

# A C<sub>60</sub>-Embedded Artificial Bilayer Membrane Film Electrode Device: Phase-Transition-Dependent Electrochemistry

Naotoshi Nakashima,\* Yuko Nonaka, Takashi Nakanishi, Takamasa Sagara, and Hiroto Murakami

Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-cho, Nagasaki 852-8521, Japan

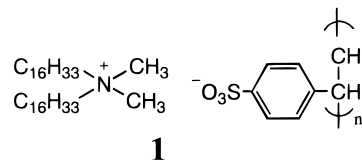
Received: June 24, 1998

We describe here regulated electrochemistry of C<sub>60</sub> embedded in a cast film of an artificial lipid, dihexadecyldimethylammonium poly(styrene sulfonate) (**1**) on an electrode. The X-ray diffraction diagram for a cast film of C<sub>60</sub>/**1** (molar ratio, 1/19) showed a diffraction peak at  $2\theta = 1.8^\circ$ , suggesting that the film forms multilayer structure with the molecular layers tilting by  $47^\circ$  from the basal plane. Phase-transition temperature for a cast film of **1**/C<sub>60</sub> (molar ratio, 1/19) in the presence of water determined by differential scanning calorimetry was 27 °C, which was almost identical with that of the single component of **1**. At temperatures above the phase transition, a cast film of C<sub>60</sub>/**1** on a basal plane pyrolytic graphite electrode in aqueous solution gave quasi-reversible two-consecutive one-electron-transfer processes leading to C<sub>60</sub><sup>2-</sup> with the formal potential of  $E_1^{0'} = -0.35$  V and  $E_2^{0'} = -0.99$  V vs SCE corresponding to C<sub>60</sub>/C<sub>60</sub><sup>•-</sup> and C<sub>60</sub><sup>•-</sup>/C<sub>60</sub><sup>2-</sup>, respectively. At temperatures below the phase-transition temperatures, the redox current for the electrode was very small or nondetectable. This temperature dependence was reversible; that is, temperature-driven “on–off” switching of C<sub>60</sub> electrochemistry was possible. The observed phenomenon would be applicable to C<sub>60</sub>-derivatives, higher fullerenes, and metallofullerenes. The present study opens possibilities for the construction of fullerene/artificial lipid electrical devices based on the nature of self-organized lipid bilayer membranes.

## Introduction

Characterization and functionalization of fullerenes and related compounds are of great interest from both a fundamental and a practical point of view.<sup>1</sup> Our interest is focused on the combination of fullerene chemistry and the chemistry of lipid bilayer membranes.<sup>2</sup> Lipid bilayer membranes are reported to provide suitable microenvironments for functionalization of fullerenes.<sup>3</sup> The electrochemical properties of fullerenes and related molecules from both experimental and theoretical aspects are currently the subject of intense research focus.<sup>4</sup> In comparison with the electrochemistry of fullerenes dissolved in organic solvents<sup>5</sup> and of a C<sub>60</sub>/γ-cyclodextrin complex dissolved in aqueous solution,<sup>6</sup> the electrochemistry of *fullerene films* on electrodes in both organic solvents<sup>4,7</sup> and aqueous solution<sup>8</sup> is rather complicated. Moreover, aqueous solution electrochemistry for C<sub>60</sub> cast films has been reported to be very unstable.<sup>8</sup> In contrast, we recently found that cast films of ammonium amphiphiles provide suitable microenvironments for the stable electrochemistry of C<sub>60</sub>.<sup>9</sup> Our current interest is focused on the construction of molecular electrode devices using fullerene film materials that are tunable. The goal is to regulate the electrochemistry of fullerene thin films on electrodes on the basis of the nature of self-assembled lipid bilayer membranes. To this end, we have designed and constructed a C<sub>60</sub>/artificial lipid bilayer film electrode device. We describe here the novel finding that the electrochemistry of C<sub>60</sub>, when embedded in a poly(ion-complexed) lipid film cast on an electrode, can be tuned by changing from/to the crystalline to/from the liquid crystalline phases of the film. An artificial lipid,

## CHART 1

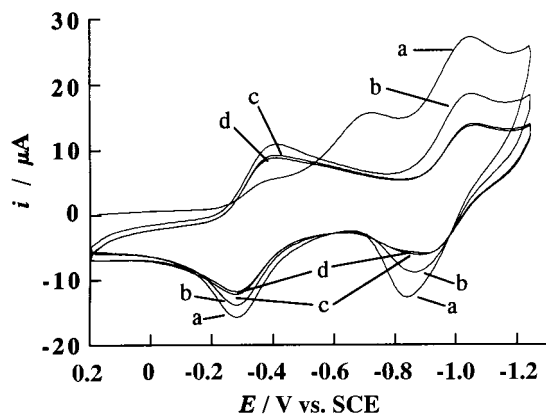


dihexadecyldimethylammonium poly(styrene sulfonate) (**1**) (see Chart 1), which forms water-insoluble multilamellar bilayer films with fundamental lipid bilayer characteristics,<sup>10</sup> was used as the electrode modifier.

## Experimental Section

Compound **1** was synthesized according to the previously described method<sup>10</sup> and analyzed by IR, NMR, and elemental analysis. X-ray diffraction study and differential scanning calorimetry<sup>11</sup> for cast films of C<sub>60</sub>/**1** or single component of **1** were conducted with a Rigaku RINT 2200 X-ray diffractometer or a Shimadzu DSC-60 differential scanning calorimeter, respectively. Modified electrodes were prepared using the following procedure. Thirty microliters of C<sub>60</sub>/**1** in benzene (C<sub>60</sub> = 0.80 mM) was placed on a basal plane pyrolytic graphite (BPG) disk electrode<sup>12</sup> (geometric area, 0.25 cm<sup>2</sup>) and allowed to air-dry. These obtained modified-electrodes were then annealed in 0.5 M tetraethylammonium chloride (TEAC) aqueous solution at 50 °C for 30 min. The electrochemistry of C<sub>60</sub>/**1** cast films on BPG electrodes was examined using cyclic voltammetry (equipment, BAS-100BW electrochemical ana-

\* Corresponding author. E-mail: nakasima@net.nagasaki-u.ac.jp.



**Figure 1.** Typical cyclic voltammograms for a cast film of  $C_{60}/1$  (molar ratio, 1/19) on a BPG electrode in a 0.5 M TEAC aqueous solution at 35.2 °C: (a) first cycle; (b) second cycle; (c) 20th cycle; (d) 30th cycle. Scan rate, 0.1 V/s.

lyzer, Bioanalytical Systems). A saturated calomel electrode (SCE) and a Pt plate electrode were used as the reference and the counter electrode, respectively. Temperatures were controlled within  $\pm 0.1$  °C in the range of 10–50 °C.

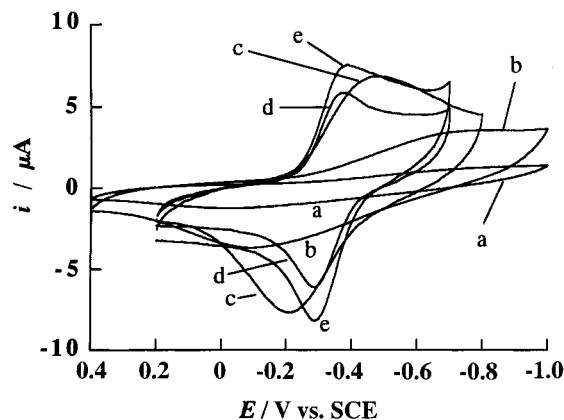
## Results and Discussion

The X-ray diffraction diagram for a film of  $C_{60}/1$  (molar ratio, 1/19) cast from benzene solution showed a diffraction peak at  $2\theta = 1.8^\circ$  (data not shown), which is identical with that for a cast film of single component of **1**. The  $d$ -spacing calculated from the Bragg equation to be 4.8 nm is shorter than the molecular length<sup>13</sup> of **1** by a factor of 2, suggesting that the film forms a multilayer structure with the molecular layers tilting by  $47^\circ$  from the basal plane.

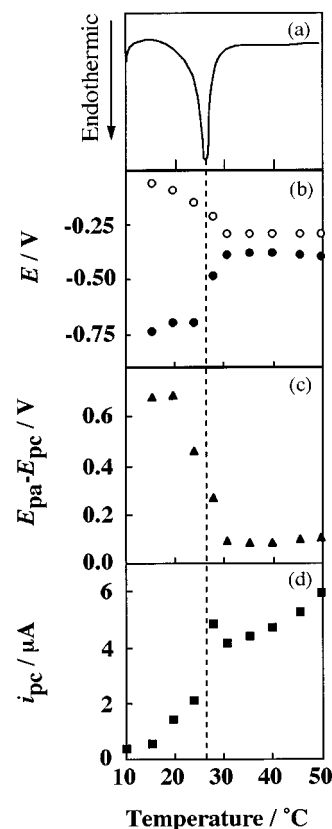
One of the most fundamental characteristics of lipid bilayer membranes is the existence of a phase transition.<sup>14</sup> A cast film of  $C_{60}/1$  (molar ratio, 1/19) in water was found to give a single endothermic peak at 27 °C (see Figure 3a), corresponding to the transition temperature ( $T_c$ ) between the crystalline and liquid crystalline phases. This is almost the same as that of single component of **1**, indicating that  $C_{60}$  does not change the bilayer membrane structure substantively.

Typical cyclic voltammograms (CVs) of a  $C_{60}/1$  cast film on BPG at 35.2 °C are shown in Figure 1. During potential cycling at a scan rate of 100 mV/s, the current of the first and second redox couples decreased to constant values.<sup>15</sup> Well-defined quasi-reversible two-consecutive one-electron-transfer processes leading to  $C_{60}^{2-}$  with the formal potential of  $E_1^{0'} = -0.35$  V and  $E_2^{0'} = -0.99$  V vs SCE corresponding to  $C_{60}/C_{60}^{\bullet-}$ ,  $C_{60}^{\bullet-}/C_{60}^{2-}$  are evident. Note that both  $C_{60}^{\bullet-}$  and  $C_{60}^{2-}$  are stable; this is in sharp contrast with the result for a cast film of  $C_{60}$  only on the electrode in aqueous solution. In that case, the redox current for the first and second redox couples disappears in the CVs after 6–7 scans at 100 mV/s.<sup>8c</sup>

Temperature experiments were conducted for the first redox couple in the CV for the modified electrode and the result is shown in Figure 2. It is evident that the electrochemistry shows a strong temperature dependence; at the lower temperatures, the electrode gave almost no electrochemical communication attributable to  $C_{60}$ . Figure 3 shows plots of the anodic and cathodic potentials,  $E_p$  (b), the peak separation (c), and the reduction peak current (d) in the CVs of the modified electrodes as a function of temperature. The observed break near 28 °C is very close to the phase transition of the bilayer films as shown



**Figure 2.** Temperature dependence of cyclic voltammograms for a cast film of  $C_{60}/1$  (molar ratio, 1/19) on a BPG electrode in a 0.5 M TEAC aqueous solution: (a) 10.3 °C; (b) 19.8 °C; (c) 27.8 °C; (d) 39.8 °C; (e) 49.7 °C. Scan rate, 0.1 V/s.



**Figure 3.** DSC thermogram for a cast film of  $C_{60}/1$  (molar ratio, 1/19) in the presence of water (a) and temperature dependence of anodic (open circles) and cathodic (closed circles) peak potential (b), peak separation (c), and cathodic peak current (d) in the voltammograms, at 0.1 V/s, for a cast film of  $C_{60}/1$  (molar ratio, 1/19) on a BPG electrode in a 0.5 M TEAC aqueous solution.

in Figure 3a. The temperature-dependent peak separation indicates that the phase transition of the bilayer film and the electron-transfer rate constants for  $C_{60}$  in the bilayer film are closely related. This temperature dependence was reversible; that is, the temperature-driven “on–off” switching of  $C_{60}$ -electrochemistry was possible.

In conclusion, we have demonstrated that the electrochemistry of  $C_{60}$  embedded in the artificial lipid film is tunable by the temperature-controlled phase transition of the bilayer films. This phenomenon could be generally applicable to  $C_{60}$ -derivatives, higher fullerenes, and metallofullerenes. The present study

opens possibilities for the construction of fullerene/lipid electrical devices based on the nature of self-organized lipid bilayer membranes.

**Acknowledgment.** This work was supported, in part, by the Iketani Science Foundation and the Grant-in-Aids from the Ministry of Education, Science, Sports, and Culture, Japan.

## References and Notes

- (1) (a) *Fullerenes*; Hammond, G. S., Kuck, V. J., Eds.; ACS Symposium Series 481; American Chemical Society: Washington, DC, 1992. (b) *Buckminsterfullerenes*; Billups, W. E., Ciufolini, M. A., Eds.; VCH Publishers: New York, 1993. (c) *Physics and Chemistry of the Fullerenes*; Prassides, K. Ed.; Kluwer Academic Publishers: Boston, MA, 1994. (d) *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1997. (e) *The Fullerenes; New Horizons for the Chemistry, Physics and Astrophysics of Carbon*; Kroto, H. W., Ed.; Cambridge University Press: New York, 1997.
- (2) (a) Murakami, H.; Watanabe, Y.; Nakashima, N. *J. Am. Chem. Soc.* **1996**, *118*, 4484–4485. (b) Hetzer, M.; Bayerl, S.; Camps, X.; Vostrowsky, O.; Hirsch, A.; Bayerl, T. M. *Adv. Mater.* **1997**, *9*, 913–917.
- (3) (a) Hungerbühler, H.; Guldi, D. M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1993**, *115*, 3386–3387. (b) Bensasson, R. V.; Garaud, J.-L.; Leach, S.; Miquel, G.; Seta, P. *Chem. Phys. Lett.* **1993**, *210*, 141–148. (c) Garaud, J. L.; Janot, J. M.; Miquel, G.; Seta, P. *J. Membr. Sci.* **1994**, *91*, 259–264. (d) Niu, S.; Mauzerall, D. *J. Am. Chem. Soc.* **1996**, *118*, 5791–5795. (e) Janot, J. M.; Seta, P.; Bensasson, R. V.; Leach, S. *Synth. Met.* **1996**, *77*, 103–106. (f) Tien, H. T.; Wang, L.-G.; Wang, X.; Ottova, A. L. *Bioelectrochem. Bioenerg.* **1997**, *42*, 161–167.
- (4) Chlistunoff, J.; Cliffl, D.; Bard, A. J. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, 1997; pp 333–412.
- (5) Xie, Q.; P.-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980.
- (6) Boulas, P.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1994**, *98*, 1282–1287.
- (7) Chlistunoff, J.; Cliffl, D.; Bard, A. J. *Thin Solid Films* **1995**, *257*, 166–184.
- (8) (a) Szucs, A.; Loix, A.; Nagy, J. B.; Lamberts, L. *J. Electroanal. Chem.* **1995**, *397*, 191–203. (b) Szucs, A.; Loix, A.; Nagy, J. B.; Lamberts, L. *J. Electroanal. Chem.* **1996**, *402*, 137–148. (c) Davis, J. J.; Hill, H. A. O.; Kurz, A.; Leighton, A. D.; Safronov, A. Y. *J. Electroanal. Chem.* **1997**, *429*, 7–11.
- (9) (a) Nakashima, N.; Kuriyama, T.; Tokunaga, T.; Murakami, H.; Sagara, T. *Chem. Lett.* **1998**, 633–634. (b) Nakashima, N.; Tokunaga, T.; Nonaka Y.; Nakanishi, T.; Murakami, H.; Sagara, T. *Angew. Chem.* **1998**, in press.
- (10) Nakashima, N.; Yamaguchi, Y.; Eda, H.; Kunitake, M.; Manabe, O. *J. Phys. Chem. B* **1997**, *101*, 215–220 and references therein.
- (11) Twenty microliters of water was added to cast films of C<sub>60</sub>/1 (the amount of **1**, 0.5 mg) or **1** (0.5 mg) in DSC sample vessels.
- (12) Scotch tape was used to expose a fresh plane.
- (13) The molecular length of **1** estimated from the space filling model was 3.3 nm.
- (14) Chapman, D. *Biomembrane and Functions*; Verlag Chemie: Weinheim, 1984.
- (15) The first scan voltammogram would contain the reduction current of dioxygen still remaining in the film after deoxygenation with argon (purity, 99.998%).