Molecular Bilayer-Based Superstructures of a Fullerene-Carrying Ammonium Amphiphile: Structure and Electrochemistry

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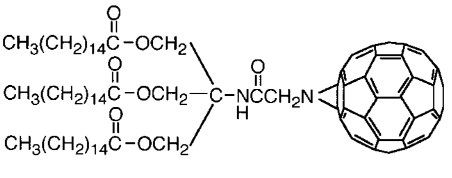
Abstract: The synthesis of a water-soluble C_{60}-carrying single-chain ammonium amphiphile, 10-(*N*-methyl-2-fulleropyrrolidyl)decyltrimethylammonium bromide (**1**) as well as the characterization of aqueous solutions and cast films of **1** are described. X-ray diffraction study suggests that cast films of **1** form a multilayer structure based on biomembrane-like molecular bilayers. Electron microscopy has revealed that **1** produces both fibrous and disk-like aggregates with 10–12 nm of thickness through self-organization of **1** in aqueous solution. Differential scanning calorimetry, dynamic light scattering, FTIR, and UV-visible absorption studies were also carried out to characterize aqueous solutions and cast films of **1**. Electrochemistry for an aqueous solution and for cast films of just **1** and **1** incorporated in lipid films on electrodes was conducted. It was found that films of just **1** and of **1**/lipid cast on electrodes showed electron transfer reactions leading to the generation of the fullerene dianion or trianion. In contrast, electrochemistry of aqueous solution of **1** at a bare electrode gives a cathodic current near −0.5 to −0.6 V against SCE; however, an anodic current for the solution did not appear.

Keywords: electron transfer · fullerenes · membranes · supramolecular chemistry · surfactants

Introduction

Since the first finding of C_{60},[1] studies on the chemistry, physics, and biochemistry of fullerenes and related compounds are at the forefront of research.[2] The combination of fullerene chemistry and the chemistry of lipid bilayer membranes (both have been extensively developed independently in recent years) would be expected to produce a new field in chemistry.[3] The goal of this study is to design and construct a novel fullerene-based, carbon nanomaterial that possesses biomembrane-mimetic structures and properties. Such a study is of interest from both a fundamental and a practical point of view. We have already reported that a water-insoluble artificial fullerene lipid, $\mathbf{3C_{16}C_{60}}$, forms organized multibilayer membrane films that exhibit a main-phase transition as well as a subphase transition that regulates the spectral properties of the fullerene moieties.[3d] We also described unique electrochemical properties of cast films of $\mathbf{3C_{16}C_{60}}$[3d] and of a C_{60}/artificial-ammonium-lipid composites[3i–k, m] on electrode surfaces. Although fullerenes can be solubilized in water by several means, reports describing the synthesis of water-soluble fullerene-bearing amphiphiles and their aggregation structure in water have been very limited.[4–7]



$\mathbf{3C_{16}C_{60}}$

In this article, we describe in detail the morphology and structure of aqueous aggregates of a water-soluble C_{60}-terminating ammonium amphiphile **1** (Figure 1), as well as the electrochemistry for aqueous solution and cast films of **1**, and for **1** embedded in lipid films on electrodes. Scheme 1 shows the synthetic route for the preparation of **1**. As matrix lipids, we have used tridodecylmethylammonium bromide (**2**), dioleoyl-phosphatidylcholine (**3**), and didodecylphosphate (**4**). A preliminary report on this study has been published elsewhere.[4] Tour and co-workers[5] recently reported the formation of supramolecular nanorods from C_{60}-*N*,*N*-dimethylpyrrolidinium iodide in dimethylsulfoxide with one part water and then adding one part benzene. They also reported that an aqueous solution of the compound treated with ultrasonication and then filtered gives vesicles with diameters of 10–70 nm. Sano and co-workers[6] described the vesicle formation by a bola-amphiphilic fullerene, though the bilayer

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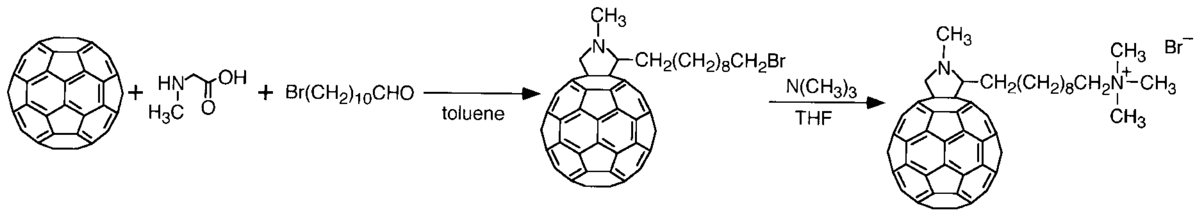

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Scheme 1. Synthesis of **1**.

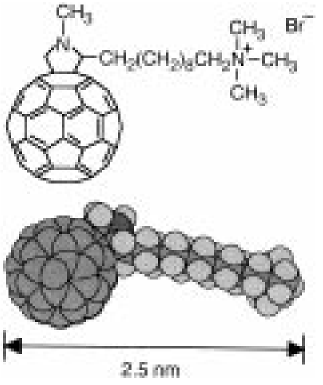

Figure 1. The chemical structure (above) and a CPK model (below) of **1**.

structure is not evident. Hirsch and co-workers[7] described the synthesis and the membrane and vesicle formation of a C_{60}-carrying globular amphiphile in water.

Results and Discussion

Molecular bilayer formation and aggregate structure: Compound **1** is soluble in DMF, DMSO, hot chloroform, and hot alcohols, but is insoluble in THF, acetonitrile, ethylacetate, hexane, and toluene. Cast films of **1** from a hot methanol solution before and after the hot-water treatment were studied by X-ray diffraction. Figure 2 shows the result. The reflection peak that appears at $2\theta = 2.04^\circ$ for the sample before the hot-water treatment is attributed to diffraction from the (001) plane. This suggests the existence of regular molecular layers in the film. For the sample taken after the hot-water treatment, a very weak peak appeared at around $2\theta = 3.96^\circ$ as well as a stronger peak at $2\theta = 1.98^\circ$. This weak peak is attributed to diffraction from the (002) plane. Hot-water treatment may cause the film structure to become slightly more ordered. The d spacing from the Bragg's equation is calculated to be 4.33 and 4.46 nm for the films before and after the hot-water treatment, respectively. The molecular length of **1** estimated from a CPK space-filling model is 2.5 nm. One possible model for the molecular bilayer structure is illustrated in Figure 3.

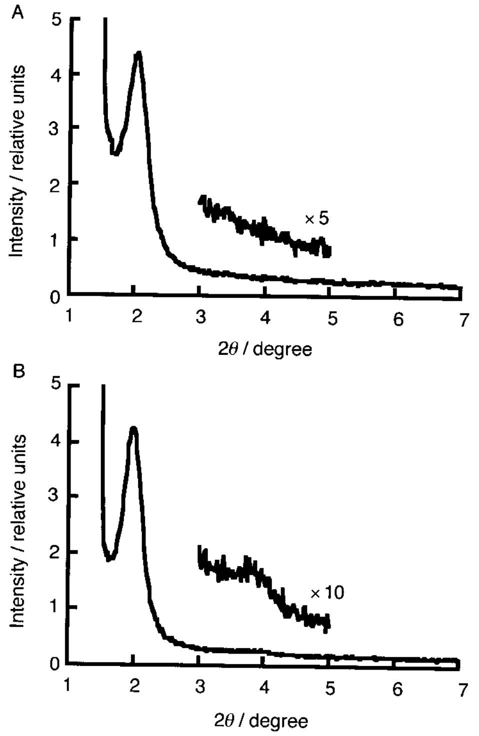

Figure 2. X-ray diagrams for a cast film of **1** A) before and B) after the hot-water treatment.

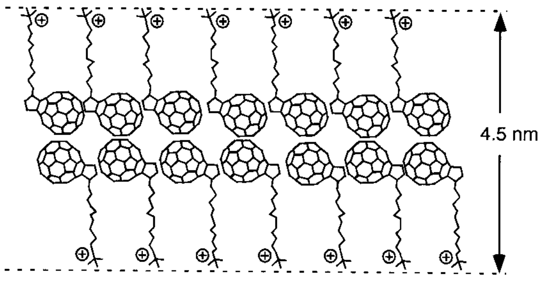

Figure 3. A schematic drawing for the molecular bilayer of **1**.

A transparent light brown aqueous solution was obtained by sonicating a film that was cast from a solution of **1** in hot methanol, as described in the Experimental Section. Negative-stained transmission electron microscopy (TEM) revealed that the aqueous solution of **1** forms both fibrous (Figure 4) and disk-like aggregates with 10–12 nm of thickness (Figure 4, below, indicated by arrows). Although detailed structure at the molecular level is unknown at present, the superstructure should be formed through self-organization of **1** in aqueous solution. Because the thickness of the disk-like aggregates is approximately 4–5 times larger than that of the molecular length, we can propose a model for this aggregate (Figure 5). Kunitake and co-workers[8] reported the formation of stacked disk-like aggregates from a single-chain ammonium amphiphile bearing a terphenoxy moiety in a dispersed aqueous solution prepared by ultrasonication.

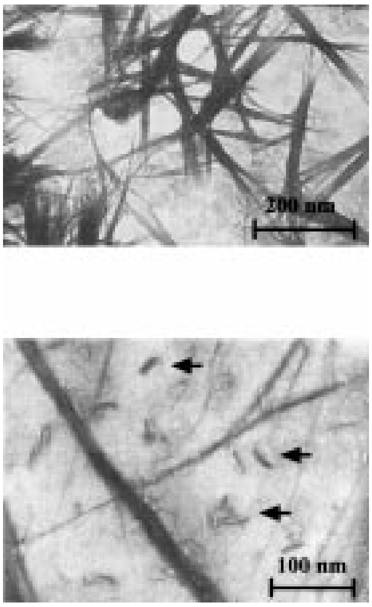

Figure 4. Typical TEM images for an aqueous solution of **1**.

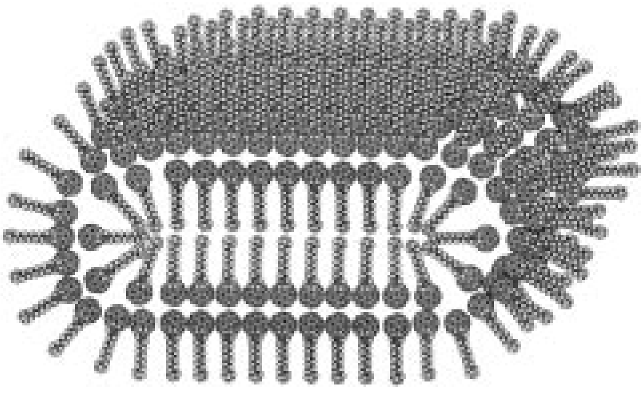

Figure 5. A schematic model for the disk-like structure of **1**.

Dynamic light scattering (DLS) study was conducted for aqueous solutions of **1** in order to get information regarding aggregation in pure water that does not contain stain. As shown in Figure 6, a size histogram for an aqueous solution of **1** demonstrates broad size distribution. For a solution prepared by ultrasonication with a bath-type sonicator, almost all of the particles were found to have a particle size of 240–600 nm, but a very small number of particles were seen around 2000 nm. When a solution of **1** was prepared by sonication with the immersion probe, particle sizes of 150–400 nm were observed (data not shown). It is known that sonication at higher power for aqueous suspensions of lipids gives rise to smaller molecular bilayer aggregates.[9] It is evident from these results that **1** forms very large aggregates with a large size distribution in pure water. This is consistent with the TEM observation.

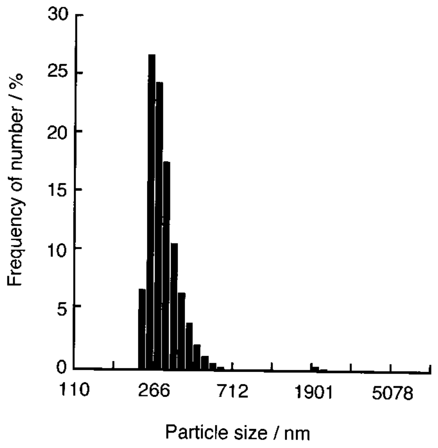

Figure 6. A DLS size distribution histogram (plot of abundance) for an aqueous solution of **1**.

Differential scanning calorimetry (DSC) study and spectral properties: The phase transition between the crystalline phase and the liquid crystalline phase is a fundamental characteristic of molecular bilayer membranes. The DSC thermogram of a cast film of **1** shows no endothermic peak in the range of 5–90 °C, indicating that there is no phase transition at this temperature range. This result is in accord with our prediction, since compound **1** is a single-chain amphiphile with a relatively short alkyl-chain length. The wavenumber of the asymmetric and symmetric methylene stretching vibrations in the FTIR spectra of cast films of **1** from both methanol and aqueous solutions appeared at 2922 ± 0.1 and $2850 \pm 0.1\,cm^{-1}$, respectively, over a temperature range of 10–40 °C (data not shown); this indicates that the methylene chain in **1** contains a *gauche* conformation[10].

UV-visible absorption spectra indicate an electronic interaction between fullerene moieties. As we described previously,[3m] the UV-visible absorption maximum for an aqueous solution of **1** is seen at 271 nm; this maximum is shifted to longer wavelength by 3 and 5 nm relative to those found in micellar solutions of hexadecyltrimethylammonium bromide (HTAB) or sodium dodecylsulfate (SDS), respectively. These shifts are due to the electronic interaction of the fullerene moieties in **1** in an aggregated state.[3d]

Electrochemistry: Although fullerenes dissolved in organic solutions form multiply charged anions upon reduction because of their high degrees of degeneracy of LUMO, the electrochemistry of fullerene films is rather complicated.[11–15] We have recently found that C_{60} incorporated in molecular bilayer films of cationic artificial lipids cast on electrodes shows stable electron transfer reactions with the underlying electrode leading to a C_{60} dianion or trianion.[3i–l] We examined the electrochemistry of **1** in film states and in aqueous solution using cyclic voltammetry in an argon atmosphere.

Figure 7 shows cyclic voltammograms (CVs) for neat cast films of **1** on basal plane graphite (BPG) electrodes in a 0.5 M aqueous electrolyte solution. When KCl, tetramethylammonium chloride, tetraethylammonium chloride, and tetrapropylammonium chloride were used as electrolytes, **1**-modified electrodes exhibited redox responses that could be attributed to the generation of radical monoanion of the fullerene moiety in **1** (Figure 7A–D). The observed CV responses were broad and the potential cycling caused gradual decrease in the

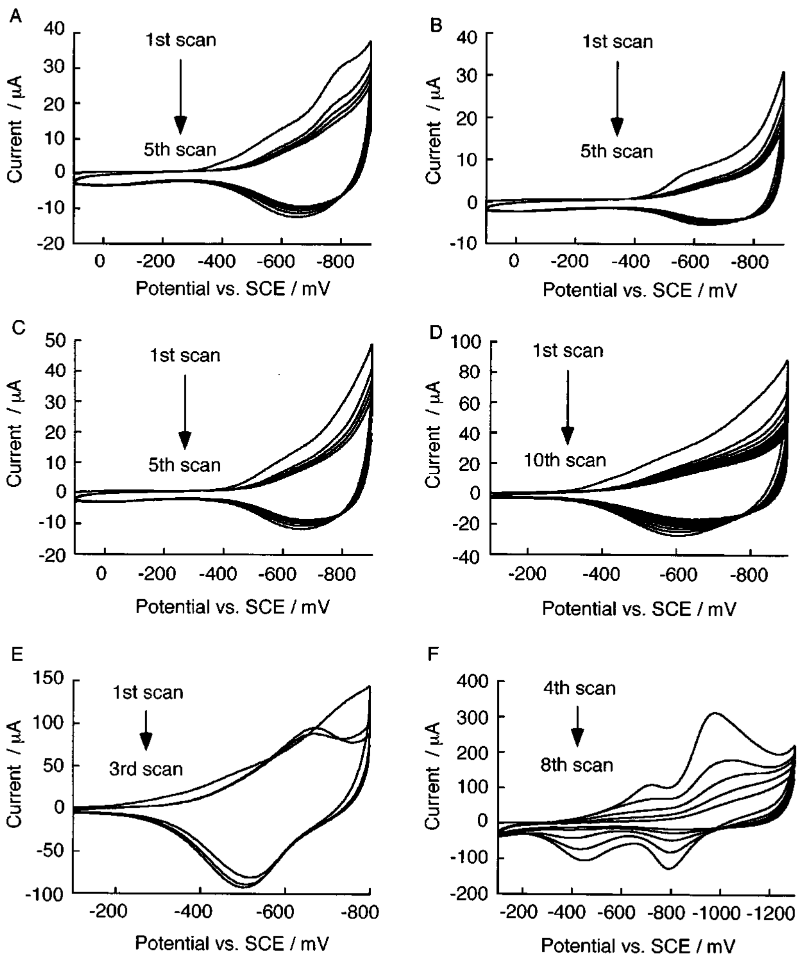

Figure 7. CVs for films of **1** cast on BPG electrodes in aqueous solution containing 0.5 M of A) KCl, B) tetramethylammonium chloride, C) tetraethylammonium chloride, D) tetrapropylammonium chloride, or E) and F) tetrabutylammonium chloride. Scan rate, 0.1 V s^{-1}.

current. The broad voltammograms suggest inhomogeneity in the structure of **1** in the film state. The second reduction peak was not seen in CVs scanned down to -1.4 V. In contrast, when *n*-tetrabutylammonium chloride was used as an electrolyte, better defined voltammograms with enhanced current intensity leading to the generation of the fullerene dianion was evident, though the dianion was very unstable (Figure 7, E and F). Expected strong binding between the fullerene radical monoanion and *n*-tetrabutylammonium chloride may change the structure of the film of **1** on the electrode in such a way as to lead to the generation of the fullerene dianion.

The electrochemistry of **1** embedded in cast films of cationic lipids on electrodes gives well-defined voltammograms.[3i–l] CVs for a **1**/**2**-modified electrode are shown in Figure 8. It is evident that in this system three consecutive one-electron electron processes occur at the electrode; this leads to the fullerene trianion in aqueous solution. The current intensity for the radical monoanion gradually increased over potential cycling and reached the steady state value (Figure 8A). The observed first reduction was stable for potential cycling of more than 50 scans. On the other hand, the fullerene dianion and trianion generated in this system were not so stable (Figure 8B,C), suggesting progressive decomposition and/or deactivation of the fullerene moiety in **1**.

In order to understand the importance of the charge on lipids for the electron transfer reaction of **1**, we have also investigated the use of a zwitterionic lipid **3** or an anionic lipid **4** instead of **2**. It is evident that a **1**/**3**-modified electrode generates the fullerene radical monoanion and dianion (Figure 9A). The first reduction peak, which is very stable, and the second reduction peak appear at -0.68 and -1.2 V, respectively. These reduction peaks are more negative by 0.3 and 0.26 V, respectively, relative to those observed at the **1**/**2**-modified electrode; this indicates weaker binding of the fullerene radical anion and dianion to the cationic moiety on **3**. The generated fullerene dianion at the **1**/**3**-modified electrode was very unstable over potential cycling as shown in the figure. Figure 9 (B and C) shows CVs at a **1**/**4**-modified electrode. Both the first (Figure 9, B) and second (Figure 9, C) reduction currents were found to be very unstable, and the reduction peaks shifted to significantly more negative potential relative to those found at the **1**/**2**-modified electrode. Since compound **4** is a negatively charged lipid under the experimental conditions (pH 9), the fullerene anions in this system are believed to interact with the electrolyte cation during the reduction processes. The results obtained indicate that ion pairing between the fullerene anions and electrolyte cations plays important role for the generation of fullerene anions.

As shown in Figure 10, CVs at a bare electrode for an aqueous solution of **1** were found to be different from that of **1** in the film states. For a bare electrode in the solution, we can see evident cathodic current near -0.5 to -0.6 V, while an anodic counterpart did not appear. Potential cycling caused a gradual decrease in the current. The first scan of the voltammograms may involve the reduction of oxygen that remained in the solution. Similar CV behavior was obtained for a solution of **1** containing HTAB (data not shown). In contrast, no faradaic current was observed for a solution of **1** containing SDS. The obtained voltammograms for **1** in aqueous solution are not identical with that of a C_{60}/γ-cyclodextrin complex dissolved in aqueous solution, for which the reversible electron transfer reaction of C_{60} is evident.[16] The absence of anodic current may come from disproportionation and/or other chemical reactions or non-electrochemical oxidation of the radical anion of **1**. The cationic

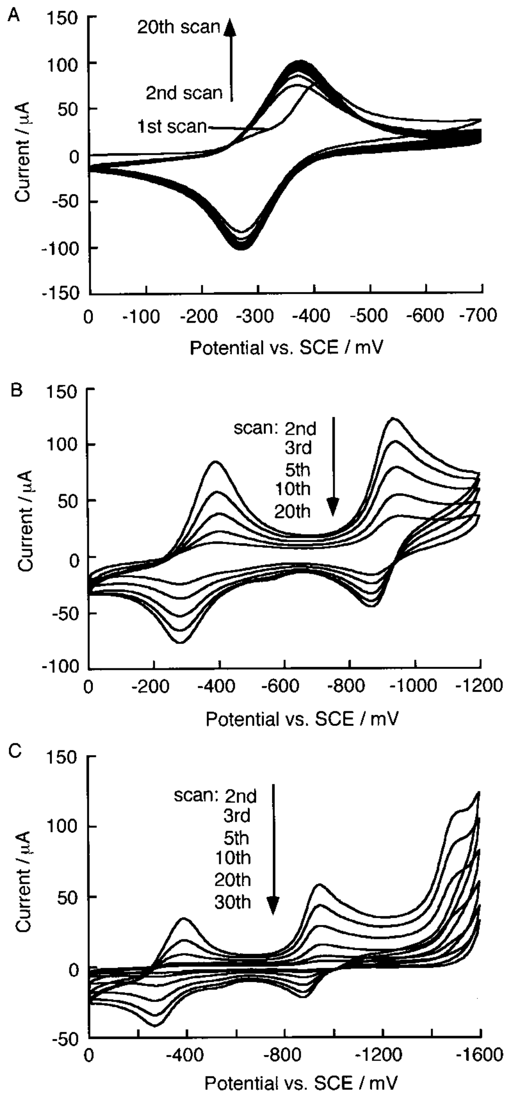

Figure 8. CVs for a cast film of **1**/**2** (molar ratio 1:19) on a BPG electrode in water containing 0.5 M tetraethylammonium chloride. A, B and C are CVs representing the first, second, and third reduction processes, respectively. Scan rate, 0.1 Vs^{-1}.

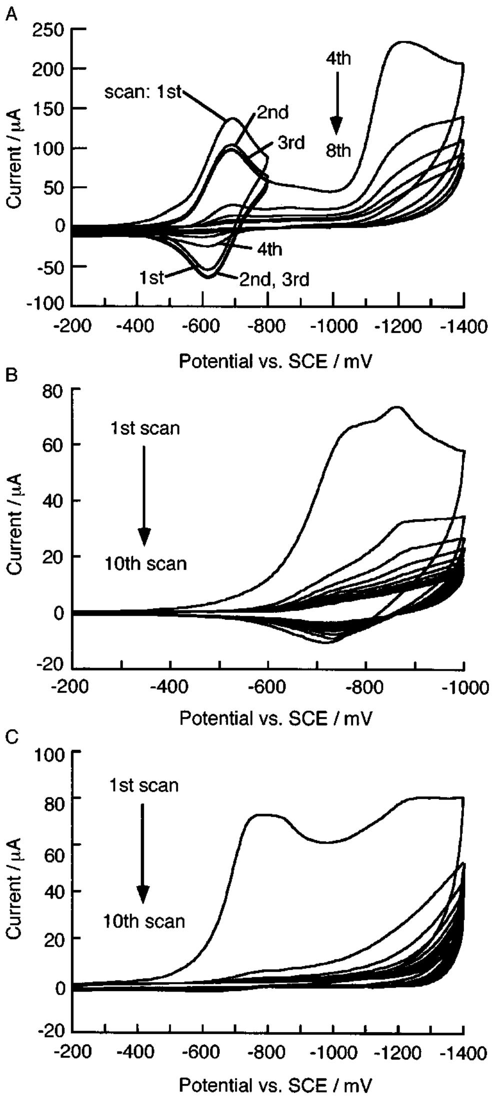

Figure 9. CVs for a cast film of A) **1**/**3** and of B) and C) **1**/**4** on BPG electrodes in water containing 0.5 M tetraethylammonium chloride. Molar ratios for **1**/**3** and for **1**/**4** are both 1:19. Scan rate, 0.1 Vs^{-1}.

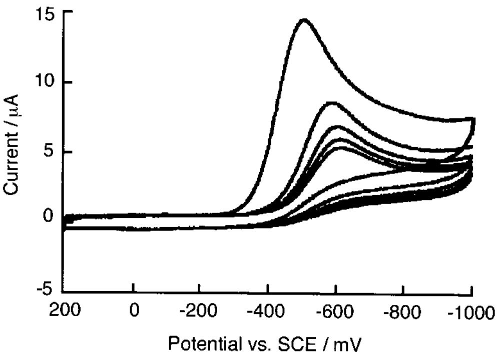

Figure 10. CVs at a bare BPG electrode for an aqueous solution of **1** (1×10^{-4} M) containing 0.02 M tetraethylammonium chloride. Scan rate, 0.1 Vs^{-1}.

charge on **1** plays an important role for the electrochemistry in the solution as well as that of **1** in film states as described above.

Conclusion

We have demonstrated that the simple C_{60}-carrying ammonium amphiphile **1** forms both fibrous aggregates and disk-like aggregates with 10–12 nm of thickness. Although detailed structure at the molecular level is unknown at present, the superstructure should be formed through self-organization of **1** in aqueous solution. This kind of fullerene-based, biomembrane-like, carbon nanosuperstructure in aqueous solution is of interest from aspects of both fundamentals and biological applications. The electron transfer reactions that lead to the generation of the fullerene trianion was observed for **1** incorporated in cast films of a cationic artificial lipid on an electrode. In this case the reduction peak potentials for both fullerene radical anion and dianion shifted significantly to more positive vlaues relative to those observed in the electrode systems in which zwitterionic or anionic lipids were used. The present study opens possibilities for the construction of electroactive fullerene nanoarchitectures with ordered structure based on self-assembled molecular organization.

Experimental Section

11-Bromoundecanal: 11-Bromoundecanal was synthesized from 11-bromoundecanol according to the method described in the literature[17] and was used immediately.

2-(10-Bromodecyl)-*N*-methylfulleropyrrolidine: C_{60} (>99.5%) was purchased from MER Corporation and used without further purification. 11-Bromoundecanal (30 mg, 0.12 mmol), *N*-methylglycine (55 mg, 0.62 mmol), and C_{60} (107 mg, 0.15 mmol) in dry toluene (90 mL) were heated under reflux for 18 h under a nitrogen atmosphere.[18] The solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (toluene). 2-(10-Bromodecyl)-*N*-methylfulleropyrrolidine was obtained as a dark brown solid. Yield: 23 mg (19%); m.p. 196 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.25–1.50 (m, 12H; $C^*C_2(\mathit{CH_2})_6C_2Br$), 1.84 (m, 2H; $C^*C\mathit{CH_2}C_8Br$), 1.89 (m, 2H; $C^*C_8\mathit{CH_2}CBr$), 2.36, 2.52 (2m, 1H each; $C^*\mathit{CH_2}C_9Br$), 2.98 (s, 3H; $N\mathit{CH_3}$), 3.38 (t, 2H; $C^*C_9\mathit{CH_2}Br$), 3.88 (t, 1H; $C^*\mathit{H}$), 4.15 (d, ^2J(H,H) = 9.5 Hz, 1H; $NC\mathit{H}HC_{60}$), 4.81 (d, ^2J(H,H) = 9.5 Hz, 1H; $NCH\mathit{H}C_{60}$); IR (KBr): $\tilde{\nu}$ = 2916, 2848, 2773 cm^{-1} (CH).

10-(*N*-Methyl-2-fulleropyrrolidyl)decyltrimethylammonium bromide (1): An excess amount of trimethylamine gas was introduced to 2-(10-bromodecyl)-*N*-methylfulleropyrrolidine (80 mg, 0.08 mmol) in dry THF (25 mL) at room temperature, and the solution was stirred for 3 days. A precipitate produced was separated and then was dried under reduced pressure to give a fullerene amphiphile **1** as a brown solid. Yield: 50 mg (60%); m.p. >400 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 1.25 (m, 6H; $C^*C_3(\mathit{CH_2})_3C_4N^+$), 1.45 (m, 2H; $C^*C_2\mathit{CH_2}C_7N^+$), 1.63 (m, 2H; $C^*C_6\mathit{CH_2}C_3N^+$), 1.77, (m, 2H; $C^*C\mathit{CH_2}C_8N^+$), 1.85 (m, 2H; $C^*C_7\mathit{CH_2}C_2N^+$), 2.40 (m, 4H; $C^*CH_2C_9N^+$, $C^*C_8CH_2CN^+$), 2.90 (s, 3H; $N\mathit{CH_3}$), 3.01 (s, 9H; $N^+(CH_3)_3$), 3.62 (t, 2H; CH_2N^+), 3.98 (t, 1H; $C^*\mathit{H}$), 4.18 (d, ^2J(H,H) = 9.6 Hz, 1H; $NC\mathit{H}HC_{60}$), 4.90 (d, ^2J(H,H) = 9.6 Hz, 1H, $NCH\mathit{H}C_{60}$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 21.95, 25.03, 25.69, 26.51, 28.45, 28.65, 52.08, 65.27, 66.94, 98.32, 139.53, 141.17, 141.52, 142.06, 142.61, 143.77, 144.75, 145.49, 146.65; IR (KBr): $\tilde{\nu}$ = 2918, 2846, 2773 cm^{-1} (CH); elemental analysis calcd (%) for $C_{76}H_{35}N_2Br \cdot 2.9H_2O$ (1056.0): C 82.36, H 3.71, N 2.53, Br 7.21; found C 82.39, H 3.73, N 2.56, Br 7.17.

X-ray measurements: Compound **1** (3 mg) in hot methanol was placed on a glass plate, followed by air-drying to obtain a cast film of **1**. X-ray diffraction measurements were carried out on a Rigaku RINT 2000 at ambient temperature.[3d]

Transmission electron microscopy (TEM): Pure water (15 mL; a Milli-Q Plus Ultrapure water system, Millipore) was added to a cast film of **1** (1 mg) from methanol. This mixture was ultrasonicated at 105 mW with an immersion-probe-type sonicator (UR-200P, Tomy Seiko Co.) for 7 min, followed by a rest period of 1 min while cooling the mixture with ice. This was repeated three times to obtain a transparent solution. A stain of either uranyl acetate or uranyl nitrate (0.4 wt%) was then added, and the solution was then ultrasonicated again for 1 min. One droplet of the solution was placed on a carbon-coating copper grid (Ouken Shoji, 200-A mesh) at ambient temperature, followed by air-drying. TEM images were taken on a JEOL JEM-100S at an accelerating voltage of 100 kV.[3m, 8]

Dynamic light scattering measurements: A cast film of **1** (0.5 mg) was immersed in pure water (10 mL), followed by ultrasonication with a bath-type sonicator (Branson 2210) or with the immersion-probe sonicator. A transparent, light brown aqueous solution was obtained by sonicating with the probe-type sonicator. The supernatant of the mixture prepared by sonication with the bath-type sonicator was used for the measurement, because the mixture was not completely transparent even after sonication for several hours. DLS measurements were carried out on a Model ELS-800 (Otsuka Electronics) at 26 ± 0.5 °C. A vertically polarized light from HeNe laser (632.8 nm, 10 mW) was irradiated to a sample cell, and the scattered light was detected at 90° to the incident beam.

Differential scanning calorimetry (DSC): DSC for a cast film of **1** (0.5 mg) was performed on a Shimadzu DSC-60 at a heating rate of 2 °C min^{-1}.[19]

FTIR and UV-visible spectral measurements: A cast film of **1** from a hot methanol or from an aqueous solution prepared on a CaF_2 plate was assembled in a temperature-controlled flow-through cell (Harrick Scientific Corporation). FTIR measurements were conducted on a Nicolet Protégé 460. Temperatures were maintained at a constant value within ± 0.1 °C (Neslab Instruments, Circulator RTE-100). The UV-visible spectral measurements for aqueous solutions of **1** were carried out on a Hitachi U-3000 spectrophotometer.

Electrochemistry: A homemade basal plane graphite (BPG) disk electrode (Scotch tape was used to expose a fresh basal plane) was used as a bare electrode for the electrochemistry of aqueous solution of **1**. A typical procedure for the preparation of a modified BPG electrode is as follows. Twenty microliters of a 0.4 mM solution of **1** in methanol (or **1**/**2** in chloroform) were placed on a BPG disk electrode (geometric area, 0.25 cm^2) and then allowed to air-dry. The electrochemistry was examined by cyclic voltammetry in an argon atmosphere (99.998% purity) at 25 °C by employing BAS-100BW electrochemical analyzer (Bioanalytical Systems). A saturated calomel electrode (SCE) and a Pt plate were used as the reference and the counter electrodes, respectively.

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