, 0.37 nm^2/molecule, respectively which are almost identical with those of the cross-section area estimated by the CPK space-filling model. Note that such rigid amphiphilic compounds without alkyl long chains can form monolayers on the water surface by the Langmuir technique. Watakabe and Kunitake[16] described monolayer formations of compounds with similar π-conjugated chain, but not possessing electroactive group. Langmuir monolayer of **1** and **2** could easily be transferred to a gold plate electrode (Fig. 2). Totally π-conjugated aromatic compounds possessing monolayer formation ability should be interesting as materials for molecular electronics and nonlinear optics apart from their fundamental characteristics.

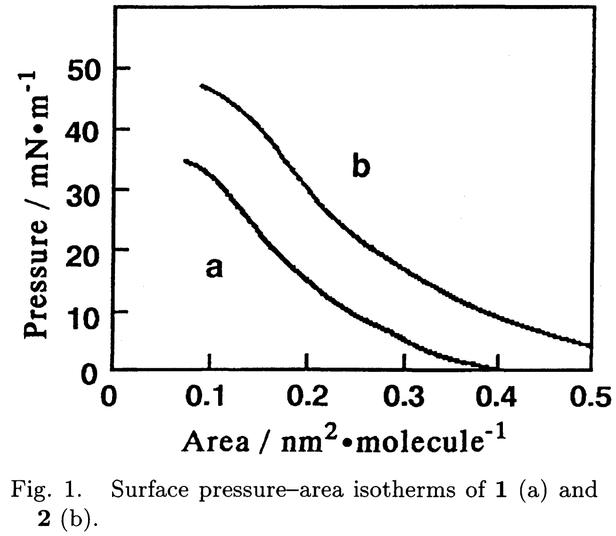

Fig. 1. Surface pressure–area isotherms of **1** (a) and **2** (b).

Cyclic Voltammograms of LB Monolayer Modified Electrodes. Figure 3 (trace a) shows a typical cyclic voltammogram (first scan) for a **1**/Au electrode where the monolayer was transferred to the electrode at 25 mN m^{-1}, which is a critical value and there would be either a partial collapse or dissolution of **1** monolayer into the subphase; still the transferred LB film possesses homogeneous structure by electrochemically as is described later. Obtained redox peaks ($E_{\mathrm{pa}}=-0.86$ V and $E_{\mathrm{pc}}=-1.08$ V) are attributable to one-electron reduction/oxidation couple of **1**. Despite

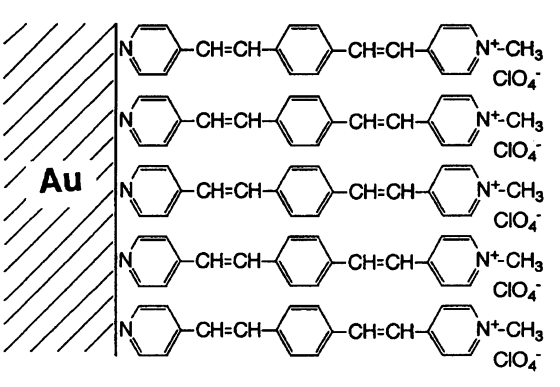

Fig. 2. Possible structure of a monolayer of **1** on an electrode.

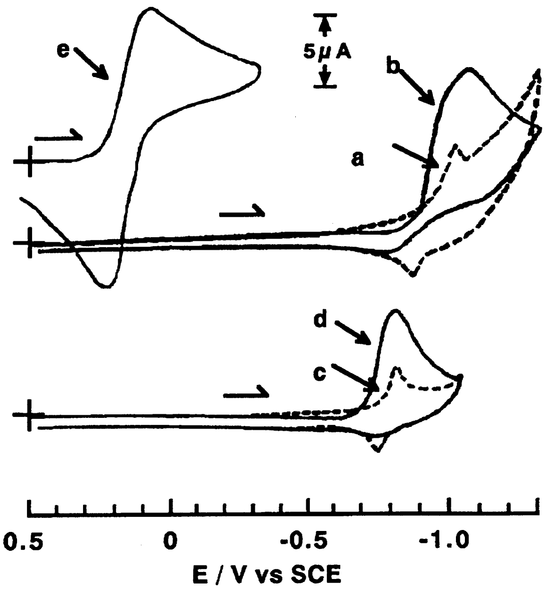

Fig. 3. Typical cyclic voltammograms for a **1**/Au in the absence (a) and presence (b) of 1.0 mM $\mathrm{K_3[Fe(CN)_6]}$ and for a **2**/Au in the absence (c) and presence (d) of 1.0 mM $\mathrm{K_3[Fe(CN)_6]}$. Trace (e) shows a cyclic voltammogram of $\mathrm{K_3Fe(CN)_6}$ with a bare electrode. Scan rate, 0.2 V s^{-1}. Temperature, 20 °C.

the voltammogram is come from adsorbed species on the electrode, rather large peak separation (about 0.2 V) is observed, indicating that the electron transfer between the electrode and **1** monolayer is relatively slow.

Figure 3 (trace c) shows a typical cyclic voltammogram (first scan) for a **2**/Au electrode. The redox peaks ($E_{pa}=-0.78$ V and $E_{pc}=-0.84$ V) shifts to positive potential than those of **1**/Au by ca. 160 mV. This comes from lowered reductive potential due to the extended π-conjugated chain of **2**. Occupied areas of the electroactive monolayer on the electrode calculated from the areas of the reductive peaks for **1** and **2** were 0.29±0.03 and 0.31±0.05 nm^2/molecule respectively, which are close those of molecular occupied area described above. The redox currents of **1**/Au and **2**/Au electrodes decreased gradually by repeated scans; the current at second scan decreased by 25% in comparison with the first.

Figure 3 (trace b and d) show typical voltammograms (first scan) of **1**/Au and **2**/Au in the presence of 1 mM $[Fe(CN)_6]^{3-}$ in solution, respectively. In both cases, there are drastic increase in the reduction current and the disappearance of the oxidation peak. As shown in Fig. 4, the intensity of reduction current increased in proportion to $[Fe(CN)_6]^{3-}$ concentration in solution. The observed enhanced redox current at the corresponding reduction potentials for each redox compound showed that the measured currents are not tunnel current but catalytic via the redox mediators in the LB monolayers.

Figure 3 (trace e) shows a cyclic voltammogram of $[Fe(CN)_6]^{3-}$ with a bare electrode. Note that the LB monolayer modified electrodes show no peak near 0.1 V corresponding to the redox potential of $[Fe(CN)_6]^{3-}$. This indicates that the degree of surface coverage of the electrode with **1** and **2** is rather high and subsequently the monolayer blocks the direct electron transfer of $[Fe(CN)_6]^{3-}$ with the electrode. Usually it is not easy for many LB monolayer modified electrodes to prohibit the direct electron transfer reactions of electroactive species in solution, because monolayers on electrodes often possess some macroscopic defects.

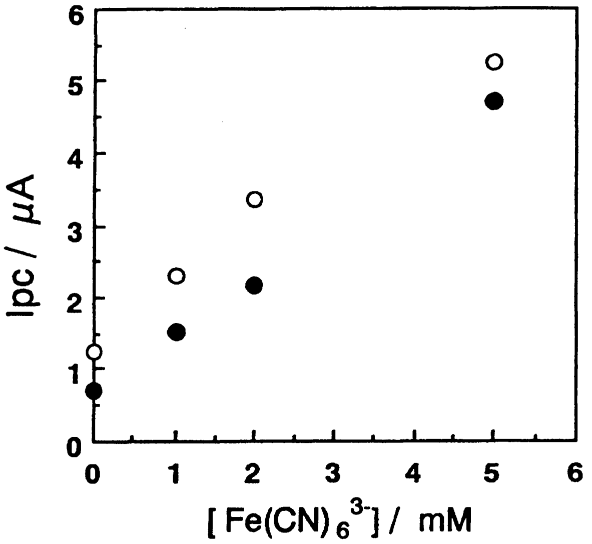

Fig. 4. Influence of $K_3[Fe(CN)_6]$ concentration on reduction peak currents of **1**/Au (○) and **2**/Au (●) electrodes. The solutions are 0.1 M $KClO_4$ aqueous solution at 20 °C.

From all results described above, it is evident that the stepwise electron transfer from the monolayer assemblies of **1** and **2** on the gold to $[Fe(CN)_6]^{3-}$ in solution is achieved in these system. Figure 5 shows schematic presentation for the rectified electron transfer of this system.

Chronocoulometric Responses of Monolayer Modified Electrodes. Double potential step chronocoulometry was introduced to examine the rectified electron transfer for the **1** (or **2**)/Au–$[Fe(CN)_6]^{3-}$ system at the voltage range between reductive potential of **1** (or **2**) and oxidative potential of $[Fe(CN)_6]^{3-}$. At forward step (0—200 ms), cumulative charge increased almost linearly with the increase of $[Fe(CN)_6]^{3-}$ concentration and at reverse step (200—400 ms) the charges are constant (Fig. 6 (trace a—c)). This result shows sharp contrast with that for a bare gold electrode which shows large decrease of charge at the reversal step; at 400 ms relatively large rest charge is caused for the bare electrode by the irreversible background charge at −1.1 V (Fig. 6, trace d). A similar chronocoulometric experiment with **2** instead of **1** gave similar result (data not shown). These are the direct proofs of vectorial electron transfer from the electroactive monolayer **1** and **2** on the gold to $[Fe(CN)_6]^{3-}$ in solution.

The slope of Anson plot (Q vs. $t^{1/2}$ plot) gives an apparent effective electrode area by the following Cottrell equation (1),

$$Q(t) = 2nFAD^{1/2}Ct^{1/2-1/2}, \tag{1}$$

where Q is charge, n is electron number, F is faradaic constant, A is apparent electrode area, D is diffusion constant, and C is concentration of $[Fe(CN)_6]^{3-}$. The apparent electrode area (A) of **1**/Au system is 2.0±0.1

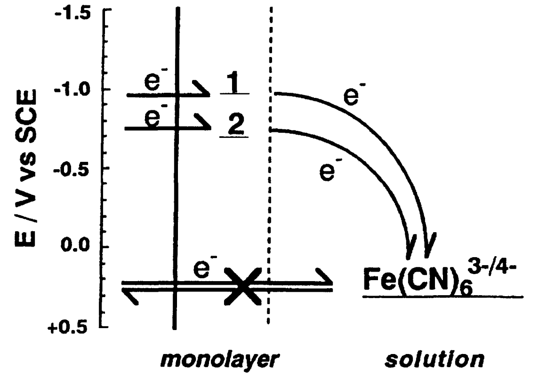

Fig. 5. Schematic presentation for the stepwise rectified electron transfer system.

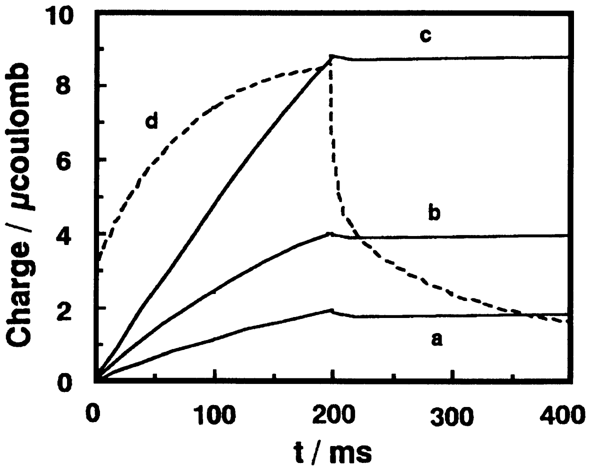

Fig. 6. Double-step chronocoulometric responses for a **1**/Au electrode (a—c) and for a bare electrode (d). Concentrations of $K_3[Fe(CN)_6]$ are: a and d, 1.0 mM; b, 2.0 mM; c, 5.0 mM. Step-up potential, −1.1 V. Final potential, 0.4 V. Pulse width, 200 ms.

which is the same as the value, $A_0=2.0\pm0.1$ for the bare electrode. This indicates that *the efficiency of the electron transfer reaction of the monolayer modified electrode does not lower even after modification.*

Conclusion

The rectified transmembrane electron transfer via the LB monolayer of the electroactive amphiphile has been proved by using cyclic voltammetry and chronocoulometry. Extended aromatic π-conjugated amphiphiles **1** and **2** are candidates of "*molecular wire*" compounds. Lehn and co-workers[17] have reported an electron transfer across a caroviologen molecular wire compound embedded in bilayer membranes dispersed in an aqueous solution. It is not easy to elucidate whether the electron transfer occurs "through bond" or "through space" in the LB monolayer on the electrode; however, apart from this difficulty, development of novel vectorial electron transfer systems using LB monolayers should be important both from the aspects of fundamentals on vectorial electron transfer mechanisms at electrode interfaces and of applications for molecular electronics based on assembled organizates.

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References

1) H. Daifuku, K. Aoki, K. Tokuda, and H. Matsuda, *J. Electroanal. Chem.*, **183**, 1 (1985).
2) H. Daifuku, I. Yoshimura, I. Hirata, K. Aoki, K. Tokuda, and H. Matsuda, *J. Electroanal. Chem.*, **199**, 47 (1986).
3) M. Fujihira and T. Araki, *Bull. Chem. Soc. Jpn.*, **59**, 2375 (1986).
4) C. W. Lee and A. J. Bard, *Chem. Phys. Lett.*, **170**, 57 (1990).
5) D. H. Charych, E. M. Landau, and M. Majda, *J. Am. Chem. Soc.*, **113**, 3340 (1991).
6) C. E. D. Chidsey, C. R. Bertozzi, T. M. Putvinski, and A. M. Mujsce, *J. Am. Chem. Soc.*, **112**, 4301 (1990).
7) J. Li and A. E. Kaifer, *Langmuir*, **9**, 591 (1993).
8) H. O. Finklea and D. D. Hanshew, *J. Electroanal. Chem.*, **347**, 327 (1993).
9) E. Katz, N. Itzhak, and I. Willner, *Langmuir*, **9**, 1392 (1993).
10) S. E. Creager, D. M. Collard, and M. A. Fox, *Langmuir*, **6**, 1617 (1990).
11) S. Ueyama and S. Isoda, *J. Electroanal. Chem.*, **310**, 281 (1991).
12) Y. Sato, H. Itoigawa, and K. Uosaki, *Bull. Chem. Soc. Jpn.*, **66**, 1032 (1993).
13) M. Kunitake, K. Akiyoshi, K. Kawatana, N. Nakashima, and O. Manabe, *J. Electroanal. Chem.*, **292**, 277 (1990).
14) M. Kunitake, S. Kawahara, N. Nakashima, and O. Manabe, *J. Electroanal. Chem.*, **309**, 341 (1991).
15) L. P. Nethsinghe, P. H. Plesch, and D. J. Hodge, *Angew. Makromol. Chem.*, **148**, 161 (1987).
16) A. Watakabe and T. Kunitake, *Thin Solid Films*, **186**, 21 (1990).
17) S. Kugimiya, T. Lazrak, M. B-Desce, and J-M. Lehn, *J. Chem. Soc., Chem. Commun.*, **1991**, 1179.