Construction of Monolayers and Langmuir-Blodgett Films of a Fullerene-Bearing Artificial Lipid

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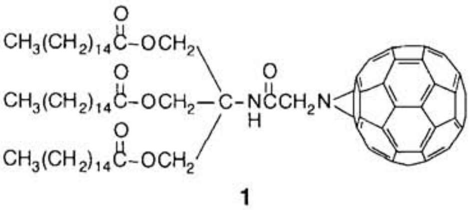
A C_{60}-bearing artificial lipid **1** forms stable monolayers at the air-water interface both in the dark and in the light. The Langmuir-Blodgett (LB) film prepared in the dark showed a phase transition by which the electronic interaction between the fullerene moieties was controllable. The LB film prepared in the light exhibited structureless electronic spectra with almost no temperature dependence.

The construction of fullerene ultrathin films with an ordered structure is of interest from both a fundamental and practical point of view.[1] C_{60} alone and amphiphilic C_{60}-derivatives form monolayers at the air-water interface and the formed monolayers can then be transferred onto solid substrates.[2] We have recently reported that the fullerene lipid **1** (see Chart 1) forms an organized multibilayer membrane film which exhibits a main phase-transition as well as a sub-phase transition that regulates the spectral properties of the fullerene moieties.[3] The goal of this study is to prepare and characterize LB films of fullerenes possessing fundamental characteristics of lipid bilayer membranes. In this communication, we demonstrate that compound **1** forms stable monolayers at the air-water interface and the monolayers are successively transferred onto a solid substrate as an LB film possessing a phase transition by which electronic interaction between the fullerene moieties is controllable.

Chart 1.



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Compound **1** was available from a previous study.[3] The surface pressure-area isotherms of **1** were measured on Millipore water (>18 MΩ) at a compression rate of 5 mm/min by using a computer-controlled film balance (USI System, Model FSD-110) at 25 °C in the light (fluorescent lamp) or in the dark. Analytical grade benzene was used as the spreading solvent.

Figure 1 shows surface pressure-area isotherms of **1**. The isotherm from the spreading solution of 1.0×10^{-4} M (1 M = 1 mol dm^{-3}) gives a limiting area of 0.27 nm^2/molecule, suggesting the formation of a multilayer. On the contrary, the isotherm with a break at 24 mN/m is exhibited for the monolayer from 1×10^{-5} M solution; the limiting areas obtained from the higher and the lower pressure regions are 0.78[2c] and 0.98[2b, 2d] nm^2/molecule, respectively, suggesting the formation of the monolayers with the hexagonal or the simple square packing, respectively. In general, monolayers of fullerenes are formed from diluted spreading solutions ($<10^{-5}$ M); instead, multilayers are formed from concentrated solutions ($>10^{-4}$ M).[4] Compound **1** gave the same phenomena. The isotherms obtained in the dark and in the light were almost identical.

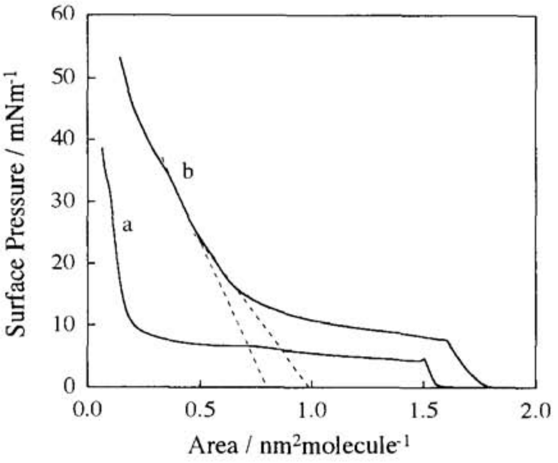

Figure 1. Surface pressure-area isotherms of **1** from 1.0×10^{-4} M benzene solution (line a) and from 1×10^{5} M benzene solution (line b) in the dark condition.

In the dark or in the light (ca. 190 lux), at a surface pressure of 30 mN/m, the monolayer of **1** from 1.0×10^{-5} M solution was transferred onto a quartz plate using a computer-controlled area controller (USI System, FSD-111). In both the light and the dark, the area-time curves (data not shown) for the deposition indicated that the monolayers were transferred as the Z-type for the first layer and the Y-type for the subsequent eight or ten layers. The transfer ratios were 1.0± 0.3.

Figure 2 shows the UV-vis absorption spectra of the LB films of **1** prepared in the dark (trace a) or in the light (traces b and c). The spectra of the LB film prepared in the dark showed an evident temperature dependence (Figure 3). At the lower temperatures, the absorption peaks appeared around 215 and 256 nm, which are shifted to longer wavelengths compared to those in hexane solution,[5] suggesting the existence of an electronic interaction between the fullerene moieties in the LB film. Upon heating to 60 °C, the peak maxima drastically changed near 47 °C, which is identical with the subphase transition temperature of the cast films of **1**.[3] The temperature dependence was reversible; that is, the electronic interaction between the fullerene moieties is controllable by the phase change of the film. On the contrary, the LB film fabricated in the light exhibited structureless electronic spectra with almost no temperature dependence (see Figure 2), suggesting the light-driven aggregate structural change[6] in the fullerene moiety in **1**. To our knowledge, there is no report describing the influence of fluorescent light on the structure of fullerenes. Cast films of **1** did not show such fluorescent light-

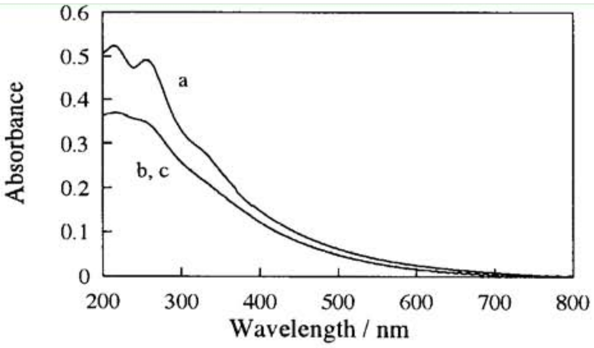

Figure 2. UV-vis spectra of LB films of **1** on quartz plates prepared in the dark (line a, 9 monolayers) or in the light (lines b and c, 11 monolayers). Measured temperature: 25 °C for a and b, 50 °C for c.

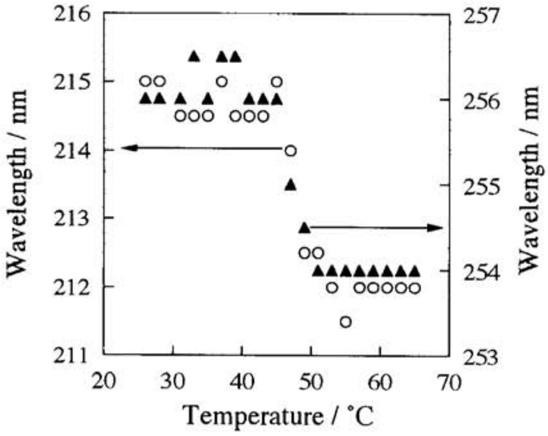

Figure 3. Temperature dependence of a LB film of **1** on a quartz plate prepared in the dark.

driven change in the spectra (data not shown).

In conclusion, we have demonstrated the formation of stable monolayers of the fullerene-bearing artificial lipid **1** and the phase transition-dependent electronic property of the LB film of **1**. The orientation of the fullerene moiety of **1** was found to be sensitive to the light from a fluorescent lamp. Together with this study and the previous study,[3] we could conclude that the molecular orientations of the fullerene moieties of the LB film and cast film of **1** are not significantly different; that is, the fundamental property of the self-assembled bilayer membrane film is maintained in the LB film. This should be important from the view point of the introduction of bilayer properties of the fullerene lipids to the organized ultrathin film system.

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5 Absorption peaks of **1** in hexane in the UV region are: 209.0, 255.0, and 322.5 nm.

6 Echegoyen and coworkers described the UV light (a medium-pressure Hg lamp)-driven structural change in the monolayers and LB films of a crown ether C_{60} derivative; see: S. Wang, R. M. Leblanc, F. Arias, and L. Echegoyen, *Langmuir*, **13**, 1672 (1997).