

Preparation of Supramolecular Assembly Films of Fullerene C₆₀ on the Aqueous Solution of Water-soluble Azocalixarene

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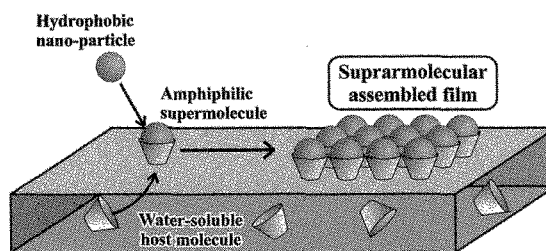
A convenient procedure was developed to prepare the ultra-thin film of supermolecules of a spherical fullerene C₆₀ and water-soluble azocalix[6]arene. C₆₀ molecule is so hydrophobic that it easily forms a three-dimensional aggregate on the water surface. When C₆₀ molecules were spread on an aqueous solution of water-soluble azocalixarene that acts as a host for C₆₀, the hydrophobic C₆₀ was captured in the cavity of the host molecule at the boundary of two phases and formed amphiphilic supermolecules. The supermolecules assembled spontaneously into the ultra-thin films, sub-mm wide. The monolayer-like film could be transferred onto the solid support by the Langmuir-Blodgett technique or the inverse Langmuir-Schaefer technique. The morphology and the transferability of the supramolecular assembled films were examined by changing the host molecules, the initial density of C₆₀ on the water surface, the subphase temperature and the metal ions in the subphase.

Key words: fullerene, host-guest interaction, supramolecular assembly, ultrathin film, azocalixarene

1. INTRODUCTION

For the achievement of a ubiquitous network, it is essential to store a large amount of information. A well-organized two-dimensional array of recordable units supports such a need. If the recordable molecules or some units are arranged in a well-organized manner, the density of the stored information in the limited area increases remarkably. Fullerene C₆₀ can act as a recordable molecule due to its excellent electronic properties, and the organization of the molecules into a structurally ordered film supports device-like properties at the macroscopic level. One of the most pursued approaches towards ordered fullerene films has been the formation of a Langmuir monolayer at the air-water interface and their subsequent transfer as Langmuir-Blodgett films onto solid supports [1,2]. The challenge in the reversible formation of stable Langmuir monolayers of fullerenes and their derivatives lies in overcoming the high aggregation tendency of the carbon sphere. With its high cohesive energy of ca. 130 kJ mol⁻¹ [3], C₆₀ prefers to undergo formation of scattered three-dimensional fullerene aggregates rather than monolayer formation [4]. In order to solve this problem, a series of amphiphilic fullerene C₆₀ were synthesized [5,6,7]. The amphiphilic fullerenes formed a monomolecular layer at the air-water interface, and the monolayer could be transferred onto quartz slides by the Langmuir-Blodgett (LB) technique [4]. To avoid the difficulty of chemical modification, the monomolecular layers of C₆₀ were prepared through molecular recognition by the host molecules. One such approach

is the co-spreading of C₆₀ and water-insoluble host molecules [8,9] and another one is the molecular recognition by the host monolayer preformed on the solid substrate [10]. The monomolecular films prepared by both approaches can be defective, such as the existence of host molecules not forming a complex. To reduce these defects, we prepared a supramolecular assembled film by spreading hydrophobic nano-particles, C₆₀, on an aqueous solution of water-soluble host molecules. When C₆₀ makes 1:2 complexes with the water-soluble host, γ -cyclodextrin, in the water, the water solubility of C₆₀ increased remarkably [11]. The C₆₀ molecule making a 1:1 complex with a hydrophilic host on the water surface, can be amphiphilic (Scheme 1). The amphiphilic supermolecules will be assembled as a monomolecular film and that will be transferred onto a solid support by the conventional LB technique.



Scheme 1. Schematic illustration for the preparation of the supramolecular assembled films of the hydrophobic nano-particle and water-soluble host molecule at the air-water interface.

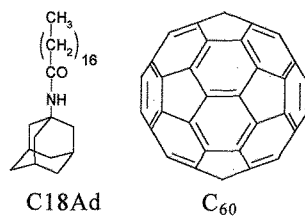
The expected merits of this procedure are that (1) the host molecule will return to the subphase when not making a complex and (2) the amphiphilic supermolecules could be aligned tightly due to the fluidity of the air-water surface. In this study, a supramolecular assembled film of C_{60} was prepared by using water-soluble azocalix[n]arene as a host molecule. The morphology of the assembled film was observed with a Brewster-angle microscope and atomic-force microscope.

2. EXPERIMENTAL

2.1 Materials

1-Octadecanoylaminoadamantane (C18Ad) was prepared by the acylation of 1-aminoadamantane with the octadecanoyl chloride. Fullerene C_{60} (>99.5% purity) was supplied by SES Research Co. and it was used without further purification. Water-soluble azocalix[n]arenes, CA4 and CA6, were synthesized as described elsewhere [12]. The chemical structures of these compounds are shown in Figure 1.

Guest nano-particles



Water-soluble hosts

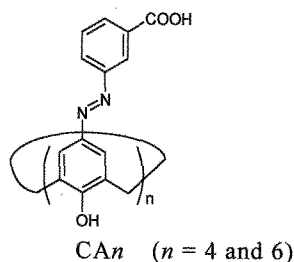


Figure 1. Chemical structures of host and guest molecules and their abbreviations.

2.2 Measurements

Surface pressure–area isotherm: The surface pressure (π) – area (A) isotherms were measured with a Langmuir trough (HBM AP3; Kyowa Kaimenkagaku Co. Ltd. and 312D; Nima technology Ltd.). Distilled water purified by EasyPure RF (Barnstead) with a resistivity of higher than 18.0 M Ω cm. The guest molecules, C_{60} and C18Ad, were dissolved into benzene or toluene, ca. 0.1 g L⁻¹, to spread on the water surface. Appropriate amounts of the solution were spread on a water surface at 20, 30 and 40 °C, and then the monolayers formed were compressed at a speed of 14 cm² min⁻¹. Homemade Brewster-angle microscope (BAM) was employed for the *in situ* observation of the surface-film morphology at the air-water interface.

Atomic force microscopy: For the observation by atomic force microscope, we transferred the surface films onto the solid support by the Langmuir-Blodgett method and the inverse Langmuir-Scheafer method [13,14]. In the inverse Langmuir-Scheafer method, the substrate is positioned horizontally under the surface. Water is removed from the trough with a syringe until a

monolayer remains above the substrate. Polished silicon wafers were used as substrates. The wafers were sonicated successively with, toluene, acetone, and ethanol. Then the substrate was exposed to O₂ plasma (Yamato Science Co., Ltd., PR300) in order to remove any trace of organic contaminant. Contact-mode observations were performed with an atomic-force microscope (Seiko Instruments Inc., SPI3700). Triangular cantilevers with a normal spring constant of 0.08 N m⁻¹ and a pyramidal Si₃N₄ tip (Olympus Optical Co., Ltd., Micro Cantilever) were used in this study. All observations were performed with a 150- μ m scanner at loading forces of 0.087 nN. The scanning area and the scanning frequency were fixed at 50 $\times$ 50 μ m² and 1 Hz, respectively.

3. RESULTS AND DISCUSSION

3.1 Preparation of supramolecular assembled film

Effect of host molecules in the subphase: Figure 2 shows the π -A isotherms of C18Ad and C_{60} on the aqueous solution at 20 °C. When C_{60} molecules were spread on ultrapure water, the surface pressure began to rise at the surface area smaller than the intrinsic molecular areas. In the hexagonal packed films, the molecular areas are estimated as 0.40 and 0.88 nm² molecules⁻¹ for C18Ad and C_{60} , respectively. BAM observation of these surface films revealed that the guest molecules form three-dimensional aggregates immediately after spreading on the water surface because of their high cohesive energy. However, when the guest molecules were spread onto the aqueous solution of CA6, the surface pressure rises sharply and the limiting molecular areas were 1.09 and 1.17 nm² molecules⁻¹ for C18Ad and C_{60} , respectively. Despite the difference in molecular area for these two molecules, they showed similar limiting areas, which indicates that they are captured in the cavity of the host molecules. If the CA4 was dissolved in the water subphase, the limiting molecular area is apparently almost the same as that for the C18Ad spread on ultrapure water. These two guest

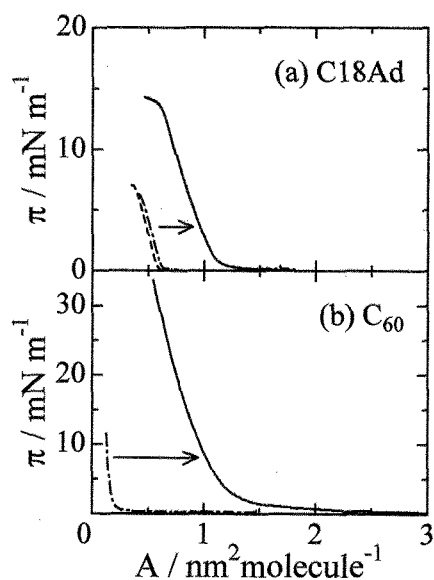


Figure 2. Surface pressure–area isotherms of (a) C18Ad and (b) C_{60} on ultrapure water (—), CA4 aq. (---) and CA6 aq. (——).

molecules, C18Ad and C₆₀, are too large to be recognized by CA4. This supports that supramolecules were formed at the air–water interface.

Effect of initial density of C₆₀ on the water surface: The limiting molecular area apparently decreased by increasing the amount of the C₆₀ molecules spread onto the water surface. In this case, the spread amounts of C₆₀ molecules were changed by using the solutions with the different concentrations and the spread volume was kept constant. There are two possibilities to explain this phenomenon: (1) the coalescence of C₆₀ in the spreading solution and (2) the aggregation of C₆₀ on the water surface after spreading. To distinguish the dominant factor, the spread volume was increased to enlarge the amount of the spread C₆₀ molecule. If C₆₀ makes an aggregate in the spreading solution, the whole surface film should have a similar limiting molecular area. However, the limiting molecular area decreased with the amount of C₆₀ spread as shown in Figure 3. These results indicate that the aggregation of C₆₀ competes with the formation of supermolecules of C₆₀ and CA6 on the water surface. There are two possible approaches to reduce the rate of aggregation. One is to increase the concentration of CA6 in the subphase, the other is to reduce the amount of C₆₀ spread. CA6 is almost saturated for the spreading condition in Figure 2. Then, it is useful to reduce the initial density of C₆₀ (d_0) for the preparation of the homogeneous film. Actually the limiting molecular area gradually increased and became almost constant when d_0 became less than 0.166 molecule nm⁻², which suggests that the aggregation of C₆₀ was almost inhibited at this planar density.

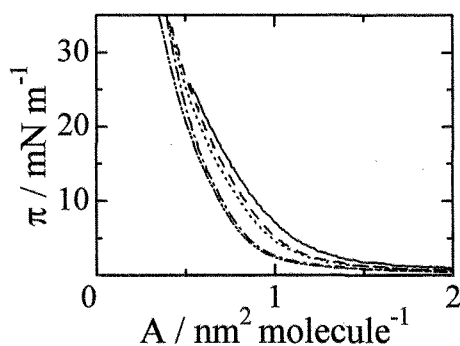


Figure 3. Surface pressure-area isotherms of C₆₀ on CA6 aq. at 10 °C. After spreading of C₆₀ solution on the aqueous solution, the planar density of fullerene C₆₀ was 0.166 (—), 0.211 (---), 0.249 (— · —), 0.277 (----) and 0.305 (— · —) molecule nm⁻².

Subphase temperature: Figure 4 shows BAM images for the surface film of C₆₀ observed on CA6 aq. at 10–30 °C. The C₆₀ film was most homogeneous when the fullerene solution was spread onto the CA6 aq. at 10 °C. At the elevated temperatures, the aggregates were recognized as bright spots and lines in the BAM images. C₆₀ molecules were spread onto the water surface as a dilute solution. If the C₆₀ molecules are trapped by CA6 before the evaporation of solvent, the C₆₀ molecules are able to stay at the air–water interface to assemble as a monomolecular thin film. Otherwise, C₆₀ molecules form three-dimensional aggregates accompanying an evaporation of the solvent. At a lower temperature, the

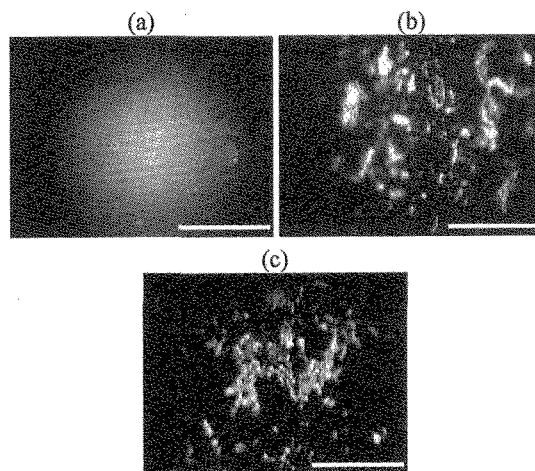


Figure 4. BAM images of C₆₀ surface film on the aqueous solution of CA6 at (a) 10 °C, (b) 20 °C and (c) 30 °C. White lines represent 500 μm.

solvent evaporates slowly, which gives C₆₀ more time to make a complex with CA6 at the air–water interface.

Metal ions in the subphase: The aggregation of CA6 has been known to be affected by the metal ions in water. Variable-temperature nuclear magnetic resonance (VT NMR) experiments indicated that the species and concentration of metal ions play important roles in regulating the molecular dynamics of calixarenes [12]. Figure 5 shows the BAM images for the CA6 surface films spread over the aqueous solution of CA6. Each subphase contains a kind of alkali metal ion; lithium, sodium, potassium or cesium. When sodium ion or cesium ion co-exists in the subphase, C₆₀ surface films showed homogeneous morphology in BAM images (Fig. 5 (b) and (d)). On the other hand, when C₆₀ molecules were spread onto the subphase containing lithium ion or potassium ion, bright regions were observed in the BAM images (Fig. 5 (a) and (c)). This means that the three-dimensional aggregates of C₆₀ were formed on that subphase even if the same concentration of CA6 existed in the subphase containing Na⁺ or Cs⁺.

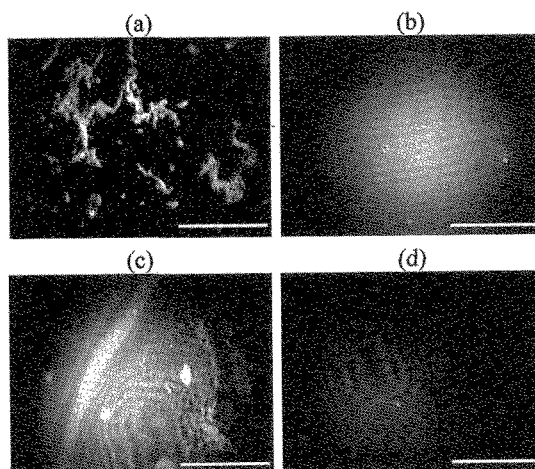


Figure 5. BAM images of C₆₀ surface film on the CA6 aq. at 10 °C. The pH of the subphase was adjusted to 11.0 by adding (a) LiOH, (b) NaOH, (c) KOH and (d) CsOH. White lines represent 500 μm.

Self-aggregation of CA6 showed that the cone conformation of CA6 was stabilized by sodium and cesium ions in the water [12]. In the present stage, we assume that such a preformed conformation of CA6 would promote the supramolecular formation at the air-water interface.

3.2 Transfer of assembled film onto the solid support

The supramolecular assembled films could be transferred onto a solid support, such as a silicon wafer or glass slide, by the Langmuir-Blodgett method and by the inverse Langmuir-Scheafer method. When the films were deposited at a surface pressure of 10 mN m^{-1} , only a smooth surface was observed in AFM and the root-mean-square roughness of the film was 0.524 nm for $25 \times 25 \mu\text{m}^2$ region. For the evaluation of film thickness, the compressed surface film was expanded until the surface pressure decreased to almost zero to make a crack in the film. The expanded film was deposited on the silicon wafer by the inverse Langmuir-Scheafer method. The AFM image of the desorbed films also showed highly smooth surfaces and a few cracks. The average depth of the cracks was 2.8 nm , which is the length of the C_{60} /CA6 1:1 complex. This feature shows that the assembled film at the air-water interface is able to be transferred onto the solid support, which expands the application probability to many devices.

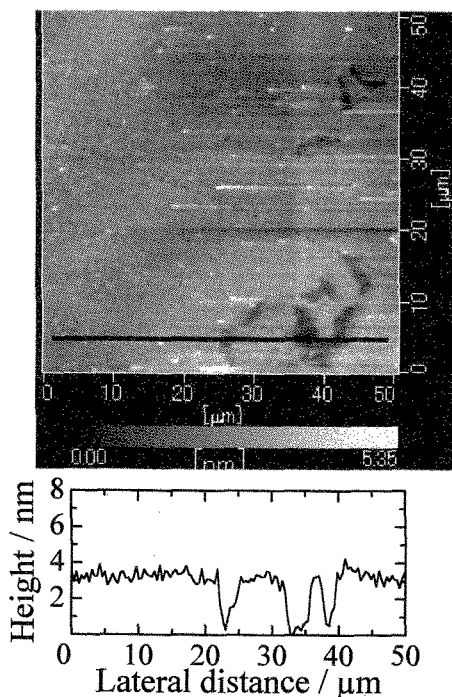


Figure 6. AFM image (top) and the height profile along with the solid line in the AFM image (bottom) for the supramolecular assembled film deposited onto the silicon wafer from the CA6 aq. at 10°C .

4. CONCLUSIONS

Supramolecular assembled films of C_{60} can be prepared at the air-water interfaces by spreading C_{60} onto the aqueous solution of the water-soluble azocalix[6]arene. When the initial density of C_{60} is less than $0.166 \text{ molecule nm}^{-2}$ on the water surface, the

monolayer-like ultrathin film spread over 1-cm long. At a lower subphase temperature, the supramolecular assembled films showed homogeneous morphology. The metal ions in the subphase play an important role in the formation of the supramolecular assembled film. The homogeneity of the assembled film was in the following order; $\text{Na}^+ \approx \text{Cs}^+ > \text{K}^+ > \text{Li}^+$. The assembled film can be transferred onto the solid support, and the film has a thickness of one supermolecule.

5. ACKNOWLEDGEMENT

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