

# Electrochemical and Chemical Reduction of Fullerenes C<sub>60</sub> and C<sub>70</sub> Embedded in Cast Films of Artificial Lipids in Aqueous Media

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In this paper, we first describe the electrochemical behavior of C<sub>60</sub> and of C<sub>70</sub> embedded in films of lipids and cationic amphiphiles on basal-plane pyrolytic graphite (BPG) electrodes in aqueous media. The electrode modifiers used were mainly tridodecylmethylammonium bromide (3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup>), tetraalkylammonium bromide (4C<sub>n</sub>N<sup>+</sup>Br<sup>−</sup>, *n* = 5, 6, 7, 8, 10, 12, and 16), and dihexadecyldimethylammonium poly(styrene sulfonate) (2C<sub>16</sub>N<sup>+</sup>PSS<sup>−</sup>). The generated radical monoanions and dianions of C<sub>60</sub> and C<sub>70</sub> on the electrodes were stable during continuous potential cycling, but the C<sub>70</sub> radical monoanion became unstable after the generation of C<sub>70</sub><sup>3−</sup>, which is not consistent with the behavior of C<sub>60</sub>. On the basis of the electrolyte dependence, a possible electron-transfer mechanism of fullerenes/lipid (amphiphile)-coated electrodes was presented. Second, a spectroelectrochemical study was conducted for C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup>-modified electrodes, and the results of simultaneous measurements of current and absorbance changes during potential cycling gave direct evidence of the generation of C<sub>60</sub><sup>•−</sup> in aqueous systems. Third, the strong phase-transition-dependent electrochemistry of fullerenes in the films on electrodes was demonstrated in which 2C<sub>16</sub>N<sup>+</sup>PSS<sup>−</sup> and 4C<sub>n</sub>N<sup>+</sup>Br<sup>−</sup> (*n* = 10, 12, 16) were used as the lipid and amphiphile matrices, respectively. Finally, chemical generation of fullerene radical anions C<sub>60</sub><sup>•−</sup> and C<sub>70</sub><sup>•−</sup> using Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> as a reducing reagent at lipid thin films containing C<sub>60</sub> or C<sub>70</sub> was investigated. Visible–near-IR spectra revealed that C<sub>60</sub><sup>•−</sup> and C<sub>70</sub><sup>•−</sup> were chemically produced in cationic lipid films in aqueous media. All results obtained suggest that the charge of the lipid matrix and the hydrophobic microenvironments in the lipid films play an important role in the generation of anions of C<sub>60</sub> and C<sub>70</sub> in these film states in aqueous media.

## Introduction

Fullerenes have been the subject of extensive investigations as to their intrinsic properties such as superconductivity,<sup>1</sup> ferromagnetism,<sup>2</sup> and photoconductivity<sup>3</sup> when they react with electron donors or acceptors. The chemistry of fullerene anions is among the most important in the study of fullerene chemistry.<sup>4</sup> The generation of fullerene anions in organic media using reducing reagents<sup>5</sup> and by electrochemical<sup>6</sup> and photochemical<sup>7</sup> methods has been reported for fullerenes dissolved in organic homogeneous solvents because fullerene anions are unstable in aqueous media.<sup>8</sup> Kadish et al. described the effects of electrolyte cations on the electrochemistry of C<sub>60</sub> in organic solutions.<sup>9c</sup> The electron-transfer mechanisms of C<sub>60</sub> and of C<sub>70</sub> on electrode surfaces are rather complicated and unstable in organic<sup>9,10</sup> and aqueous media.<sup>11,12</sup>

Szücs et al. described the electron-transfer mechanism of cast films of C<sub>60</sub> and C<sub>70</sub> on electrodes (Figure 1a) in aqueous media, showing a strong cation dependence.<sup>11b</sup> We described an electron-transfer mechanism for thin films of a fullerene lipid (3C<sub>n</sub>C<sub>60</sub>, Chart 1) on BPG electrodes in aqueous media<sup>13</sup> and

evaluated the thermodynamics of the binding of electrolyte cations to the radical monoanion and dianion of the fullerene moieties (Figure 1b). We recently reported stable electrochemistry for C<sub>60</sub>,<sup>14</sup> higher fullerenes,<sup>15</sup> and metallofullerenes<sup>16</sup> embedded in films of cationic lipids on electrodes in an aqueous system in which strong binding of electrochemically reduced fullerenes with the matrix lipid cations was suggested in order to observe stable the electrochemistry of fullerenes (Figure 1c). In related work, Echegoyen et al.<sup>17</sup> recently reported the spectroelectrochemistry and electrochemical quartz crystal microbalance (EQCM) characterization of C<sub>60</sub> embedded in a tetraoctylammonium bromide (4C<sub>8</sub>N<sup>+</sup>Br<sup>−</sup>) film in an aqueous solution, and Li et al.<sup>18</sup> reported the electrochemistry of C<sub>70</sub> embedded in a cationic didodecylmethylammonium bromide (2C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup>) film in an aqueous solution.

Yoshida et al. reported the chemical generation of C<sub>60</sub><sup>•−</sup> for a  $\gamma$ -cyclodextrin-bicapped C<sub>60</sub><sup>*n*−</sup> (*n* = 1–2) complex in an aqueous solution.<sup>19</sup> Beedy et al. reported the photochemical generation of C<sub>60</sub><sup>•−</sup> in a micellar aqueous solution.<sup>7a</sup> However, to our knowledge, no report has been published describing the chemical generation of fullerene anions in film states on substrates in aqueous media.

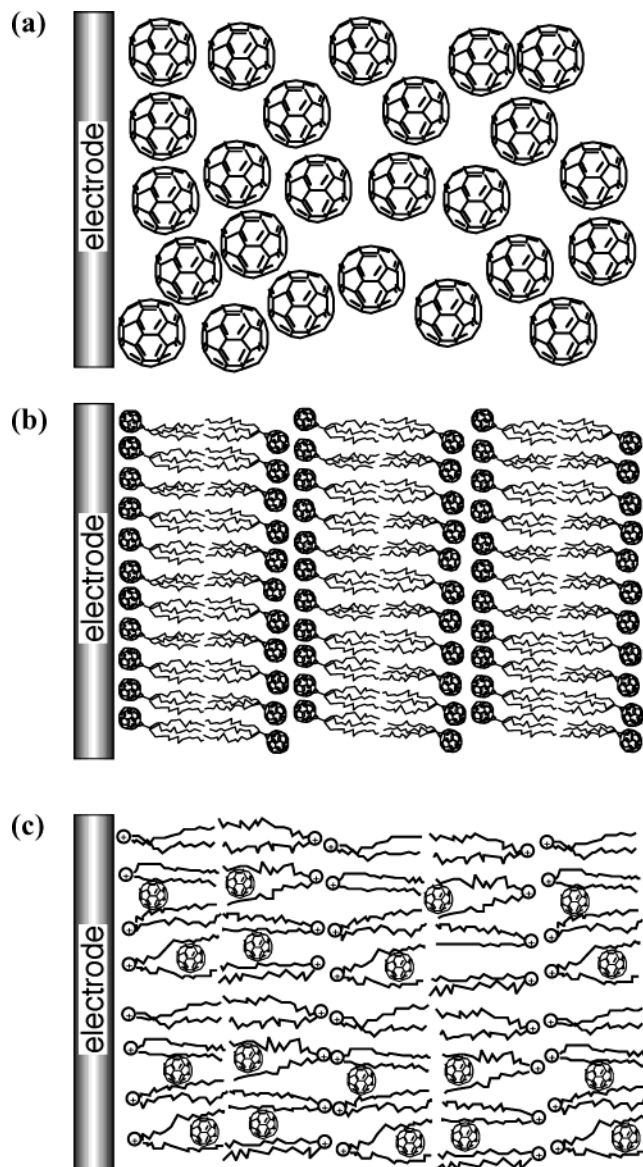
In this paper, we give a detailed description of the electrochemical properties of C<sub>60</sub> and C<sub>70</sub> embedded in cationic lipids or artificial amphiphiles on a basal-plane pyrolytic graphite (BPG) electrode in aqueous solution, comparing electron-transfer mechanisms for films of fullerenes, fullerene lipids, and fullerenes in lipids (Figure 1). Also, in situ electrochemical and

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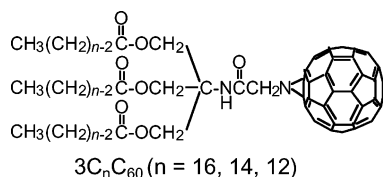
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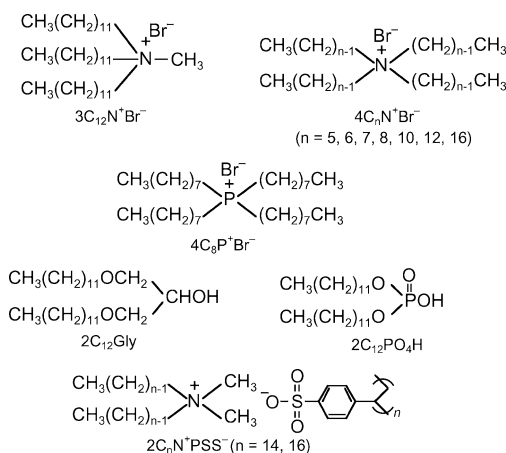
**Figure 1.** Schematic illustrations of a C<sub>60</sub>-only film-modified electrode (a), a fullerene lipid (3C<sub>n</sub>C<sub>60</sub>)-modified electrode (b), and a C<sub>60</sub>/lipid bilayer-modified electrode (c), respectively.

## CHART 1



spectroscopic properties of fullerene lipid films on an optically transparent indium tin oxide (ITO) electrode were investigated. Finally, we describe the chemical generation of C<sub>60</sub><sup>•-</sup> and C<sub>70</sub><sup>•-</sup> using Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> as a reducing agent for fullerene/lipid films on quartz substrates in aqueous media. The matrix lipids and amphiphiles used in this study were tridodecylmethylammonium bromide (3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup>),<sup>14c,20</sup> tetraalkylammonium bromide (4C<sub>n</sub>N<sup>+</sup>Br<sup>-</sup>;  $n = 5, 6, 7, 8, 10, 12, 16$ ), tetraoctylphosphonium bromide (4C<sub>8</sub>P<sup>+</sup>Br<sup>-</sup>),<sup>14d</sup> didodecylglycerol (2C<sub>12</sub>Gly), didodecyl phosphate (2C<sub>12</sub>PO<sub>4</sub>H), dimethylditetradecylammonium poly(styrene sulfonate) (2C<sub>14</sub>N<sup>+</sup>PSS<sup>-</sup>),<sup>14a,21</sup> and dihexadecyldimethylammonium poly(styrene sulfonate) (2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup>),<sup>14b,21</sup> whose chemical structures are shown in Chart 2. We reported

## CHART 2



earlier that the artificial lipids, 3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup>,<sup>20</sup> 2C<sub>14</sub>N<sup>+</sup>PSS<sup>-</sup>,<sup>21</sup> and 2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup>,<sup>21</sup> form a molecular-bilayer structure that provides suitable microenvironments for the facile electron-transfer reactions of fullerenes embedded in the lipid films.<sup>14a-c</sup> We also described initial results on the electron-transfer behavior of C<sub>60</sub> embedded in films of 4C<sub>8</sub>P<sup>+</sup>Br<sup>-</sup> and 4C<sub>8</sub>N<sup>+</sup>Br<sup>-</sup>.<sup>14d</sup> 4C<sub>8</sub>P<sup>+</sup>Br<sup>-</sup> forms a gellike viscous phase that is also a suitable medium for the electrochemistry of double-decker lutetium(III) phthalocyanines.<sup>22</sup>

## Experimental Section

C<sub>60</sub> (99.95%), and C<sub>70</sub> (99.5%) were purchased from the Material and Electrochemical Research Co. Lipid 3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> was prepared previously.<sup>14c</sup> Poly(ion-complexed) lipids 2C<sub>14</sub>N<sup>+</sup>PSS<sup>-</sup> and 2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup> were synthesized according to the previously described method.<sup>21</sup> 4C<sub>16</sub>N<sup>+</sup>Br<sup>-</sup> (Aldrich), 4C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> (Wako Pure Chemical), 4C<sub>n</sub>N<sup>+</sup>Br<sup>-</sup> ( $n = 5, 6, 7, 8, 10$ , Tokyo Kasei), and 4C<sub>8</sub>P<sup>+</sup>Br<sup>-</sup> (Aldrich) were used as received. Supporting electrolytes used in this study were tetraethylammonium chloride (TEAC), KF, KCl, KBr, KNO<sub>3</sub>, KClO<sub>4</sub>, LiBr, NaBr, RbBr, and CsBr from Wako Pure Chemical.

The procedure for the preparation of modified electrodes is as follows. A bare homemade basal-plane pyrolytic graphite (BPG, Union Carbide Co.) electrode (geometric area, 0.36 cm<sup>2</sup>) was prepared and polished with a 1500-grit SiC emery paper, rinsed with water, and then air dried. To expose a fresh basal plane, the surface of the BPG electrode was peeled off with Scotch adhesive tape immediately before use. A 15-μL portion of C<sub>60</sub> (or C<sub>70</sub>)/lipid (molar ratio 1:19) in toluene ([C<sub>60</sub>] = [C<sub>70</sub>] = 0.5 mmol dm<sup>-3</sup>) was placed on a BPG electrode and then air dried. The modified BPG electrode was used as the working electrode in a given 0.5 mol dm<sup>-3</sup> aqueous electrolyte solution. Cyclic voltammetry measurements (BAS-100BW Electrochemical Analyzer, Bioanalytical Systems) at 25 ± 1 °C were carried out under an argon atmosphere (99.998% purity). A saturated calomel electrode (SCE) and a Pt plate electrode were used as the reference and counter electrodes, respectively.

In situ electrochemical reduction of C<sub>60</sub> in lipid films on indium tin oxide (ITO) electrodes was examined under potential control by visible–near-IR spectroscopy. A 100-μL portion of C<sub>60</sub>/lipid (molar ratio 1:19) toluene solution ([C<sub>60</sub>] = 0.5 mmol dm<sup>-3</sup>) was placed on an ITO electrode surface (geometric area 1.5 cm<sup>2</sup>)<sup>23</sup> and then air dried. The modified ITO electrode was vertically inserted into a quartz cuvette with a light-path length of 10.0 mm. The electrode surface was perpendicular to the incident light. The cuvette was filled with 0.1 mol dm<sup>-3</sup> aqueous

TABLE 1: Electrochemical Half-Wave Potentials of C<sub>60</sub> and C<sub>70</sub> in Films and in Solution

conditions	electrode	supporting electrolyte	R. E.	$E_{1/2(1)}/V$	$E_{1/2(2)}/V$	$E_{1/2(3)}/V$	ref
C <sub>60</sub> /3C <sub>12</sub> N <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	Ag/AgCl <sup>a</sup>	-0.12	-0.74	-1.21	14c
C <sub>60</sub> /4C <sub>16</sub> N <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	SCE	-0.25 <sup>b</sup>	-0.75 <sup>b</sup>		tw <sup>c</sup>
C <sub>60</sub> /4C <sub>12</sub> N <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	SCE	-0.17 <sup>d</sup>	-0.73 <sup>d</sup>		tw
C <sub>60</sub> /4C <sub>10</sub> N <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	SCE	-0.17 <sup>e</sup>	-0.70 <sup>e</sup>		tw
C <sub>60</sub> /4C <sub>8</sub> N <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	SCE	-0.11	-0.64	-1.28	14d
C <sub>60</sub> /4C <sub>7</sub> N <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	SCE	-0.16	-0.63	-1.24	tw
C <sub>60</sub> /4C <sub>8</sub> P <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	SCE	-0.17	-0.66	-1.23	14d
C <sub>60</sub> film	Au	TBAB <sup>f</sup>	SCE	-0.45	-0.82		11c
C <sub>60</sub> - $\gamma$ -CD in sol <sup>g</sup>	GC	LiClO <sub>4</sub>	SCE	-0.57	-1.03	-1.34 <sup>h</sup>	23
C <sub>60</sub> - $\gamma$ -CD/Nafion <sup>i</sup>	GC	KCl	SCE	-0.58	-1.20 <sup>h</sup>		11e
C <sub>70</sub> /3C <sub>12</sub> N <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	SCE	-0.13	-0.77	-1.25	tw
C <sub>70</sub> /4C <sub>8</sub> N <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	SCE	-0.07	-0.58	-1.14	tw
C <sub>70</sub> /4C <sub>7</sub> N <sup>+</sup> Br <sup>-</sup> film	BPG	TEAC	SCE	-0.13	-0.60	-1.12	tw
C <sub>70</sub> film	GC	KOH	SHE/ <sup>j</sup>	-1.17			12a
C <sub>70</sub> /2C <sub>12</sub> N <sup>+</sup> Br <sup>-</sup> film	GC	KCl	SCE	-0.27	-0.82		18

<sup>a</sup> The value vs Ag/AgCl/saturated KCl can be calibrated from the values vs SCE by adding 0.04 V. <sup>b</sup> The values were obtained at 70 °C. <sup>c</sup> tw = this work. <sup>d</sup> The values were obtained at 55 °C. <sup>e</sup> The values were obtained at 35 °C. <sup>f</sup> TBAB indicates tetrabutylammonium bromide. <sup>g</sup> C<sub>60</sub>- $\gamma$ -CD in sol represents a water-soluble magenta  $\gamma$ -cyclodextrin inclusion complex of C<sub>60</sub>. <sup>h</sup> The values represents irreversible reduction potential. <sup>i</sup> C<sub>60</sub>- $\gamma$ -CD/Nafion represents C<sub>60</sub>- $\gamma$ -CD and a Nafion chemically modified electrode that was prepared by evaporation with an infrared lamp on the electrode surface of a few microliters of C<sub>60</sub>- $\gamma$ -CD in an aqueous solution and then by casting a Nafion protection film. <sup>j</sup> The value vs SHE can be calibrated from the values vs SCE by subtracting 0.24 V.

TEAC solution, and the reference SCE and counter Pt plate electrodes were positioned so as not to block the light path.

The procedure for preparing a C<sub>60</sub> (or C<sub>70</sub>)/lipid cast film on a quartz substrate is as follows. A 300- $\mu$ L portion of C<sub>60</sub> (or C<sub>70</sub>)/lipid (molar ratio 1:19) or C<sub>60</sub> (or C<sub>70</sub>) in toluene ([C<sub>60</sub>] = [C<sub>70</sub>] = 0.5 mmol dm<sup>-3</sup>) was placed on a quartz substrate and then air dried in a desiccator. Visible-near-IR absorption spectral measurements for the modified quartz substrate were carried out in Milli-Q water (Millipore Corp. > 18 M $\Omega$  cm) for C<sub>60</sub> and in D<sub>2</sub>O for C<sub>70</sub> in the absence and presence of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (Kishida Research Chemicals, amino acid, analysis grade) at 25  $\pm$  1 °C under an argon atmosphere. The modified quartz substrate was vertically inserted in a quartz cuvette that contains 6.0 mL of H<sub>2</sub>O or D<sub>2</sub>O, and then deoxygenated by an argon gas. Five hundred micrograms of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was placed in a disposable syringe and then dissolved in an argon degassed H<sub>2</sub>O or D<sub>2</sub>O, followed by the injection of the solution into the cuvette. The wavelength scan rate of the visible-near-IR absorption spectra was 200 nm min<sup>-1</sup>.

## Results and Discussion

**Electrochemistry of C<sub>60</sub>/Lipid (or Amphiphile) Films-Modified BPG Electrode.** The electrochemistry of films containing only C<sub>60</sub> is complicated and unstable both in organic and aqueous media; that is, the voltammetric response disappears after a single scan or several cyclic potential scans.<sup>9,11</sup> We have found that films of cationic lipids including 3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup>, 4C<sub>8</sub>N<sup>+</sup>Br<sup>-</sup>, and 4C<sub>8</sub>P<sup>+</sup>Br<sup>-</sup> on electrodes provide suitable microenvironments for the facile reduction of C<sub>60</sub>,<sup>14</sup> higher fullerenes<sup>15</sup> and metallofullerenes<sup>16</sup> in aqueous media. The C<sub>60</sub>/cationic lipid-coated electrode showed stable electrochemistry leading to the generation of C<sub>60</sub><sup>•3-</sup>. We extended this work to investigate the electrochemistry of C<sub>60</sub> embedded in 4C<sub>n</sub>N<sup>+</sup>Br<sup>-</sup> (n = 5, 6, 7, 10, 12, and 16) as a modified cast film on a BPG electrode in a 0.5 mol dm<sup>-3</sup> aqueous TEAC solution using cyclic voltammetry under an argon atmosphere.

**Chain-Length Dependence of Cationic Amphiphiles.** The electrodes coated with films of C<sub>60</sub>/4C<sub>5</sub>N<sup>+</sup>Br<sup>-</sup> and C<sub>60</sub>/4C<sub>6</sub>N<sup>+</sup>Br<sup>-</sup> on BPG electrodes did not show evidence of electron-transfer reactions. However, C<sub>60</sub>/4C<sub>7</sub>N<sup>+</sup>Br<sup>-</sup> cast film-modified electrodes showed three redox couples corresponding to C<sub>60</sub>/C<sub>60</sub><sup>•-</sup>, C<sub>60</sub><sup>•-</sup>/C<sub>60</sub><sup>2-</sup>, and C<sub>60</sub><sup>2-</sup>/C<sub>60</sub><sup>3-</sup> with  $E_{1/2}$  = -0.16, -0.63,

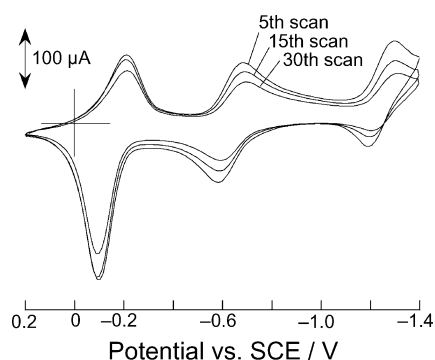


Figure 2. Cyclic voltammograms at a scan rate of 0.1 V s<sup>-1</sup> for a cast film of C<sub>60</sub>/4C<sub>7</sub>N<sup>+</sup>Br<sup>-</sup> (molar ratio 1:19) on a BPG electrode in a 0.5 M aqueous TEAC solution at 25 °C.

and -1.24 V, respectively (Figure 2). The pentyl (C<sub>5</sub>) and hexyl (C<sub>6</sub>) alkyl chain length is suggested to be too short to immobilize C<sub>60</sub> in order to conduct direct electron-transfer reactions. The electrochemical properties of the C<sub>60</sub>/4C<sub>7</sub>N<sup>+</sup>Br<sup>-</sup> cast film-modified BPG electrodes such as the redox wave shape, the formal potential, and the stability are comparable to those of our previous work.<sup>14c,d</sup> The redox reactions of the C<sub>60</sub>/4C<sub>7</sub>N<sup>+</sup>Br<sup>-</sup> cast film-modified BPG electrode were examined as a function of the potential scan rate in order to probe the electron-transfer mechanism. The cathodic peak current for the first and second redox couples in the cyclic voltammograms (CVs) increased in direct proportion to the square root of the scan rate between 0.05 and 1.0 V s<sup>-1</sup>, suggesting that fullerene electrochemistry is controlled by diffusion at the measured scan rates.<sup>24a</sup> Here, a self-exchange electron-transfer mechanism between the C<sub>60</sub> anions and C<sub>60</sub> in the film is suggested. At scan rates below 0.01 V s<sup>-1</sup>, the peak currents are directly proportional to the scan rate, indicating thin-layer electrochemical behavior.<sup>24b</sup>

Two redox couples 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> were clearly seen at the C<sub>60</sub>/4C<sub>10</sub>N<sup>+</sup>Br<sup>-</sup>, C<sub>60</sub>/4C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup>, and C<sub>60</sub>/4C<sub>16</sub>N<sup>+</sup>Br<sup>-</sup>-modified electrodes above 35, 55, and 70 °C, respectively. The temperature-dependent electrochemistry of these electrodes is described later. (See Phase-Transition Dependence.) The measured half-wave potentials for the C<sub>60</sub>/4C<sub>n</sub>N<sup>+</sup>Br<sup>-</sup> cast films and our previously reported C<sub>60</sub>/cationic lipid films<sup>14c,d</sup>-modified BPG electrodes in aqueous media are listed in Table 1 together with some reported electrochemical



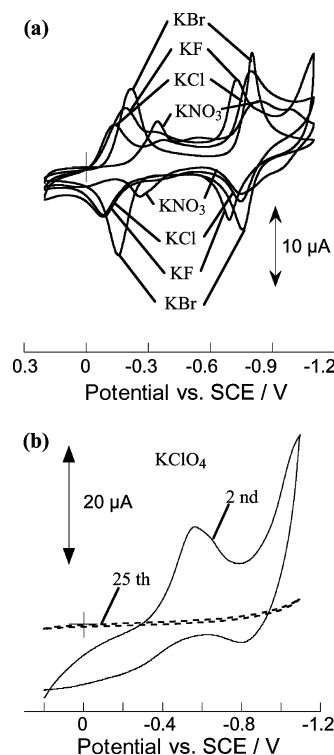
**TABLE 2: Anodic and Cathodic Peak Potentials and Half-Wave Potentials for a Cast Film of C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup> on a BPG Electrode in Aqueous Solution Containing Various 0.1 M Electrolytes at a Scan Rate of 0.01 V s<sup>−1</sup>**

electrolyte	C <sub>60</sub> /C <sub>60</sub> <sup>•−</sup> process (E/V vs SCE)			C <sub>60</sub> <sup>•−</sup> /C <sub>60</sub> <sup>2−</sup> process (E/V vs SCE)		
	E <sub>pc1</sub>	E <sub>pa1</sub>	E <sub>1/2</sub> (1)	E <sub>pc2</sub>	E <sub>pa2</sub>	E <sub>1/2</sub> (2)
LiBr	−0.226	−0.162	−0.194	−0.792	−0.759	−0.776
NaBr	−0.227	−0.152	−0.190	−0.792	−0.749	−0.771
KBr	−0.228	−0.163	−0.196	−0.790	−0.751	−0.771
RbBr	−0.227	−0.159	−0.193	−0.790	−0.756	−0.773
CsBr	−0.231	−0.131	−0.181	−0.800	−0.744	−0.772
KF	−0.192	−0.082	−0.137	−0.728	−0.692	−0.710
KCl	−0.138	−0.082	−0.110	−0.799	−0.748	−0.774
KNO <sub>3</sub>	−0.345	−0.261	−0.303	−0.838	−0.750	−0.794

data for C<sub>60</sub>. The half-wave potentials for E<sub>1/2</sub>(1) of the C<sub>60</sub>/cationic lipid film-modified BPG electrodes are all shifted positively by 0.20–0.47 V from that of the C<sub>60</sub> film alone,<sup>11c</sup> that of the C<sub>60</sub>–γ-cyclodextrin (1:2) complex dissolved aqueous solution,<sup>25</sup> and that of the C<sub>60</sub>–γ-cyclodextrin in a Nafion film.<sup>11e</sup> The C<sub>60</sub> incorporated in a cast film of a neutral lipid, 2C<sub>12</sub>Gly, and an anionic lipid, 2C<sub>12</sub>PO<sub>4</sub><sup>−</sup>, on BPG electrodes showed no evidence of electron-transfer reactions (data not shown). As discussed above, the remarkable positive potential shift suggests strong binding of C<sub>60</sub> anions with the cationic lipids in the films.<sup>13</sup> Cast films of cationic lipids including 3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup>, 4C<sub>8</sub>N<sup>+</sup>Br<sup>−</sup>, 4C<sub>7</sub>N<sup>+</sup>Br<sup>−</sup>, and 4C<sub>8</sub>P<sup>+</sup>Br<sup>−</sup> on electrodes provide suitable hydrophobic microenvironments for the electrochemical reduction of C<sub>60</sub> up to C<sub>60</sub><sup>3−</sup>.

**Electrolyte Dependence.** To understand the electron-transfer mechanism for fullerene/cationic lipid-modified electrodes in detail, we examined the electrolyte dependence. We have reported initial electrolyte cation- and anion-dependent electrochemistry elsewhere.<sup>26</sup> Echegoyen et al. also briefly described electrolyte-dependent electrochemistry for C<sub>60</sub>/4C<sub>8</sub>N<sup>+</sup>Br<sup>−</sup> cast films.<sup>17</sup> We examine here the electrolyte cation dependence for a C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup>-modified electrode at a scan rate of 0.01 V s<sup>−1</sup> in water containing a 0.1 M given electrolyte (LiBr, NaBr, KBr, RbBr or CsBr). The obtained cathodic (E<sub>pc</sub>) and anodic (E<sub>pa</sub>) peak potentials and half-wave potentials (E<sub>1/2</sub>), together with our previously reported data,<sup>26</sup> are listed in Table 2. The cathodic peak potentials for cast films containing only C<sub>60</sub> on electrodes in aqueous solutions containing a variety of cations (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Ca<sup>2+</sup>, and Ba<sup>2+</sup>) have been reported to shift positively with a decrease in the hydration energy of the electrolyte cations.<sup>11b</sup> As we described elsewhere,<sup>13</sup> differential pulse voltammograms of the cast films of the fullerene lipids, 3C<sub>n</sub>C<sub>60</sub> (Chart 1), on electrodes showed a strong electrolyte cation dependence in aqueous media. Although the stability of the generated fullerene anions is quite different, the electrodes modified with C<sub>60</sub> and with the fullerene lipids are governed by similar electron-transfer mechanisms. In sharp contrast, the CVs for C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup>-modified electrodes in aqueous media showed no electrolyte cation dependence; that is, as shown in Table 2, the half-wave potentials (E<sub>1/2</sub>) for the first and second reductions of C<sub>60</sub> in the films do not shift with electrolyte cations. (See Figure S1 in Supporting Information.) This result strongly suggests that the electrochemically generated C<sub>60</sub> anions in the films are bound not to electrolyte cations but to the ammonium moieties on 3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup>.

We have also briefly reported the electrolyte anion-dependent electrochemistry for C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup>-modified electrodes in water containing 0.1 M electrolytes including KF, KCl, KBr, and KNO<sub>3</sub>.<sup>26</sup> In sharp contrast to the electrolyte cation dependence, the CVs showed a strong electrolyte anion dependence



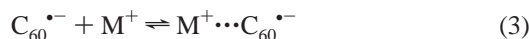
**Figure 3.** Cyclic voltammograms at a scan rate of 0.01 V s<sup>−1</sup> for a cast film of C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup> (molar ratio 1:19) on a BPG electrode in an aqueous solution containing 0.1 M KF, KCl, KBr, and KNO<sub>3</sub> (a) and KClO<sub>4</sub> (b), in which the solid line and broken line denote the 2nd and 25th scans, respectively.

(Figure 3a and b). When KClO<sub>4</sub> was used as the electrolyte, faradaic current was observed for several potential scans. After repetitive scans, the disappearance of the faradaic current in the CV is probably due to the strong binding between ClO<sub>4</sub><sup>−</sup> and the ammonium moieties on 3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup> in the film (Figure 3b). Table 2 summarizes the E<sub>pc</sub>, E<sub>pa</sub>, and E<sub>1/2</sub> values obtained from the CVs. When the obtained first and second half-wave potentials are plotted as a function of the hydration energies of the anions, for NO<sub>3</sub><sup>−</sup>, Br<sup>−</sup>, and Cl<sup>−</sup> the first and second half-wave potentials are related to the hydration energy of these anions, and for the second reduction, F<sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, and NO<sub>3</sub><sup>−</sup> ions are related to the hydration energy of these anions. (See Figure S2 in Supporting Information.) It is likely that the observed anion dependence is related to the Hofmeister series of anions<sup>27</sup> that exhibit an indication of the affinity of hydrophobic tetraalkylammonium cations in an organic phase and anions in an aqueous phase. This result suggests that the binding of electrolyte anions with the cationic lipid of 3C<sub>12</sub>N<sup>+</sup>Br<sup>−</sup> in the films results in a shift of the half-wave potentials. The potential shift might include a contribution from the Donnan potential at the modified electrode.

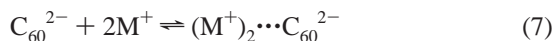
Echegoyen et al.<sup>17</sup> have recently examined a similar electrolyte dependence for the electrochemistry of the C<sub>60</sub>/4C<sub>8</sub>N<sup>+</sup>Br<sup>−</sup>-modified electrode in water containing a variety of electrolytes (KCl, NaCl, LiCl, KBr, NaI, NaF, Na<sub>2</sub>SO<sub>4</sub>, LiClO<sub>4</sub>, KClO<sub>3</sub>, KNO<sub>3</sub>, NaBrO<sub>3</sub>, CH<sub>3</sub>COONa, and tetraethylammonium chloride) by means of CV and the electrochemical quartz crystal microbalance (EQCM). They reported that the C<sub>60</sub>/4C<sub>8</sub>N<sup>+</sup>Br<sup>−</sup>-modified electrodes in aqueous solution are closely associated with the nature of the anions in the supporting electrolyte solution. Their data in the paper is in line with our results.<sup>26</sup>

**Electron-Transfer Mechanism.** Considering all of the data, one possible electron-transfer mechanism for C<sub>60</sub>/lipid

( $3C_{12}N^+Br^-$ ) film-coated electrodes is shown in Scheme 1 (the first reduction)



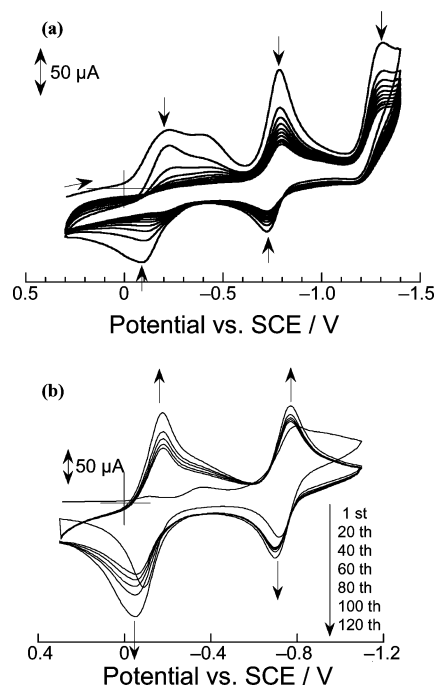
and Scheme 2 (the second reduction)



where  $M^+$  is the electrolyte cation and  $X^-$  is the electrolyte anion. For the first reduction process (eq 1) of  $C_{60}$  embedded in a film of  $3C_{12}N^+Br^-$ , the half-wave potentials in the CVs shift in a positive direction compared with those for  $C_{60}$  in organic solutions, indicating the complex formation between  $C_{60}^{\bullet -}$  and the lipid cation. The absence of an electrolyte cation dependence on the CVs of the  $C_{60}/3C_{12}N^+Br^-$ -modified electrodes suggests that the counteraction of the  $C_{60}$  anion is not an electrolyte cation but the ammonium cations on  $3C_{12}N^+Br^-$  (eq 2). Therefore, the contribution of eq 3 on the half-wave potentials is almost negligible. Unfortunately, the determination of the binding constant between the  $C_{60}$  radical monoanion and  $3C_{12}N^+$  was not possible because  $3C_{12}N^+$  is not in electrolyte but is in the film. An important feature is the anion dependence of the half-wave potentials. As described above, the half-wave potentials of the  $C_{60}/3C_{12}N^+Br^-$ -modified electrodes shifted negatively in the presence of electrolyte anions with smaller hydration energy such as  $NO_3^-$ . This shift is due to the formation of a complex between the electrolyte anion and  $3C_{12}N^+$  in the lipid films, as expressed by eq 4. That is, the negative shift is controlled by the competitive binding of  $C_{60}^{\bullet -}$  and the electrolyte anion with the lipid cation. The proposed electron-transfer mechanism is quite different from those of fullerene-coated (Figure 1a)<sup>11b</sup> and fullerene lipid-coated (Figure 1b) electrodes. For fullerene- and fullerene lipid-coated electrodes, electrolyte cations regulate the half-wave potentials of fullerenes, and for fullerenes incorporated into the cationic lipid films, electrolyte anions regulate the half-wave potentials.

The same electron-transfer mechanism for the second reduction process (Scheme 2) with the addition of eq 4 is proposed because both the cation and anion dependences on the CVs for the second reduction were very similar to those of the first reduction.

**Electrochemistry of  $C_{70}$ /Lipid Films-Modified BPG Electrodes.** The electrochemistry of  $C_{70}$  films<sup>12</sup> has been limited to aqueous solution as for  $C_{60}$  films.<sup>11</sup> Szűcs et al. reported the reduction of films of  $C_{70}$  on an electrode in an alkaline aqueous solution, but the electrochemistry was completely irreversible.<sup>12a</sup> The stable electrochemistry of  $C_{70}/C_{70}^{\bullet -}$  and  $C_{70}^{\bullet -}/C_{70}^{2-}$  redox couples embedded in a film of didodecyldimethylammonium bromide ( $2C_{12}N^+Br^-$ ) in an aqueous solution has recently been investigated by Li et al.<sup>18</sup> We used  $3C_{12}N^+Br^-$ ,  $4C_8N^+Br^-$ , and  $4C_7N^+Br^-$  as matrices instead of  $2C_{12}N^+Br^-$  because trialkyl- and tetraalkylammonium lipids (amphiphiles) gave more suitable microenvironments for the electrochemistry of  $C_{60}$  in these films.



**Figure 4.** Cyclic voltammograms showing three redox couples (a) and two redox couples (b) at a scan rate of  $0.1 \text{ V s}^{-1}$  for a cast film of  $C_{70}/3C_{12}N^+Br^-$  (molar ratio 1:19) on a BPG electrode in a  $0.5 \text{ M}$  aqueous TEAC solution at  $25^\circ\text{C}$ .

Cast films of  $C_{70}/3C_{12}N^+Br^-$ ,  $C_{70}/4C_8N^+Br^-$ , and  $C_{70}/4C_7N^+Br^-$  on BPG electrodes showed three consecutive well-defined quasi-reversible one-electron-transfer processes leading to the generation of  $C_{70}^{\bullet 3-}$ . Half-wave potentials  $E_{1/2}(1)$ ,  $E_{1/2}(2)$ , and  $E_{1/2}(3)$  versus SCE were  $-0.13$ ,  $-0.77$ , and  $-1.25 \text{ V}$  at  $C_{70}/3C_{12}N^+Br^-$  (Figure 4a),  $-0.07$ ,  $-0.58$ , and  $-1.14 \text{ V}$  at  $C_{70}/4C_8N^+Br^-$ , and  $-0.13$ ,  $-0.60$ , and  $-1.12 \text{ V}$  at  $C_{70}/4C_7N^+Br^-$ , respectively. The third reduction of  $C_{70}$  has been obtained in organic homogeneous solution<sup>6a,b,28</sup> but has not been reported in film states in aqueous media. Continuous potential cycling at a scan rate of  $0.1 \text{ V s}^{-1}$  for the  $C_{70}/3C_{12}N^+Br^-$ -modified electrode caused a gradual decrease in the second and third reduction currents and became almost constant. This process was accompanied with a drastic decrease in the first reduction current. This behavior is not observed for the  $C_{60}/3C_{12}N^+Br^-$ -modified electrode, where the first reduction is stable as we described elsewhere.<sup>14c</sup> As shown in Figure 4b, no such current decrease was observed during continuous cycling when the CVs were cycled back at  $-1.0 \text{ V}$  versus SCE. The electrochemical stability of the  $C_{70}$  radical monoanion and dianion is similar to that of  $C_{60}$  at a  $C_{60}/3C_{12}N^+Br^-$ -modified electrode.<sup>14c</sup> It is evident that the drastic decrease in the first reduction of  $C_{70}$  is caused by the generation of  $C_{70}^{\bullet 3-}$ . Similar redox properties were observed at the  $C_{70}/4C_8N^+Br^-$ - and  $C_{70}/4C_7N^+Br^-$ -modified electrodes. Because  $C_{60}$  and  $C_{70}$  have been reported to show essentially the same CV behavior in organic solutions,<sup>6a,b</sup> the observed electrochemical difference in the film state might be due to the difference in the aggregation behavior of  $C_{60}$  and  $C_{70}$  in the lipid bilayers after the third reduction.

The measured half-wave potentials for the  $C_{70}/3C_{12}N^+Br^-$ ,  $C_{70}/4C_8N^+Br^-$ , and  $C_{70}/4C_7N^+Br^-$  cast film-modified BPG electrodes are listed in Table 1 together with values for  $C_{70}$  from the literatures. Note that the half-wave potentials of the electrodes modified with films of  $C_{70}/3C_{12}N^+Br^-$ ,  $C_{70}/4C_8N^+Br^-$ , and  $C_{70}/4C_7N^+Br^-$  shifted in the positive direction by about  $0.24 \text{ V}$  compared with that of the  $C_{70}/2C_{12}N^+Br^-$  cast film,<sup>18</sup> and this positive shift is much more evident when compared

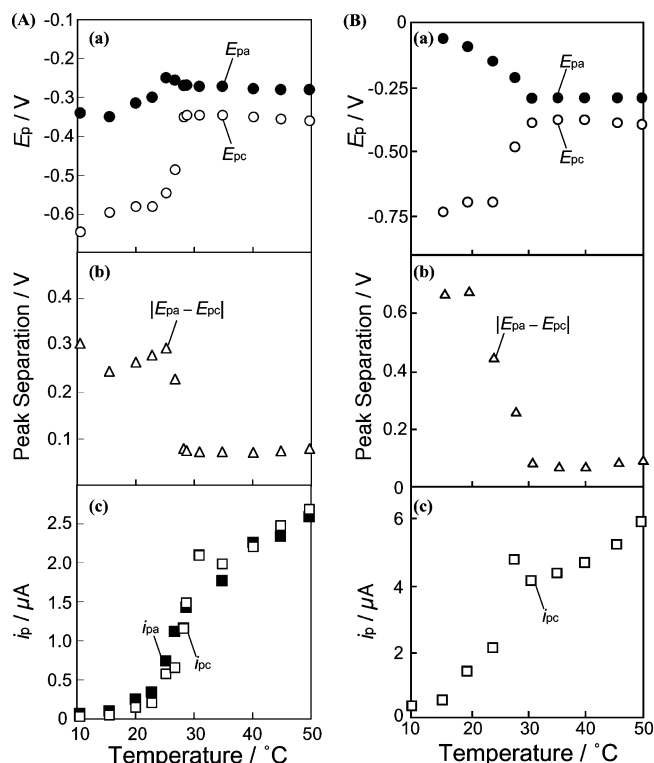
with that of the cast film of C<sub>70</sub>.<sup>12a</sup> The C<sub>70</sub> radical anion in the film state has been reported to associate with Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>, and this interaction is related to the Gibbs hydration energy of the cations.<sup>12a</sup> This association also occurs with the lipid cation moiety of the films, thus leading to a larger stabilization of the electroreduced forms of C<sub>70</sub> in the film and a positive potential shift in  $E_{1/2}$  for each redox couple. This makes it possible to detect three reduction peaks within the potential window in aqueous media.

The electrochemical behavior of C<sub>60</sub> and C<sub>70</sub> in an organic solution<sup>6a,b</sup> and in solid films<sup>9a</sup> has been reported to be almost identical. Although the generation of C<sub>70</sub><sup>•3-</sup> is possible at the C<sub>70</sub>/cationic lipid cast film-modified electrode, the C<sub>70</sub>/C<sub>70</sub><sup>•-</sup> redox couple was less stable than the C<sub>60</sub>/C<sub>60</sub><sup>•-</sup> redox couple during continuous potential cycling over three reduction processes.

**Phase-Transition Dependence.** We initially described the phase-transition-controllable electrochemistry of C<sub>60</sub> embedded in polyion complex-type artificial lipids on electrodes in aqueous media.<sup>14a,b</sup> Phase-transition-controllable electrochemistry has also been observed for C<sub>70</sub> embedded in a film of 2C<sub>14</sub>N<sup>+</sup>PSS<sup>-</sup> or 2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup> on a BPG electrode. 2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup> possesses a phase-transition temperature ( $T_c$ ) between the crystalline and the liquid-crystalline phases at 26.6 °C.<sup>14b,21</sup> The C<sub>70</sub>/C<sub>70</sub><sup>•-</sup> and C<sub>70</sub><sup>•-</sup>/C<sub>70</sub><sup>2-</sup> redox couples at the 2C<sub>14</sub>N<sup>+</sup>PSS<sup>-</sup>-modified BPG electrode in 0.5 M aqueous TEAC solution at room temperature show stable electrochemistry at  $E_{1/2}(1) = (-0.30) - (-0.32)$  V and  $E_{1/2}(2) = (-0.87) - (-1.0)$  V, respectively (data not shown). The measured half-wave potentials for the C<sub>70</sub>/2C<sub>14</sub>N<sup>+</sup>PSS<sup>-</sup>-modified electrodes were similar to those of a C<sub>60</sub>/2C<sub>14</sub>N<sup>+</sup>PSS<sup>-</sup>-modified electrode<sup>14a</sup> ( $E_{1/2}(1) = (-0.25) - (-0.36)$  V and  $E_{1/2}(2) = (-0.88) - (-0.97)$  V). The cathodic and anodic peak currents for C<sub>70</sub>/C<sub>70</sub><sup>•-</sup> in the film increased in proportion to the square root of the scan rate between 0.002 and 2.0 V s<sup>-1</sup>, indicating that the electrochemistry in the lipid film is controlled by diffusion over the range of the potential scan rates.<sup>24a</sup>

The C<sub>70</sub>/2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup>-modified electrode showed a strong temperature dependence (Figure 5A); its behavior was similar to that of the C<sub>60</sub>/2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup>-modified electrode (Figure 5B).<sup>14b</sup> At temperatures below 20 °C, there is almost no electrochemical response attributable to the reduction/oxidation of C<sub>70</sub>, whereas evident faradaic current appeared at around 25 °C and increased with temperature up to 50 °C. (See Figure S3 in Supporting Information.) The redox potentials (a), peak separation ( $|E_{pc} - E_{pa}|$ ) (b), and peak currents (c) from the CVs were plotted as a function of temperature (Figure 5A). The break appeared near 27 °C, which is close to the  $T_c$  of the bilayer film. As shown in Figure 5A(b), the peak-potential separation observed at temperatures above the phase transition is smaller than at temperatures below the phase transition. This indicates faster electron-transfer rate constants at  $T > T_c$ . We emphasize that the electrochemistry of the fullerene film can be temperature controlled and is reversible. At lower temperatures, the lipid bilayer films are electrochemically inactive because of their rigid structure, whereas at higher temperatures, the lipid bilayer films becomes fluid, which leads to the facile electron transfer of the fullerenes.

Electrodes modified with C<sub>60</sub>/4C<sub>10</sub>N<sup>+</sup>Br<sup>-</sup>, C<sub>60</sub>/4C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup>, and C<sub>60</sub>/4C<sub>16</sub>N<sup>+</sup>Br<sup>-</sup> on BPG also showed a strong temperature dependence. At low temperature (<25 °C), there is almost no electrochemical response attributable to C<sub>60</sub>, but at C<sub>60</sub>/4C<sub>10</sub>N<sup>+</sup>Br<sup>-</sup>, C<sub>60</sub>/4C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup>, and C<sub>60</sub>/4C<sub>16</sub>N<sup>+</sup>Br<sup>-</sup>-modified electrodes above 35, 55, and 70 °C, two redox couples 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> were clearly seen. This temperature



**Figure 5.** Temperature dependence of anodic (●) and cathodic (○) peak potentials (a), peak separation (b), and anodic (■) and cathodic (□) peak currents (c) in the cyclic voltammograms at a scan rate of 0.1 V s<sup>-1</sup> for cast films of (A) C<sub>70</sub>/2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup> (molar ratio 1:19) and (B) C<sub>60</sub>/2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup> (molar ratio 1:19) on BPG electrodes in a 0.5 M aqueous TEAC solution.

dependence might be due to microphase transitions of the alkyl chain of the matrices that are similar to what is known for the phase transition of artificial lipid films, which can be attributed to a trans-gauche conformational change of the alkyl chain.

The phase-transition regulation of the electrochemistry of fullerenes in lipid bilayer films on an electrode is schematically drawn in Figure 6. Construction of redox-switchable molecular devices<sup>29</sup> based on fullerene films would be of interest for the application and utilization of fullerenes.

**Electrochemical Generation of C<sub>60</sub><sup>•-</sup> and C<sub>60</sub><sup>2-</sup> at ITO Electrodes.** Absorption peaks of fullerene anions that are generated chemically<sup>5a-c,e,g</sup> and electrochemically<sup>6c-h</sup> in organic solutions are known to appear at 1078–1080, 1042, 1000, and 940 nm for C<sub>60</sub><sup>•-</sup> and at 952 and 830 nm for C<sub>60</sub><sup>2-</sup>. The bands at 1078, 952, and 830 nm are assigned to  $a_{2u} \rightarrow e_{1g}$ ,  $e_{1u} \rightarrow e_{1g}$ , and  $e_{1u} \rightarrow a_{2g}$ , respectively.<sup>6c</sup> A C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> cast film-modified ITO electrode showed well-defined CVs. The generation of C<sub>60</sub><sup>•-</sup> and C<sub>60</sub><sup>2-</sup> take place at  $E_{1/2}(1) = -0.12$  and  $E_{1/2}(2) = -0.78$  V, respectively, in a 0.1 mol dm<sup>-3</sup> aqueous TEAC solution at a scan rate of 0.1 V s<sup>-1</sup>. Figure 7 shows in situ visible-near-IR absorption spectra of these cast films. When the potential was held at -0.4 V for 10 min, characteristic C<sub>60</sub><sup>•-</sup> bands appeared at 1078, 1036 (shoulder), 1002, and 936 nm (spectrum b). Spectrum a returned to spectrum b when the potential was held at 0.3 V for 10 min. From the spectroelectrochemical data, the first reduction process of C<sub>60</sub> in the film was fully reversible. At a potential of -1.0 V, the peak at 1078 nm decreased significantly, whereas new peaks appeared at 942 and 830 nm (spectrum c). Absorption bands for C<sub>60</sub><sup>2-</sup> in organic solutions have been reported to appear at almost the same wavelength described above;<sup>5c,h,6c-h</sup> therefore, the new peak indicates the generation of C<sub>60</sub><sup>2-</sup> in the lipid film in this system. Cationic amphiphiles 4C<sub>7</sub>N<sup>+</sup>Br<sup>-</sup> and 4C<sub>8</sub>P<sup>+</sup>Br<sup>-</sup> and anionic lipid



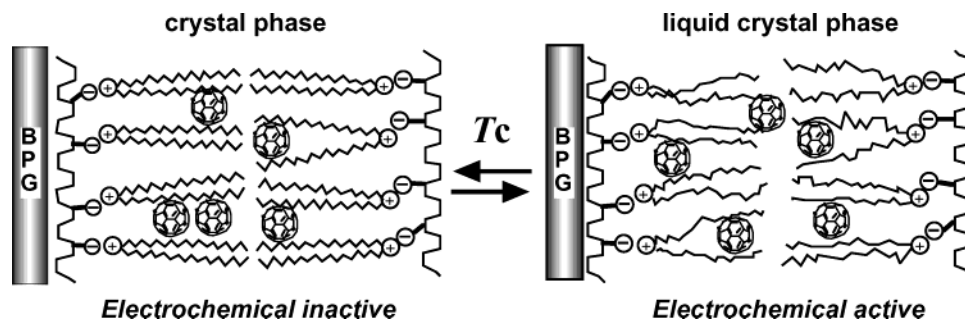


Figure 6. Schematic illustration of the phase-transition-dependent electrochemistry of a fullerene/lipid-coated electrode.

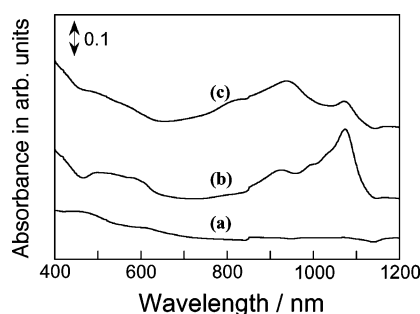


Figure 7. In situ electrochemical visible–near-IR absorption spectra for a cast film of  $C_{60}/3C_{12}N^+Br^-$  (molar ratio 1:19) on an ITO electrode in a 0.1 M aqueous TEAC solution at 25 °C. Potential was controlled at 0.3 V for 10 min (a), -0.4 V for 10 min (b), and -1.0 V for 10 min (c), respectively.

TABLE 3:  $\lambda_{max}$  of  $C_{60}^{\bullet-}$ ,  $C_{60}^{2-}$ , and  $C_{70}^{\bullet-}$  in Films of  $C_{60}(C_{70})/Lipid$  (Amphiphiles) on Quartz Generated by Chemical Reduction with  $Na_2S_2O_4$  (CR) and by in Situ Electrochemical Reduction on an ITO Electrode (ER)

cast films	method	solution	$\lambda_{max}/nm$	
			$C_{60}^{\bullet-}$	$C_{60}^{2-}$
$C_{60}/3C_{12}N^+Br^-$	CR	H <sub>2</sub> O	1077	
	ER	0.1 M TEAC	1078	940
$C_{60}/4C_8N^+Br^-$	CR	H <sub>2</sub> O	1078	
	ER	0.1 M TEAC	1078	949
	ER <sup>a</sup>	0.5 M KCl	1080	950
$C_{60}/4C_7N^+Br^-$	CR	H <sub>2</sub> O	1078	
	ER	0.1 M TEAC	1073	947
$C_{60}/4C_8P^+Br^-$	CR	H <sub>2</sub> O	1076	
	ER	0.1 M TEAC	1083	
			$C_{70}^{\bullet-}$	
$C_{70}/3C_{12}N^+Br^-$	CR	D <sub>2</sub> O	1376	
$C_{70}/4C_8N^+Br^-$	CR	D <sub>2</sub> O	1378	

<sup>a</sup> The data have been reported in ref 17.

$2C_{12}PO_4^-$  were used as matrices instead of  $3C_{12}N^+Br^-$ . Electrodes coated with  $4C_7N^+Br^-$  and  $4C_8P^+Br^-$  gave almost identical results to those from the  $C_{60}/3C_{12}N^+Br^-$  electrode. Similar spectroelectrochemical behavior was described for a  $C_{60}/4C_8N^+Br^-$ -modified ITO electrode by Echegoyen et al.<sup>17</sup> However, no absorbance was observed for the  $C_{60}/2C_{12}PO_4^-$  electrode. This coincides with the results of CVs described before. The spectroelectrochemical data obtained in this study together with the data reported by Echegoyen et al. is shown in Table 3.

Detailed analysis was carried out for the  $C_{60}/3C_{12}N^+Br^-$  cast film-modified ITO electrode. Simultaneous measurements of current and absorbance during dc cyclic potential scanning were carried out for a  $C_{60}/3C_{12}N^+Br^-$  cast film on ITO at a scan rate of 0.002 V s<sup>-1</sup> (Figure 8). The differential curve shown in Figure 8c exhibited two peak maxima near -0.16 (corresponding to  $E_{pc}(1)$ ) and -0.10 V (corresponding to  $E_{pa}(1)$ ). This supports

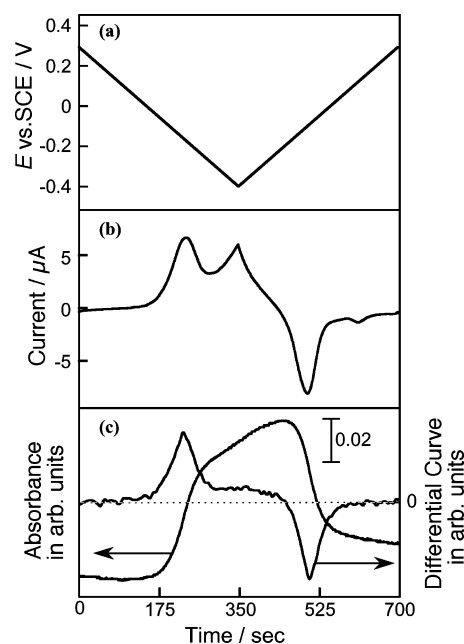
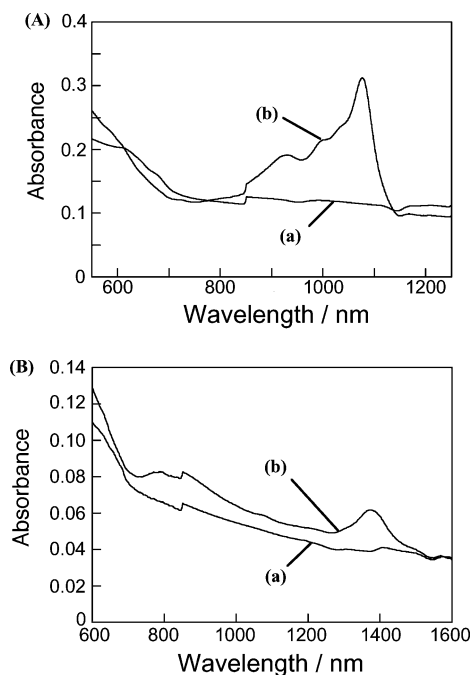


Figure 8. Result of simultaneous measurements of current and charge in absorbance at a  $\lambda_{max}$  of 1078 nm during dc cyclic potential scanning at a scan rate of 2 mV s<sup>-1</sup> for a cast film of  $C_{60}/3C_{12}N^+Br^-$  (molar ratio 1:19) on an ITO electrode in a 0.1 M aqueous TEAC solution at 25 °C. Scanning potential vs time (a), current vs time (b), and absorbance at 1078 nm and the differential curve vs time (c), respectively.

the suggestion that the absorption at 1078 nm is due to electrochemically generated  $C_{60}^{\bullet-}$  because the differential curve and the current profile are closely related.

**Chemical Generation of  $C_{60}^{\bullet-}$  in H<sub>2</sub>O.** To understand the ion-pairing interaction between the reduced forms of fullerenes and matrix lipid cations in aqueous media, we first measured the visible–near-IR absorption spectra for a cast film of a single component ( $C_{60}$ ) on a quartz substrate in a cuvette. We found that no characteristic bands of the reduced  $C_{60}$  appeared in the near-IR region in H<sub>2</sub>O in the presence of  $Na_2S_2O_4$ . (See Figure S4 in Supporting Information.) This result would be related to the fact that the facile reduction/oxidation reaction of films of only  $C_{60}$  on electrodes is difficult.

In contrast, when  $C_{60}$  is incorporated into cationic lipids, chemical reduction with  $Na_2S_2O_4$  occurs easily. A cast film of  $C_{60}/3C_{12}N^+Br^-$  on quartz substrates in H<sub>2</sub>O turned reddish brown on adding  $Na_2S_2O_4$  to solution. The intensity of the near-IR absorption bands of the film increased gradually for ca. 20 min to a constant value remaining constant for a couple of hours and then gradually decreased. As shown in Figure 9A, the film showed characteristic bands at 1077, 1034 (shoulder), 1000, and 934 nm that are assignable to  $C_{60}^{\bullet-}$ . The observed absorption maxima were almost identical to those of chemically<sup>5a–c,e,g</sup> and



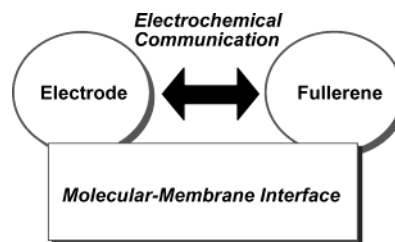
**Figure 9.** Visible-near-IR absorption spectra for a cast film of (A) C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> (molar ratio 1:19) on a quartz plate in H<sub>2</sub>O and (B) C<sub>70</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> (molar ratio 1:19) on a quartz plate in D<sub>2</sub>O in the absence (a) and the presence (b) of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> under an Ar atmosphere.

electrochemically<sup>6c-h</sup> generated C<sub>60</sub><sup>•-</sup> in organic solvents. It is clear that Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> reduces C<sub>60</sub> in the cationic lipid film to generate C<sub>60</sub><sup>•-</sup>. The instability of C<sub>60</sub><sup>•-</sup> could be due to the reaction of C<sub>60</sub><sup>•-</sup> with some oxygen that might remain in the film even after argon bubbling.

Because cationic amphiphiles such as 4C<sub>8</sub>N<sup>+</sup>Br<sup>-</sup>, 4C<sub>7</sub>N<sup>+</sup>Br<sup>-</sup>, and 4C<sub>8</sub>P<sup>+</sup>Br<sup>-</sup> provide suitable microenvironments for the electrochemistry of fullerene films in aqueous media, these lipid films containing C<sub>60</sub> all showed visible-near-IR absorption spectra due to the generation of C<sub>60</sub><sup>•-</sup> in the presence of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. The obtained data for the chemical generation of C<sub>60</sub><sup>•-</sup> using Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> for the composite thin films of C<sub>60</sub> and lipids (amphiphiles) are summarized in Table 3 along with the results of the electrochemical generation of C<sub>60</sub><sup>•-</sup> at the modified ITO electrodes.

To understand the effect of the charge of the lipids (amphiphiles) for the chemical generation of C<sub>60</sub><sup>•-</sup>, we have examined the use of a neutral artificial lipid, 2C<sub>12</sub>Gly, and an anionic artificial lipid, 2C<sub>12</sub>PO<sub>4</sub><sup>-</sup> (at pH 10). The visible-near-IR absorption spectra for both cast films of C<sub>60</sub>/2C<sub>12</sub>Gly and C<sub>60</sub>/2C<sub>12</sub>PO<sub>4</sub><sup>-</sup> on quartz substrates did not show the generation of C<sub>60</sub><sup>•-</sup> in water in the presence of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. (See Figure S5 Supporting Information.) All obtained results indicate that the ion-pairing capability between chemically generated C<sub>60</sub><sup>•-</sup> and lipid matrix cations is the key factor in the generation of C<sub>60</sub><sup>•-</sup>.

**Chemical Generation of C<sub>70</sub><sup>•-</sup> in D<sub>2</sub>O.** A characteristic band around 1370 nm for C<sub>70</sub><sup>•-</sup>, when being generated by chemical<sup>5d,f,j,k</sup> and electrochemical<sup>6d</sup> reduction, is observed in organic homogeneous solutions. Because H<sub>2</sub>O has absorption bands near 1400 nm, the detection of C<sub>70</sub><sup>•-</sup> should be difficult in H<sub>2</sub>O. Hence, we used D<sub>2</sub>O instead of H<sub>2</sub>O. Like the film of C<sub>60</sub>, as described above, a cast film of a single component (C<sub>70</sub>) also did not exhibit the C<sub>70</sub><sup>•-</sup> peak in the presence of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. Visible-near-IR absorption spectra for a cast film of C<sub>70</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> on a quartz substrate in argon-saturated D<sub>2</sub>O are shown in Figure 9B. By adding Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, the film turned dark red, and the absorbance at 1376 and 790 nm increased to reach maximum



**Figure 10.** Lipid films are an interface of electron transfers between electrodes and fullerenes toward the construction of molecular devices.

intensity in ca. 20 min. The characteristic bands for C<sub>70</sub><sup>•-</sup> were retained for a couple of hours, as in the case of the C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> film. The band at 1376 nm is assigned to the a<sub>2</sub> → e<sub>1</sub> allowed electronic transition.<sup>6d</sup> Similar near-IR spectra were obtained when 4C<sub>8</sub>N<sup>+</sup>Br<sup>-</sup> was used in place of 3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> (Table 3). The chemical generation of C<sub>70</sub><sup>•-</sup> was also found to show a strong matrix-lipid (amphiphile) charge dependence similar to that of C<sub>60</sub><sup>•-</sup>. We emphasize the importance of the strong ion-pairing formation between the fullerene anions and the matrix-lipid cations that are formed in the hydrophobic microenvironments in the films on the quartz substrate. (See Figure S6 in Supporting Information.)

## Concluding Remarks

In conclusion, we have described in detail the stable electrochemistry of C<sub>60</sub> and C<sub>70</sub> incorporated into films of artificial lipids and cationic amphiphiles on electrodes. We highlighted the importance of the cationic charge of the lipids and amphiphiles and formed hydrophobic microenvironments in the films for the stable electrochemistry of the fullerenes. A possible electron-transfer reaction mechanism of the fullerenes in the films with regard to the ionic interactions was presented. We have also demonstrated that the electrochemistry of the fullerene films on the electrodes is tunable and that this result come from a phase change of the lipid bilayer phase in the films. We have presented spectroelectrochemical data for the generation of anions of C<sub>60</sub> embedded in the films of the cationic lipid. We also have stated that the generation of C<sub>60</sub><sup>•-</sup> and C<sub>70</sub><sup>•-</sup> by chemical reduction with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> is possible when the fullerenes are embedded in the cationic lipid films. Finally, we emphasize that the lipid bilayer structure functions as an interface of the electron transfer of fullerene thin films on electrodes (Figure 10). This should be a great advantage for the construction fullerene devices in many applications.

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**Supporting Information Available:** Electrolytes' cation-dependent CVs and relationship between the hydration energy of anions and the peak potentials for a cast film of C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> on BPG electrodes, temperature-dependent CVs for a cast film of C<sub>70</sub>/2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup> and C<sub>60</sub>/2C<sub>16</sub>N<sup>+</sup>PSS<sup>-</sup>, visible-near-IR absorption spectra for an as-cast film of C<sub>60</sub>, C<sub>60</sub>/2C<sub>12</sub>Gly, and C<sub>60</sub>/2C<sub>12</sub>PO<sub>4</sub><sup>-</sup> on a quartz plate, and schematic depiction of the structure of a cast film of C<sub>60</sub>/3C<sub>12</sub>N<sup>+</sup>Br<sup>-</sup> on a quartz plate. This material is available free of charge via the Internet at <http://pubs.acs.org>.



## References and Notes

- (1) (a) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600–601. (b) Tanigaki, K.; Ebbesen, T. W.; Sato, J.; Mizuki, J.; Tsai, J. S.; Kudo, Y.; Kuroshima, S. *Nature* **1991**, *352*, 222–223. (c) Spam, G.; Thompson, J. D.; Huang, S. M.; Kaner, R. B.; Diederich, F.; Whetten, R. L.; Gruener, G.; Holczer, K. *Science* **1991**, *252*, 1829–1830. (d) Gunnarsson, O. *Rev. Mod. Phys.* **1997**, *69*, 575–606.
- (2) (a) Allemand, P.-K.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Gruner, G.; Thompson, J. D. *Science* **1991**, *253*, 301–303. (b) Stephens, P. W.; Cox, D.; Lauher, J. W.; Mihaly, L.; Wiley, J. B.; Allemand, P.-M.; Hirsh, A.; Holczer, K.; Li, Q.; Thompson, J. D.; Wudl, F. *Nature* **1992**, *355*, 331–332. (c) Hino, S.; Umishima, K.; Iwasaki, K.; Tanaka, K.; Sato, T.; Yamabe, T.; Yoshizawa, K.; Okahara, K. *J. Phys. Chem. A* **1997**, *101*, 4346–4350. (d) Ishii, K.; Fujiwara, A.; Suematsu, H.; Kubozono, Y. *Phys. Rev. B* **2002**, *65*, 134431. (e) Margiolaki, I.; Margadonna, S.; Prassides, K.; Hansen, T.; Ishii, K.; Suematsu, H. *J. Am. Chem. Soc.* **2002**, *124*, 11288–11289.
- (3) (a) Wang, Y. *Nature* **1992**, *356*, 585–587. (b) Wang, Y.; West, R.; Yuan, C.-H. *J. Am. Chem. Soc.* **1993**, *115*, 3844–3845. (c) Kraabel, B.; McBranch, D.; Sariciftci, N. S.; Moses, D.; Heeger, A. J. *Phys. Rev. B* **1994**, *50*, 18543–18552.
- (4) (a) Chlistunoff, J.; Cliffl, D.; Bard, A. J. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley & Sons: Chichester, England, 1997; Vol. 1, pp 333–412. (b) Echegoyen, L.; Diederich, F.; Echegoyen, L. E. In *Fullerenes: Chemistry, Physics, and Technology*; Kadish, K. M.; Ruoff, R. S., Ed.; Wiley-Interscience: New York, 2000; Chapter 1, pp 1–51. (c) Shergara, B. S.; Kutner, W.; D'Souza, F. *Electroanalysis* **2003**, *15*, 753–772. (d) Nakashima, N. *Structure and Electrochemistry of Fullerene Lipid-Hybrid and Composite Materials*; Ottov, A.; Tien, H. T., Eds.; Membrane Science and Technology; 2003; Vol. 7, Chapter 29.
- (5) (a) Stinchcombe, J.; Pénicaud, A.; Bhyrappa, P.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 5212–5217. (b) Subramanian, R.; Boulas, P.; Vijayashree, M. N.; D'Souza, F.; Jones, M. T.; Kadish, K. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1847–1848. (c) Boyd, P. D. W.; Bhyrappa, P.; Paul, P.; Stinchcombe, J.; Bolskar, R. D.; Sun, Y.; Reed, C. A. *J. Am. Chem. Soc.* **1995**, *117*, 2907–2914. (d) Gherghel, L.; Baumgarten, M. *Synth. Met.* **1995**, *70*, 1389–1390. (e) Wu, M.; Wei, X.; Qi, L.; Xu, Z. *Tetrahedron Lett.* **1996**, *37*, 7409–7412. (f) Konarev, D. V.; Drichko, N. V.; Graja, A. *J. Chim. Phys.* **1998**, *95*, 2143–2156. (g) Fukuzumi, S.; Nakanishi, I.; Maruta, J.; Yorisue, T.; Suenobu, T.; Itoh, S.; Arakawa, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 6673–6680. (h) Fukuzumi, S.; Suenobu, T.; Hirasaka, T.; Arakawa, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 9220–9227. (i) Fujitsuka, M.; Luo, C.; Ito, O. *J. Phys. Chem. B* **1999**, *103*, 445–449. (j) Konarev, D. V.; Drichko, N. V.; Semkin, V. N.; Graja, A. *Synth. Met.* **1999**, *103*, 2384–2385. (k) Wei, X.; Suo, Z.; Zhou, K.; Zhang, W.; Wang, P.; Shen, H.; Li, X. *J. Chem. Soc., Perkin Trans. 2* **1999**, 121–126.
- (6) (a) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050–1051. (b) Xie, Q.; P-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1991**, *114*, 3978–3979. (c) Lawson, D. R.; Feldheim, D. L.; Foss, C. A.; Dorhout, P. K.; Elliott, C. M.; Martin, C. R.; Parkinson, B. *J. Electrochem. Soc.* **1992**, *139*, L68–L71. (d) Lawson, D. R.; Feldheim, D. L.; Foss, C. A.; Dorhout, P. K.; Elliott, C. M.; Martin, C. R.; Parkinson, B. *J. Phys. Chem.* **1992**, *96*, 7175–7177. (e) Khaled, M. M.; Carlin, R. T.; Trulove, P. C.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1994**, *116*, 3465–3474. (f) Trulove, P. C.; Carlin, R. T.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1995**, *117*, 6265–6272. (g) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075–1120. (h) Rapt, P.; Bartl, A.; Gromov, A.; Stasko, A.; Dunsch, L. *Chem. Phys. Chem.* **2002**, *351*–356.
- (7) (a) Beedy, A.; Eastoe, J.; Crooks, E. R. *Chem. Commun.* **1996**, 901–902. (b) Brezová, V.; Gügel, A.; Rapt, P.; Stasko, A. *J. Phys. Chem.* **1996**, *100*, 16232–16237. (c) Konishi, T.; Fujitsuka, M.; Ito, O. *Chem. Lett.* **2000**, 202–203.
- (8) Ohlendorf, V.; Willnow, A.; Hungerbühler, H.; Guldi, D. M.; Asumus, K.-D. *J. Chem. Soc., Chem. Commun.* **1995**, 759–760.
- (9) (a) Jehoulet, C.; Obeng, Y. S.; Kim, Y.-T.; Zhou, F.; Bard, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 4237–4247. (b) Koh, W.; Dubois, D.; Kutner, W.; Thomas Jones, M.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 4163–4165. (c) Dubois, D.; Moninot, G.; Kutner, W.; Thomas Jones, M.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137–7145. (d) Koh, W.; Dubois, D.; Kutner, W.; Thomas Jones, M.; Kadish, K. M. *J. Phys. Chem.* **1993**, *97*, 6871–6879. (e) Chlistunoff, J.; Cliffl, D.; Bard, A. J. *Thin Solid Films* **1995**, *257*, 166–184. (f) Suárez, M. F.; Marken, F.; Compton, R. G.; Bond, A. M.; Miao, W.; Raston, C. L. *J. Phys. Chem. B* **1999**, *103*, 5637–5644. (g) Winkler, K.; Costa, D. A.; Balch, A. L. *Pol. J. Chem.* **2000**, *74*, 1–37 and references therein. (h) Bond, A. M.; Miao, W.; Raston, C. L. *J. Phys. Chem. B* **2000**, *104*, 2320–2329.
- (10) Wang, W.; Chiu, H.; Chang, C.; Chuang, K.; Lin, S. *Synth. Met.* **1999**, *103*, 2450–2451.
- (11) (a) Szűcs, A.; Loix, A.; Nagy, J. B.; Lamberts, L. *J. Electroanal. Chem.* **1995**, *397*, 191–203. (b) Szűcs, 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. (d) Szűcs, A.; Tölgyesi, M.; Szűcs, E.; Nagy, J. B.; Novák, M. *J. Electroanal. Chem.* **1997**, *429*, 27–35. (e) Li, M.; Li, N.; Gu, Z.; Zhou, X.; Sun, Y.; Wu, Y. *Anal. Chim. Acta* **1997**, *356*, 225–229. (f) Szűcs, A.; Tölgyesi, M.; Csizsár, M.; Nagy, J. B.; Novák, M. *J. Electroanal. Chem.* **1998**, *442*, 59–66. (g) Szűcs, A.; Tölgyesi, M.; Csizsár, M.; Nagy, J. B.; Novák, M. *Electrochim. Acta* **1998**, *44*, 613–621. (h) Hatano, T.; Ikeda, A.; Akiyama, T.; Yamada, S.; Sano, M.; Kanekiyo, Y.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 909–912. (i) Szűcs, A. *J. Electroanal. Chem.* **2001**, *505*, 159–164.
- (12) (a) Csizsár, M.; Szűcs, A.; Tölgyesi, M.; Nagy, J. B.; Novák, M. *J. Electroanal. Chem.* **1998**, *441*, 287–292. (b) Liu, T.; Li, M.; Li, N.; Shi, Z.; Gu, Z.; Zhou, X. *Synth. Met.* **1999**, *107*, 175–181.
- (13) (a) Nakanishi, T.; Murakami, H.; Sagara, T.; Nakashima, N. *J. Phys. Chem. B* **1999**, *103*, 304–308. (b) Nakanishi, T.; Morita, M.; Murakami, H.; Sagara, T.; Nakashima, N. *Chem.—Eur. J.* **2002**, *8*, 1641–1648.
- (14) (a) Nakashima, N.; Tokunaga, T.; Nonaka, Y.; Nakanishi, T.; Murakami, H.; Sagara, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 2671–2673. (b) Nakashima, N.; Nonaka, Y.; Nakanishi, T.; Sagara, T.; Murakami, H. *J. Phys. Chem. B* **1998**, *102*, 7328–7330. (c) Nakashima, N.; Kuriyama, T.; Tokunaga, T.; Murakami, H.; Sagara, T. *Chem. Lett.* **1998**, 633–634. (d) Nakanishi, T.; Murakami, H.; Sagara, T.; Nakashima, N. *Chem. Lett.* **2000**, 340–341.
- (15) Nakashima, N.; Wahab, N. W. B.; Mori, M.; Murakami, H.; Sagara, T. *Chem. Lett.* **2001**, 748–749.
- (16) Nakashima, N.; Sakai, M.; Murakami, H.; Sagara, T.; Wakahara, T.; Akasaka, T. *J. Phys. Chem. B* **2002**, *106*, 3523–3525.
- (17) Song, F.; Echegoyen, L. *J. Phys. Chem. B* **2003**, *107*, 5844–5850.
- (18) Li, M.; Xu, M.; Li, N.; Gu, Z.; Zhou, X. *J. Phys. Chem. B* **2002**, *106*, 4197–4202.
- (19) (a) Takekuma, S.; Takekuma, H.; Matsumoto, T.; Yoshida, Z. *Tetrahedron Lett.* **2000**, *41*, 1043–1046. (b) Takekuma, S.; Takekuma, H.; Matsumoto, T.; Yoshida, Z. *Tetrahedron Lett.* **2000**, *41*, 2929–2932. (c) Takekuma, S.; Takekuma, H.; Matsumoto, T.; Yoshida, Z. *Tetrahedron Lett.* **2000**, *41*, 4909–4912.
- (20) Kunitake, T.; Kimizuka, N.; Higashi, N.; Nakashima, N. *J. Am. Chem. Soc.* **1984**, *106*, 1978–1983.
- (21) Nakashima, N.; Yamaguchi, Y.; Eda, H.; Kunitake, M.; Manabe, O. *J. Phys. Chem. B* **1997**, *101*, 215–220.
- (22) (a) Kadish, K. M.; Nakanishi, T.; Gürek, A.; Ahsen, V.; Yilmaz, I. *J. Phys. Chem. B* **2001**, *105*, 9817–9821. (b) Yilmaz, I.; Nakanishi, T.; Gürek, A.; Kadish, K. M. *J. Porphyrins Phthalocyanines* **2003**, *7*, 227–238. (c) Nakanishi, T.; Yilmaz, I.; Nakashima, N.; Kadish, K. M. *J. Phys. Chem. B* **2003**, *107*, 12789–12796.
- (23) An indium tin oxide substrate (surface resistivity, 10  $\Omega$ /sq, supplied from Sony Co.) was cut to a size of 1.0 cm  $\times$  1.5 cm and then sheathed in an epoxy resin and connected to a glass tube. The ITO electrode was sonicated in water with surfactant (VISTA no. 50), rinsed with water, immersed in concentrated H<sub>2</sub>SO<sub>4</sub>/water (1:1 v/v) for 30 s, and then rinsed with a copious amount of water and ethanol.
- (24) (a) *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Bard, A. J., Faulkner, L. R., Eds.; Wiley & Sons: New York, 2001; pp 228–234. (b) *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Bard, A. J., Faulkner, L. R., Eds.; Wiley & Sons: New York, 2001; pp 452–458.
- (25) Boulas, P.; Kutner, W.; Thomas Jones, M.; Kadish, K. M. *J. Phys. Chem.* **1994**, *98*, 1282–1287.
- (26) Ohwaki, H.; Nakashima, N. *Trans. Mater. Res. Soc. Jpn.* **2001**, *26*, 933–936.
- (27) Hofmeister, F. *Arc. Exp. Pathol. Pharmacol.* **1888**, *24*, 247–260.
- (28) (a) Xie, Q.; Arias, F.; Echegoyen, L. *J. Am. Chem. Soc.* **1993**, *115*, 1818–1819. (b) Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Herrmann, A.; Rüttimann, M.; Crassous, J.; Cardullo, F.; Echegoyen, L.; Diederich, F. *J. Am. Chem. Soc.* **1998**, *120*, 7860–7868.
- (29) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2000.