

## Electroconductive Langmuir–Blodgett Films Containing a Carotenoid Amphiphile for Sugar Recognition

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The fabrication of electroconductive molecules has attracted the most interest in nanotechnology. Especially, the conducting molecule incorporated in a two-dimensionally organized matrix could function as an electric wire in nanoscale electric circuits. To date, the molecules which have a long conjugated bond such as carotenoid derivatives,<sup>1,2</sup> phenylene–vinylene,<sup>3,4</sup> and phenylene–ethynylene<sup>5</sup> have been synthesized and incorporated into Langmuir–Blodgett (LB) films<sup>1,3</sup> and self-assembled monolayers (SAM).<sup>2,4,5</sup> These studies have demonstrated that the conjugated molecules provided electric conduction to organic molecular layers, which are generally insulators. If molecular recognition sites could be attached to the conducting molecules, the molecules can then be connected to each other or wired to the desired joints via the guest molecules, and further be applied to the chemical sensors or the nanoelectronics device.

In the present study, we synthesized a novel electroconductive amphiphile functionalized with a boronic acid. The electroconductive amphiphile was incorporated into the LB film on an electrode. Using this electrode, the redox current of the redox-active sugar derivative was selectively observed. As already mentioned, this provides a key step for designing molecular electronic devices based on molecular assembling.

The boronic acid-functionalized, electroconductive LB film was fabricated by the polymerization of a 1:10 mixture of a carotenoid type amphiphile **1**<sup>6</sup> and a polymerizable amphiphile **2**<sup>8</sup> (Figure 1). The amphiphile **1** was designed as follows: (1) The amphiphile **1** has a long conjugated double bond chain, (2) a boronic acid is attached as a binding site for sugar derivatives, and (3) the length of **1**, 39.0 Å from the CPK model, is almost the same as that of **2**, 38.3 Å. The third point should work advantageously in preparing the mixed monolayer of **1** and **2**.

The mixed monolayer of **1** and **2** was prepared by spreading a solution of the 1:10 mixture of **1** and **2** in chloroform/methanol (10:1) onto the water surface (pH 11.0, KOH) of a Langmuir trough (USI system, FSD 50). Ten minutes after the spreading, the monolayer was compressed at a surface pressure of  $20.0 \pm 0.1$  mN/m, which was maintained for 10 min. The monolayer was then polymerized by irradiation at 254 nm using a UV lamp ( $200 \mu\text{W}/\text{cm}^2$ ) for 10 min.<sup>9</sup> The polymerized mixed monolayer was deposited by the horizontal lifting method on a hydrophobic gold electrode, which was prepared by immersing a gold electrode in a  $1.0 \times 10^{-3}$  M solution of octanethiol in methylenechloride.<sup>10</sup> Furthermore, the LB film on the electrode thus prepared was doped with iodine by exposure to an iodine vapor under atmospheric pressure for 5 min. As a reference, the monolayer composed of only **2** was prepared and deposited on the hydrophobic gold electrode following the same procedure.

The cyclic voltammetry (CV) of a  $5.0 \times 10^{-5}$  M aqueous solution of **3** on the LB modified electrodes was examined. The mannoside **3** is composed of a nitrobenzene moiety as a redox-active site and

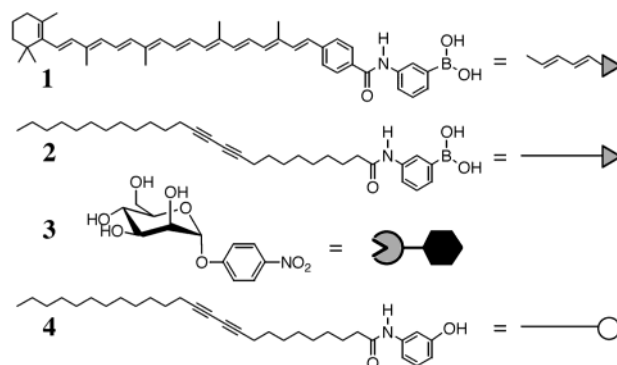


Figure 1. Structures of molecules examined in this study.

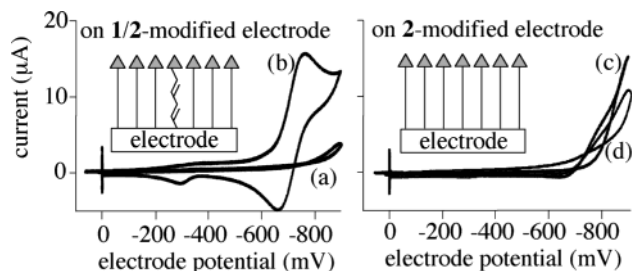
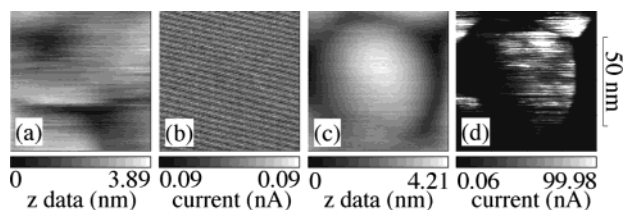


Figure 2. Cyclic voltammograms in a  $5.0 \times 10^{-5}$  M aqueous solution of **3** at pH 11, room temperature. The working electrodes were gold plates ( $3.9 \text{ cm}^2$ ) successively modified with the octanethiol SAM and (a,b) the mixed monolayer of **1** and **2**, and (c,d) the monolayer of **2**. The working electrodes in (b,d) were exposed to iodine before use. Reference electrode, Ag/AgCl; counter electrode, Pt; electrolyte, 0.10 M sodium sulfate; and scan rate, 10 mV/s.

a mannoside moiety as a binding site. The pH of the solutions of **3** was adjusted to 11.0 because the formation of the boronic acid ester is promoted at higher pH's.<sup>11</sup> Without the doping with iodine, no current peaks were observed on the 1/2- and 2-modified electrodes (Figure 2a,c). Both of the undoped LB films did block the electron flow which was observed on a bare gold electrode (Figure S4). On the other hand, the reversible redox reaction of **3** was observed on the 1/2-modified electrode after the doping (Figure 2b); the reduction and the oxidation peak currents were  $+15.5 \mu\text{A}$  at  $-768 \text{ mV}$  and  $-5.0 \mu\text{A}$  at  $-665 \text{ mV}$ , respectively, while no current peaks were observed on the 2-modified electrode even after the doping. The observed voltammogram of **3** on the 1/2-electrode was reproducible, and the profile did not change after 10 scans. This electron conduction should be attributable to the iodine-doped carotenoid moiety. Shirakawa et al. have demonstrated the markedly increased conductivity of the polyacetylene (polyene) film by exposure to iodine vapor. They proposed that a charge-transfer complex and/or a carbonium ion complex were formed. The similar complex should be formed between the polyene chain of **1** and



**Figure 3.** (a,c) AFM topographs and (b,d) current images of the polymerized mixed monolayer of **1** and **2** (1:10) on the gold electrode (a,b) before and (c,d) after doping with iodine. The tip bias was +0.1 V, and the load was  $\pm 2$  nN.

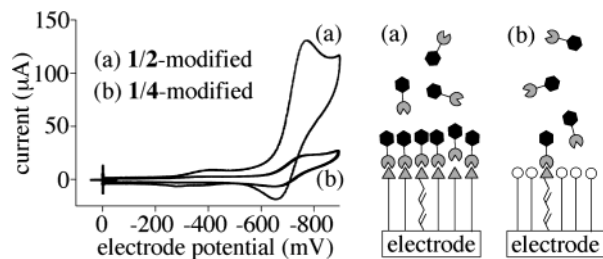
iodine. One may note that no redox peak was observed for the iodine-doped carotenoid in the range between  $-0.9$  and  $+0.7$  V (Figure S5).

The difference in the oxidative and reductive electrochemical half wave potentials might seem relatively large for a redox reaction of the immobilized species. Such large peak separations have been reported for the immobilized species on the SAM-modified electrodes where the redox reactions were charge-transfer controlled.<sup>13</sup> The large peak separation observed here should be attributed to the overpotential required for the charge transfer across the thick organic monolayer (ca. 4 nm).

The CVs of ferrocyanide and nitrobenzene were also examined on the **1/2**-modified electrode after the iodine doping to investigate the molecular selectivity of the electrode. The modified electrodes exhibited no redox peaks for either of them, although they are well known to be redox-active species on gold electrodes (Figures S6, S7). These results ensured that the **1/2**-LB film was free of defects and of diffusing redox species. This control experiment also supported that the redox reaction of **3** on the **1/2**-electrode proceeded through molecular recognition.

The microscopic electric conduction of the modified electrode was examined by AFM-current imaging (Seiko Instrument, Inc., SPA400). The current between a rhodium-coated tip and the modified electrodes was recorded simultaneously with the topographs. The bias voltage and the load between the tip and the modified electrodes were maintained at +0.1 V and within  $\pm 2$  nN, respectively. The roughness of several nanometers in the topographs originated from the deposited gold film (Figure 3a,c). On the **2**-modified electrode, the observed current was only at noise level (less than  $10^{-10}$  A, similar with Figure 3b) both after and before the iodine doping, which demonstrated that the **2**-LB film worked as an insulator. On the other hand, the **1/2**-modified electrode showed electrically conductive domains, where a current of ca.  $10^{-7}$  A was observed, only after the doping (Figure 3d). This microscopic observation demonstrated that the **1/2**-LB film developed the electronic conduction by doping with iodine, and these results agreed well with the result of the CV measurement.

The boronic acid amphiphile **2** in the **1/2**-modified electrode was replaced with the phenol amphiphile **4** to strictly assess the molecular recognition property of the boronic acid moiety of **1**. The **1/4**-modified (1:10) electrode was prepared as described above, and the CV of **3** was measured (Figure 4). The reduction peak current of **3** on the **1/4**-modified electrode was only  $+23.0 \mu\text{A}$  at  $-770$  mV at the scan rate of 200 mV/s, while that on the **1/2**-modified electrode was  $+132 \mu\text{A}$  at  $-770$  mV. The decrease in the reduction current to 17% reflected the decreased surface density of the boronic acid group. In the 1:10 mixed LB film of **1/2**, most of the amphiphile **2** should be placed adjacent to the amphiphile **1**. Therefore, not only the **3** binding to **1** but also the **3** binding to **2** can undergo the redox reaction through **1**. On the **1/4**-modified electrode, only the **3** bound to the boronic acid moiety of **1** must



**Figure 4.** Cyclic voltammograms in a  $5.0 \times 10^{-5}$  M aqueous solution of **3** at pH 11, room temperature. The working electrodes were gold plates ( $3.9 \text{ cm}^2$ ) successively modified with the octanethiol SAM and (a) the 1:10 mixed monolayer of **1** and **2**, and (b) the 1:10 mixed monolayer of **1** and **4**. The working electrodes were exposed to iodine before use. Reference electrode, Ag/AgCl; counter electrode, Pt; electrolyte, 0.10 M sodium sulfate; and scan rate, 200 mV/s.

have undergone the redox reaction, which evidenced that **1** acted as the molecular wire.

In conclusion, the electrically conductive LB film was fabricated by incorporating the conjugated molecule into a monolayer and successively doping the monolayer with iodine. The selectivity of the electrode for a sugar derivative was achieved by attaching the molecular recognition site to the conjugated molecule. The conducting molecule with binding site, that is, the molecular wire with the connecting terminal, as designed in this study would open the possibility of designing well-defined complex molecular devices based on the rich library of molecular assembly chemistry.

**Acknowledgment.** This work was supported by Grant-in-Aids for Scientific Research (14740372) and for the COE project, Giant Molecules and Complex Systems, from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and by the NEDO International Joint Research Grant Program.

**Supporting Information Available:** The surface pressure–area isotherms of the monolayers; the time-course of the area of the **1/2** monolayer during the photoirradiation; the UV–visible and IR spectra of the polymerized monolayers; and the voltammograms of **3**, nitrobenzene, and potassium ferrocyanide. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Sereno, L.; Silber, J. J.; Otero, L.; Bohorquez, M. d. V.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem.* **1996**, *100*, 814.
- Leatherman, G.; Durantini, E. N.; Gust, D.; Moore, T. A.; Moore, A. L.; Stone, S.; Zhou, Z.; Rez, P.; Liu, Y. Z.; Lindsay, S. M. *J. Phys. Chem. B* **1999**, *103*, 4006.
- Kunitake, M.; Nasu, K.; Manabe, O.; Nakashima, N. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 375.
- Kunitake, M.; Akiyoshi, K.; Kawatana, K.; Nakashima, N.; Manabe, O. *J. Electroanal. Chem.* **1990**, *292*, 277.
- Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L. II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.
- The amphiphile **1** was synthesized from 7'-apo-7'-(4-carboxyphenyl)- $\beta$ -carotene<sup>7</sup> and 3-aminophenylboronic acid.
- Gust, D.; Moore, T. A.; Bensasson, R. V.; Mathis, P.; Land, E. J.; Chachaty, C.; Moore, A. L.; Liddell, P. A.; Nemeth, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 3631.
- Miyahara, T.; Kurihara, K. *Chem. Lett.* **2000**, 1356–1357.
- The area of the monolayer decreased by the photoirradiation, and the shrinkage finished in less than 10 min (Figure S2). The polymerization was confirmed by UV–visible spectroscopy (Figure S3).
- Octanethiol exhibited the best performance among the thiols we examined. The gold electrode modified with ethane-, butane-, or hexanethiol did not give reproducible results. The SAM of octadecanethiol completely blocked the current.
- Tsukagoshi, K.; Shinkai, S. *J. Org. Chem.* **1991**, *56*, 4089.
- Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578.
- Bowden, E. F. *Electrochem. Soc. Interface* **1997**, winter, 40.

JA0390101