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Langmuir Films of Amphiphilic [60]Fullerene Derivatives

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The stability of Langmuir films of [60]fullerene bisphenols **1**—**3**, monophenols **4** and **5**, and monocatechol **6** was investigated on the basis of surface pressure–area (π–A) isotherms. The films of **1**—**3** were found to be more stable than those of **4**—**6**. Among bisphenols **1**—**3**, *cis*-3-isomer **2** forms less stable Langmuir films than *cis*-2- (**1**) or *e*-isomer (**3**). This is ascribable to the lower hydrophilicity due to the intramolecular hydrogen bonding between the OH groups in **2**, as demonstrated by the ^{1}H NMR and IR spectroscopies. The contribution of intramolecular hydrogen bonding was also observed in monocatechol **6**.

Many chemists are investigating the applications of [60]-fullerene (derivatives) to advanced materials,[1] which require an arrangement of molecules in well-ordered two- or three-dimensional networks. However, it is usually difficult to obtain appropriate single crystals of [60]fullerene (derivatives). The difficulty concerning the processibility of [60]fullerene is a major problem for practical applications.

One of the most useful methods for constructing ordered networks is to make thin solid films of good quality.[2] In the thin-film form, [60]fullerene is known to exhibit some marvelous properties, such as superconductivity,[3,4] second-order non-linear optical properties,[5] and unique electrochemical properties.[6,7] This method also has an advantage of employing only a small amount of expensive [60]fullerene.

Several techniques have been utilized for the preparation of potentially useful fullerene films: thermally-evaporated, cast, Langmuir–Blodgett (LB), and self-assembled monolayer (SAM's) methods.[2] Among them, the LB technique is one of the simplest methods for obtaining organized thin solid films of fullerene derivatives. The main advantage of this technique involves the facility in the control of molecular orientation, especially for amphiphilic molecules possessing both hydrophilic and hydrophobic ends.

Some research groups have reported that [60]fullerene, itself, usually fails to form Langmuir monolayers at the air/water interface due to a lack of hydrophilic groups.[8—13] The limiting area per molecule experimentally observed at $\pi = 0$ mN m^{-1} is 10—40 Å^2/molecule, whereas the theoretical value for [60]fullerene should be at least 86.6 Å^2/molecule based on the assumption of a tight hexagonal packing of the carbon spheres with a nearest center-to-center distance of 10 Å.[14—16] [60]Fullerene easily aggregates to form multilayer films due to their strong hydrophobic interaction. Other groups have reported, however, that even pristine [60]fullerene could form a Langmuir monolayer from an extremely dilute solution,[17—19] although transferring the films to solid substrates by the LB method generally resulted in films of only a poor quality.[7,16,19] A modification of [60]fullerene with a hydrophilic group(s) usually reduces the tendency to aggregate randomly. Some research groups have already obtained amphiphilic fullerene derivatives, prepared their Langmuir films of good quality,[13,19—22] transferred them to solid substrates, and investigated their properties and stability.[23—29]

Recently, we have achieved a regioselective synthesis of [60]fullerene bisadducts **1**—**3** possessing two hydrophilic groups on a nanoparticle surface within only one hemisphere (Fig. 1).[30] These bisadducts are expected to be sufficiently amphiphilic to form well-ordered Langmuir films, whose stability seems to depend on the relative arrangement of the

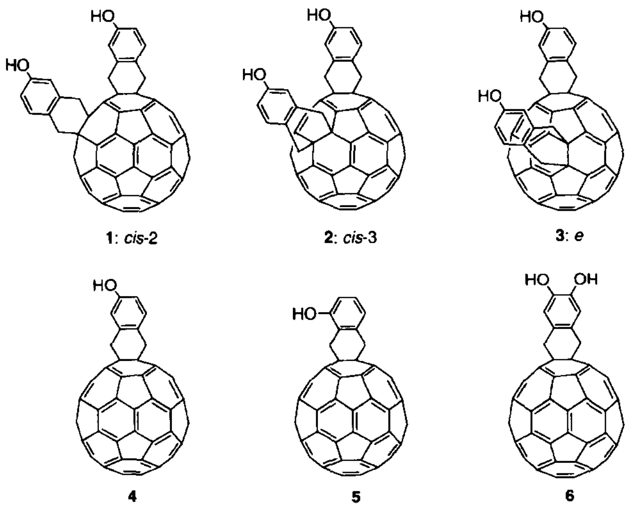

Fig. 1. Various amphiphilic [60]fullerene derivatives: [60]-fullerene bisphenols **1**—**3**, monophenols **4** and **5**, and monocatechol **6**.

two OH groups. Thus, we are prompted to systematically investigate the ability to form Langmuir films for a series of [60]fullerene derivatives, bisphenols **1**—**3**, monophenols **4** and **5**, and monocatechol **6**. Here, we disclose the effects of the number and positions of the OH groups toward the formation of Langmuir films containing [60]fullerene.

Experimental

Sample Preparation and Instruments. The synthesis, purification, and characterization of [60]fullerene derivatives **1**—**4** were described in our previous report.[30] Compounds **5** and **6** were prepared in a manner similar to that in the literature[30] and characterized mainly by ^{1}H NMR spectroscopy. All of the organic solvents used in this study were of spectroscopic grade. The distilled pure water used for the monolayer study was purified by a Yamato-WG240 autostill water purification system. The water had a resistivity of 18.2×10^4 Ω m. All equipments for the surface chemistry experiments were in a class 1000 clean room. NMR spectra were recorded on a JEOL α-500 FT NMR spectrometer. IR spectra were taken on a JASCO FT-IR 5300 spectrophotometer.

Surface Pressure–Area (π–A) Isotherms and Film Deposition. All surface pressure–area (π–A) isotherms were measured on a Nippon Laser-LB240N-MWC Langmuir trough system at room temperature (26.6 ± 0.2 °C). The temperature of water as a subphase was 25.0 ± 0.2 °C. The trough had an area of 246 cm^2, and the surface pressure sensor had a resolution of 0.1 mN m^{-1}. All [60]fullerene derivatives were dissolved at a concentration of 0.1 mM. For each isotherm experiment, the solution (250 μL) was spread evenly on the water surface, followed by a 10-min wait for the solvent evaporation before compression. The barrier was compressed at a speed of 10.0 mm min^{-1} and isotherms of the [60]fullerene derivatives were obtained. The surface of the water was cleaned by repeated compression, aspiration, and expansion cycles.

Results and Discussion

Surface Pressure–Area (π–A) Isotherms of [60]Fullerene Derivatives. Surface pressure–area (π–A) isotherms of [60]fullerene derivatives **1**—**5** on pure water subphase from benzene as a spreading solvent are shown in Fig. 2. The π–A curves of monophenols **4** and **5** suggest the formation of multilayers (Fig. 2b); their limiting areas per molecule are smaller than the theoretical value mentioned above. In addition, their isotherms are not always reproducible. These phenomena are characteristic of unstable Langmuir films of [60]fullerene (derivatives).[9,18] Thus, the weak hydrophilicity of a single OH group is insufficient to pull the molecule toward the water surface, leading to a random aggregation of the molecules (see below).

The introduction of another OH group is expected to enhance the hydrophilicity of [60]fullerene derivatives. Actually, the spreading ability of the bisphenols, especially that of **1** and **3**, was dramatically improved compared to monophenols **4** and **5**, as shown in Fig. 2a. The limiting areas per molecule of **1**—**3** were found to be 96, 60, and 84 Å^2/molecule, respectively, and their isotherms were sufficiently reproducible. The values of **1** and **3** were close to the theoretical cross-sectional area of [60]fullerene.

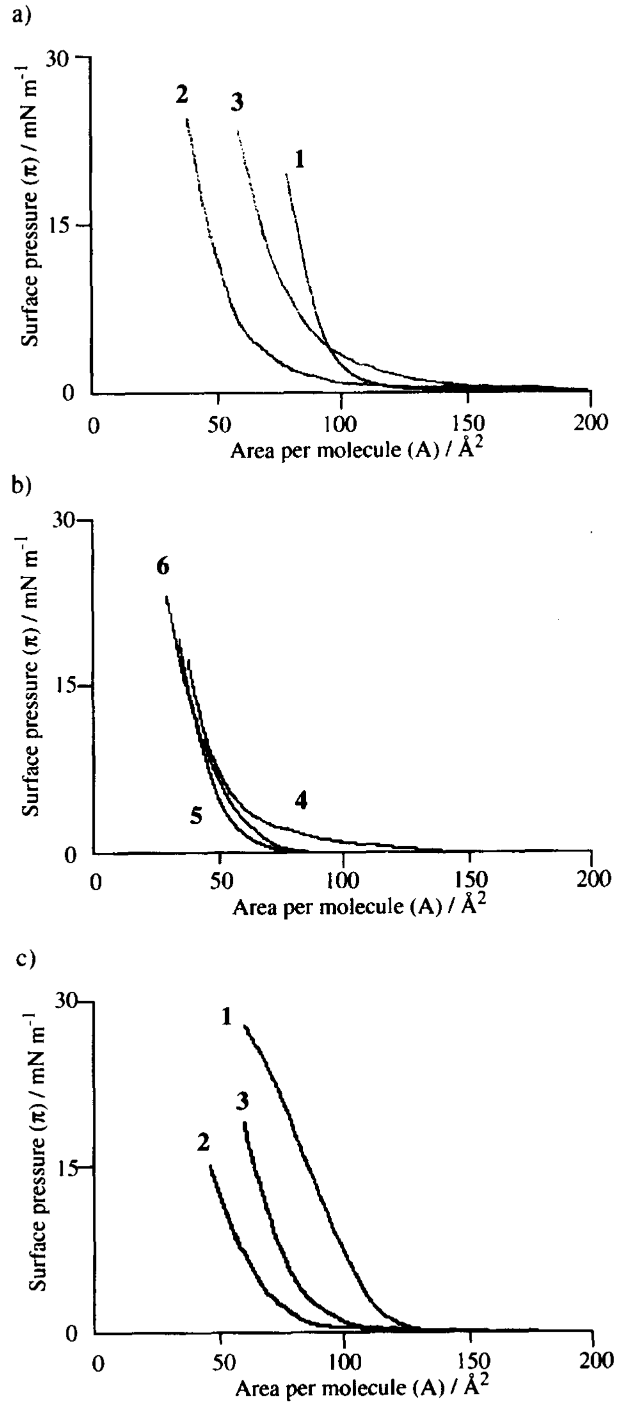

Fig. 2. Surface pressure–area (π–A) isotherms of a) **1**—**3** and b) **4**—**6** at the air/water interface from benzene solution, and c) **1**—**3** at the air/water interface from benzene/EtOH (12 : 1) solution.

We also investigated the decompression of these films in order to estimate their stability and to probe aggregation. Figure 3a shows the π–A curves of *e*-bisphenol **3** corresponding to different compressions of the same floating film. Upon the initial compression, the surface pressure began to slowly increase at A = ca. 130 Å^2/molecule, reaching 5 mN m^{-1}. When the film was decompressed, the surface pressure sharply dropped to 0. After the film was kept in the expanded state for 10 min to give it enough time for reorganization, a second compression cycle exhibited a shift

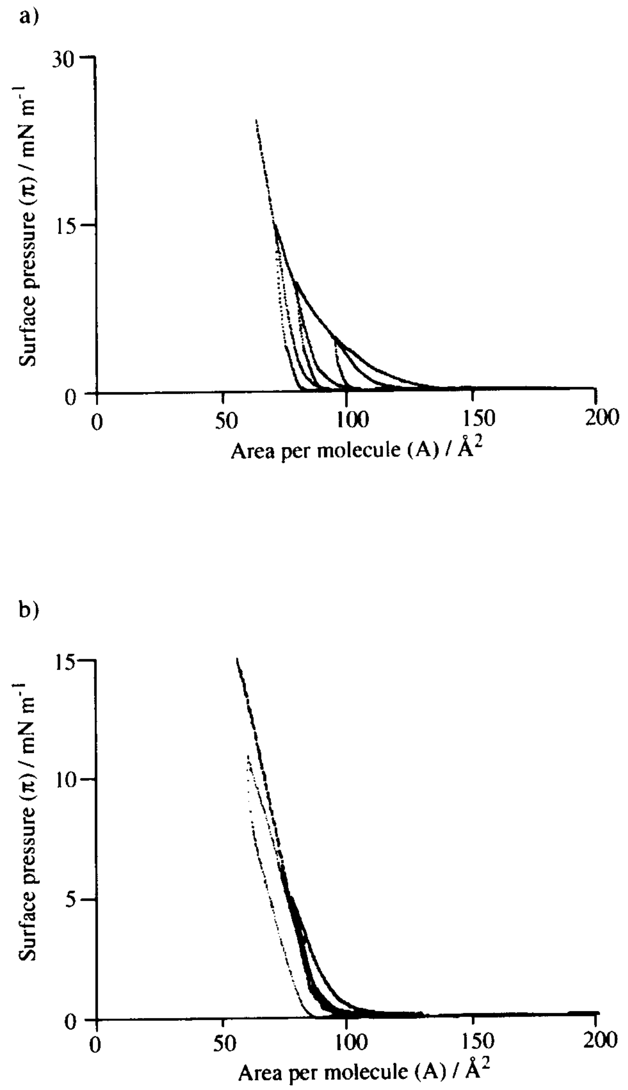

Fig. 3. Successive compression and expansion cycles (hysterisis) with a monolayer of a) *e*-bisphenol **3**, showing the irreversibility of the compression, and b) *cis*-2-bisphenol **1**, showing the reversibilityof the compression.

in the onset of the surface pressure towards a lower value (A = ca. 120 Å^2/molecule), and the isotherm commenced with a steeper slope. The curves crossed at the point where the first compression ends ($\pi = 5$ mN m^{-1}), and the second compression followed the π–A isotherm measured previously. A similar behavior was observed when repeating the procedure for π = 10 and 15 mN m^{-1}. These results clearly indicate some irreversible molecular aggregation.[21] For the Langmuir films of the other derivatives, except for *cis*-2-bisadduct **1**, similar results were obtained in hysteresis experiments where the floating film was repeatedly compressed and expanded. On the contrary, the measured surface pressure of **1** followed a similar curve in the π–A isotherm upon both compression and expansion (Fig. 3b), obviously indicating the formation of high-quality Langmuir monolayers at the air/water interface. Thus, the film stability of bisphenols **1**—**3** is different from one another, which seems to result from the steric factors of the hydrophilic OH groups.

MM2 Calculations and Spectroscopic Studies of [60]-Fullerene Bisphenols. As one of such steric factors, the intramolecular hydrogen bonding between the two OH groups seems to play an important role. Thus, molecular-mechanics (MM2) calculations were performed for possible conformations of **1**—**3**. In the most stable conformation, the O–O distances were calculated to be 4.0, 3.2, and 6.8 Å for **1**, **2**, and **3**, respectively. Since the two OH groups in **2** can be located most closely among the three bisphenols, they are likely to form intramolecular hydrogen bonding, which may affect the formation of Langmuir films. The intramolecular hydrogen bonding in **1**—**3** was examined by ^{1}H NMR and IR spectroscopies.

We previously reported that the ^{1}H NMR spectra of **1**—**3** in DMSO-d_6 exhibited broad signals due to the cyclohexene protons at room temperature, resulting from the slow flipping motion of the cyclohexene rings.[30] Their ^{1}H NMR spectra were measured in non-polar benzene-d_6 again. The signals of the cyclohexene protons of **1** and **3** were found to be extremely broadened, similarly to those in DMSO-d_6. In these bisphenols, the intramolecular hydrogen bonding is too weak to be detected in the NMR time scale. In contrast, **2** afforded four sharp doublet peaks in the cyclohexene region, apparently indicating that the flipping motion of the cyclohexene rings is highly restricted due to the intramolecular hydrogen bonding.[30] Even in MeOH-d_4/benzene-d_6 (1 : 2), **2** gave similar four doublet peaks in this region. It is noteworthy that the intramolecular hydrogen bonding of **2** was so strong that it was not broken even in such a polar medium. This intramolecular hydrogen bonding, however, was broken in DMSO-d_6, as described above.

The intramolecular hydrogen bonding in **2** was also confirmed by IR spectroscopy. Its IR spectrum was measured in KBr disk and dilute CS_2 solution (3×10^{-2} M) along with **3** for a comparison (Fig. 4). In KBr disks, both **2** and **3** afforded a broad band around 3420 cm^{-1} due to the intermolecularly hydrogen-bonded OH groups, as reported previously.[30] In dilute CS_2 solution, where the intermolecular hydrogen bonding is considerably depressed, the behavior of **2** and **3** is rather different from each other. Bisadduct **3** gives only a sharp band around 3580 cm^{-1}, corresponding to the stretching of free OH groups. In contrast, another distinct band is observed at 3486 cm^{-1} in **2**, in addition to the band at 3581 cm^{-1} due to the free OH groups. The former band apparently suggests the participation of hydrogen bonding. Since no similar band is observed in **3**, the extra band in **2** is ascribable to not intermolecularly, but intramolecularly hydrogen-bonded OH groups.

These spectroscopic results apparently demonstrate the contribution of intramolecular hydrogen bonding in **2**. As a result, its OH groups cannot sufficiently contribute to the intermolecular hydrogen bonding with water, leading to the formation of the poorest film among the three bisphenols.

Surface Pressure–Area (π–A) Isotherms of [60]-Fullerene Monocatechol. In order to confirm the idea that the intramolecular hydrogen bonding destabilizes Langmuir films, we also examined the π–A isotherm of [60]fullerene

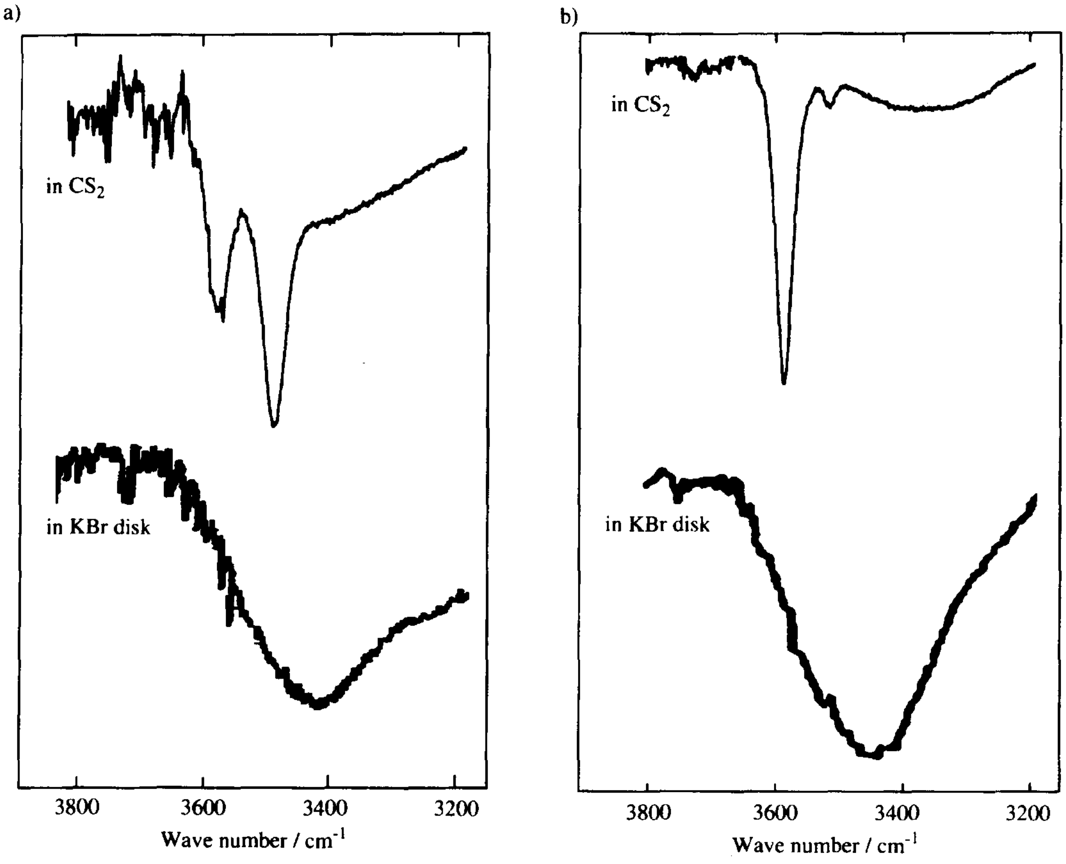

Fig. 4. IR spectra of a) **2** and b) **3** in KBr disk and CS_2 solution (3×10^{-2} M) (1 M = 1 mol dm^{-3}).

monocatechol **6** possessing two OH groups located closely to each other. As shown in Fig. 2b, the *π–A* curve of **6** indicated the formation of remarkably poor Langmuir films compared to bisphenols **1**—**3**. Its behavior is rather similar to that of monophenols **4** and **5**. Intramolecular hydrogen bonding appears to participate in the two OH groups of **6**, although it cannot be verified by ^{1}H NMR spectroscopy, since the flipping motion of the cyclohexene ring is not substantially disturbed by this hydrogen bonding, in contrast with **2**. The IR spectrum of **6** in dilute CS_2 solution, however, exhibits two bands at 3589 and 3559 cm^{-1}, which are located close to those in catechol, itself (3584 and 3559 cm^{-1}). The former band is reasonably assigned as free OH groups, while the latter is assigned as intramolecularly hydrogen-bonded OH groups.

The results in **2** and **6** obviously indicate that two OH groups located so close together form the intramolecular hydrogen bonding, which suppresses the interaction with water molecules, resulting in the formation of an unstable Langmuir film. The quality of [60]fullerene Langmuir films depends on the various factors, such as the shape of molecules, the intermolecular π–π interaction, or the balance between hydrophilicity and hydrophobicity, but the intramolecular hydrogen bonding apparently plays an important role.

Spreading Solvent Effect. Attempting to break the intramolecular hydrogen bonding between the OH groups as well as intermolecular hydrogen bonding and to prevent random aggregation, the *π–A* isotherms of bisphenols **1**—**3** were recorded by using a mixed solvent of benzene/EtOH (12 : 1) instead of benzene as a spreading solvent (Fig. 2c). Note that all films exhibited more reproducible isotherms.

e-Bisphenol **3** that failed to form intramolecular hydrogen bonding gave the same limiting area per molecule (84 Å^2/molecule) as in benzene. The addition of EtOH had no significant effect on the stability of the films. In contrast, the limiting area per molecule for *cis*-2-bisphenol **1** was enhanced in this mixed solvent compared to that in benzene (96 vs. 112 Å^2/molecule), though intramolecular hydrogen bonding was hardly detected, even in benzene. This result may reflect some kind of intermolecular interaction that expands the packing or the incorporation of ethanol molecules in the films. Although a higher limiting area per molecule was observed for **2** (60 vs. 69 Å^2/molecule), the value is much less than the theoretical value, suggesting that most of intramolecular hydrogen bonding still remains under this condition (see the above section).

Conclusion

We have been engaged in the systematic study aiming to determine the factors that govern the stability of LB films of fullerene bisphenols **1**—**3**. Their stability was found to be different from each other. The films of **1** and **3**, especially **1**, were of higher quality than those of **4** and **5**, indicating that the two OH groups efficiently pull the molecules toward the water surface and prevent random aggregation of the molecules. On the other hand, **2** formed rather unstable films in spite of possessing two OH groups. Thus, the steric factors of hydrophilic groups apparently influence the spreading behavior. The smaller stability in the films of **2** was ascribed to the intramolecular hydrogen bonding, which was clarified by ^{1}H NMR and IR spectroscopies. The contribution of intramolecular hydrogen bonding was also observed in monocatechol **6**, in which two OH groups are located close together.

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