

# Effect of Heat Treatment on Langmuir–Blodgett Films of a C60 Adduct

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A thermal dissociation method was employed to fabricate the Langmuir–Blodgett (LB) films of C60. A C60 adduct with an amphiphilic anthracene bearing a carboxylic group (C60–AN) was synthesized as the precursor molecule. C60–AN formed a monolayer at the air–water interface. The monolayers were transferred on solid substrates to form LB films using a horizontal lifting method. The LB films were subjected to heat treatments and their structural change was investigated by using UV–visible and IR spectroscopies. Most of the C60–AN molecules were dissociated to C60 and amphiphilic anthracenes at 100 °C, followed by the exclusion of the anthracene moiety from the LB films. The thermal dissociation proceeded more at higher temperatures. At 200 °C, the dissociation proceeded completely, although a certain form of hydrocarbon remained in the LB films. All the materials disappeared when the films were heated above 350 °C.

## 1. Introduction

Interesting physical properties of fullerene (C60)<sup>1</sup> and its covalently functionalized derivatives<sup>2,3</sup> have been revealed since the discovery of facile methods for the synthesis of C60 molecules in large quantities. One of the important issues is to construct ultrathin C60 films with well-defined structures. The Langmuir–Blodgett (LB) technique is one of the most promising methods to serve this purpose.<sup>4–7</sup> Actually, ultrathin films of C60 have been fabricated using the LB technique.<sup>8–26</sup> In the initial stage, efforts were made to obtain monolayers and LB films of C60. Some researchers reported that C60 forms a monolayer at the air–water interface.<sup>8,12,14,18,20,25</sup> Others noted multilayer formation of C60 at the air–water interface,<sup>9–11,13,17</sup> which can be deposited by the LB technique. In the second stage, C60 molecules were chemically modified to render the molecules amphiphilic. Since C60 is hydrophobic, hydrophilic substituents have been introduced to the C60 core.<sup>14–16,19,21–24,26</sup> These amphiphilic C60 molecules formed monolayers at the air–water interface, and the monolayers were transferred on various substrates as monolayer LB films. However, the introduction of substituents on the C60 core reduces the symmetry of the molecule and affects the electronic structure of C60 significantly.

Amphiphilic precursors have been employed for the fabrication of the LB films of polyimide<sup>22,27,28</sup> and poly(*p*-phenylenevinylene).<sup>29,30</sup> The LB films of the amphiphilic precursors have been treated thermally or chemically to yield the target LB films. The adducts of C60 with a variety of 1,3-dienes have been prepared by Diels–Alder reaction.<sup>2,3</sup> Among the C60 adducts, the cyclopentadiene and anthracene adducts undergo retro-Diels–Alder reaction by heating the solution even below 100 °C.<sup>31–33</sup> We chose a C60 adduct with an amphiphilic anthracene as the precursor molecule, since the anthracene can be eliminated easily by simple heat treatments. It has been reported that the C60 adduct decomposes by heating the precursor LB films in solution, but the decomposition has not been complete yet.<sup>23</sup>

In this paper, we report the preparation of C60 LB films by heating the C60 adduct under vacuum. We have synthesized C60 adduct with an amphiphilic anthracene, 6-(2-anthryl)-hexanoic acid. The amphiphilic C60 adduct formed a monolayer at the air–water interface, and the monolayer was transferred as LB films. The effect of heat treatments of the LB films was investigated using UV–visible and infrared absorption spectroscopies.

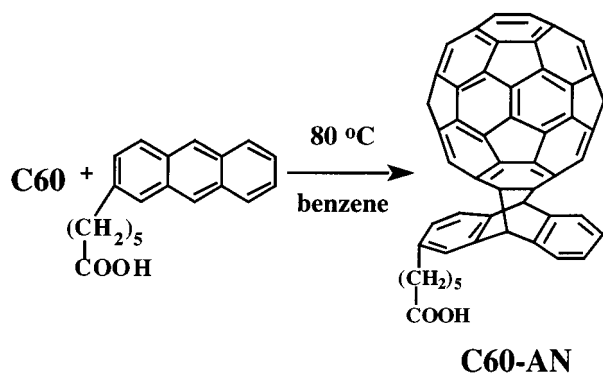
## 2. Experimental Section

**2.1. Materials.** The amphiphilic anthracene molecule, 6-(2-anthryl)hexanoic acid, was prepared in a similar way as described earlier.<sup>34</sup> The amphiphilic adduct was synthesized by Diels–Alder reaction of C60 and 6-(2-anthryl)hexanoic acid in benzene at 80 °C following the procedure reported in the literature (Figure 1).<sup>31,32</sup> The measurements of <sup>1</sup>H NMR, <sup>13</sup>C NMR, and IR spectra revealed that the purified product was a 1:1 adduct of C60 and the anthracene derivative (C60–AN). The yield was 25%.

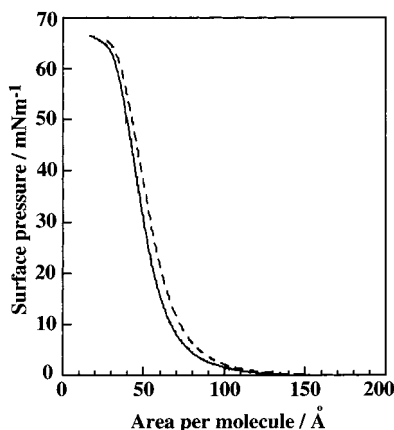
**2.2. LB Film Preparation.** A chloroform solution of C60–AN at the concentration of 0.1 mM was spread on pure water or a cadmium buffer solution containing  $4.0 \times 10^{-4}$  M of CdCl<sub>2</sub> and  $5.0 \times 10^{-5}$  M of KHCO<sub>3</sub>. The surface pressure–area ( $\pi$ –*A*) isotherms were measured at 17 °C using a Lauda film balance. The monolayers were transferred at 20 mN m<sup>-1</sup> by a horizontal lifting method on quartz plates for UV–visible absorption measurements, on CaF<sub>2</sub> plates for IR transmission measurements, and on vacuum-evaporated Au film on glass plates for IR reflection–absorption (RA) measurements. The dissociation reaction of C60–AN in the LB films was investigated by heating the films under a reduced pressure of 0.5 mmHg. After the heat treatments, the LB films were cooled to room temperature prior to the spectroscopic measurements.

**2.3. Characterization.** UV–visible absorption spectra of the LB films of the C60–AN adduct were measured on a Shimadzu UV-265FS spectrophotometer. Fourier transform transmission and RA spectra were measured on a Perkin-Elmer Spectrum 2000 FT-IR equipped with a liquid nitrogen-cooled MCT detector. For RA measurements, the incident angle was 80°.

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**Figure 1.** Synthesis of the C60 adduct with an amphiphilic anthracene, 6-(2-anthryl)hexanoic acid (C60-AN).



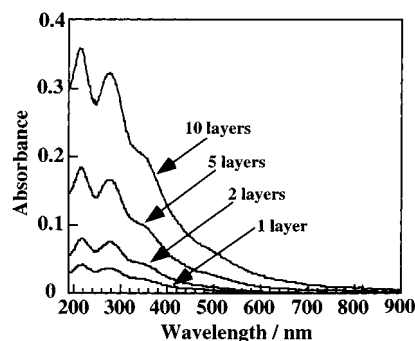
**Figure 2.** Surface pressure–area isotherms of the C60-AN adduct on pure water (solid line) and a cadmium buffer solution containing  $4.0 \times 10^{-4}$  M of  $\text{CdCl}_2$  and  $5.0 \times 10^{-5}$  M of  $\text{KHCO}_3$  (dashed line) at 17 °C.

All the IR spectra were recorded at a resolution of  $4 \text{ cm}^{-1}$  with the coaddition of 512 scans.

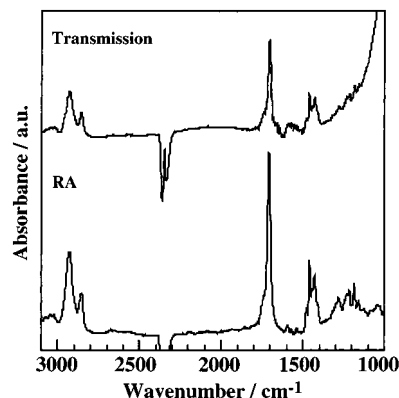
### 3. Results and Discussion

**3.1. Behavior at the Air–Water Interface.** Figure 2 shows the  $\pi$ -A isotherms of the C60-AN adduct on pure water and the cadmium buffer solution. Both isotherms showed an initial increase in surface pressure at  $150 \text{ Å}^2$ . The limiting area per molecule was 70 and  $80 \text{ Å}^2$  for the monolayer on pure water and the cadmium buffer solution, respectively. Assuming that the C60-AN molecules were hexagonally closed-packed on the water surface, the intermolecular distance on pure water and the cadmium buffer solution was 9.0 and  $9.6 \text{ Å}$ , respectively. These values are in good agreement with that of the monolayer of the amphiphilic C60 molecules ( $9.5 \text{ Å}$ ) reported previously.<sup>16</sup> This suggests that the molecular area is governed by the bulky C60 core.

**3.2. Structure of LB Films.** Figure 3 shows the UV–visible absorption spectra of the LB films of C60-AN with various layer numbers. The spectral shape was the same for all the LB films. Two absorption bands are observed at 214 and 267 nm with a shoulder around 340 nm. The intensity of each absorption band was almost proportional to the layer number, indicating that the C60-AN monolayers are transferred successfully on solid substrates. Compared with the absorption spectra of parent C60 LB films,<sup>9</sup> both absorption bands were broader, which is due to the reduction of symmetry caused by the introduction of a substituent on the C60 core. Similar features have been reported for the LB films of another amphiphilic C60.<sup>16</sup>



**Figure 3.** UV–visible absorption spectra of C60-AN LB films with various layer numbers.

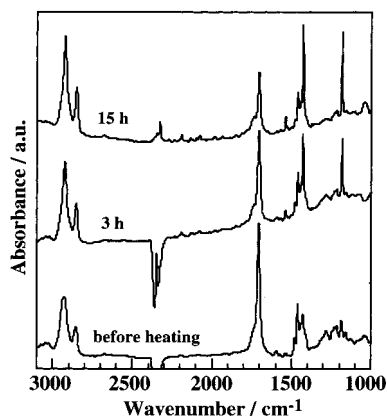


**Figure 4.** Infrared transmission and reflection–absorption (RA) spectra of 20-layer C60-AN LB films.

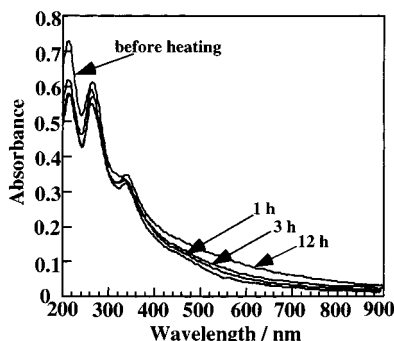
The LB films were further characterized using FT-IR spectroscopies. The transmission and RA spectra of the LB films are shown in Figure 4. The absorption bands in the  $3000\text{--}2800 \text{ cm}^{-1}$  region are assigned to the  $\text{CH}_2$  symmetric and asymmetric stretching modes, and those in  $3100\text{--}3000 \text{ cm}^{-1}$  region are assigned to the stretching vibration modes of aromatic C–H. The absorption bands in the  $1500\text{--}1400$  and  $1250\text{--}1100 \text{ cm}^{-1}$  regions are due to the C=C stretching vibration modes of C60 and the anthracene moiety of C60-AN, respectively. In addition, an intense absorption band is observed at  $1706 \text{ cm}^{-1}$ , which is assigned to the carbonyl stretching band of the carboxylic group. The position of this band is known to be sensitive to the state of the carboxylic acid. This band appears around  $1760\text{--}1740 \text{ cm}^{-1}$  for a monomeric carboxylic acid. The position of  $1706 \text{ cm}^{-1}$  in the present case corresponds to the well-known hydrogen-bonded dimer of carboxylic groups.<sup>35,36</sup> Similar absorption of carboxylic acid was also reported for another amphiphilic C60 in the LB films.<sup>16</sup> From these results, it is clear that the monolayer of the C60-AN adduct was transferred on solid substrates without decomposition.

In addition, the spectral profile was almost the same for both transmission and RA spectra (i.e., all the characteristic bands appeared in both spectra). This lack in out-of-plane anisotropy in the vibration modes of the hydrocarbon chain and the carboxylic group indicates that these groups are tilted with respect to the normal of the substrate. This result may be related to the finding that the molecular area obtained from the  $\pi$ -A isotherm was mainly governed by the bulky C60 core.

**3.3. Heat Treatment.** The LB films of C60-AN were subjected to heat treatments, and the structural changes were investigated using IR and UV–visible absorption spectroscopies. Figure 5 shows the change in the RA spectrum of the LB film of C60-AN when the film was heated at  $100 \text{ °C}$  for different treatment times under reduced pressure. Several changes were



**Figure 5.** Infrared reflection-absorption (RA) spectra of 20-layer C60-AN LB films after the heat treatment at 100 °C for the given time under reduced pressure.

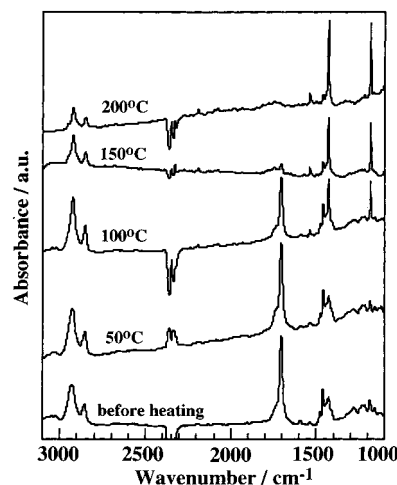


**Figure 6.** UV-visible absorption spectra of 20-layer C60-AN LB films after the heat treatment at 100 °C for the given time under reduced pressure.

observed: (1) a large increase in the intensities of 1429- and 1183-cm<sup>-1</sup> bands, (2) an increase in the intensities of the CH<sub>2</sub> stretching bands, and (3) a decrease in the intensity of the carbonyl stretching band. The large increase in the absorption of the C60 core (change 1) indicates the dissociation of the C60-AN adduct into the parent C60 and the anthracene derivative in the LB film; this is in accord with the report that a C60-anthracene adduct dissociated at 90 °C.<sup>31-33</sup> The behavior of the CH<sub>2</sub> stretching bands (change 2) can be explained by the orientational effect. The tilt angle of the hydrocarbon chain increased with heating because the intensity of the vertical component of the transition moment with respect to the film surface is enhanced in the RA spectrum. It is possible that a fraction of hydrocarbon may be excluded from the LB film, but this effect, if any, should be hidden by the orientational effect. The decrease in the intensity of the carbonyl stretching band (change 3) may be explained both by the exclusion of this group from the LB film and by the orientation effect.

The dissociation of the C60-AN adduct was also supported by the UV-visible absorption measurements. Figure 6 shows the change in the UV-visible absorption spectrum of the LB film of C60-AN when the film was heated at 100 °C for a given time under reduced pressure. The absorption bands shifted to longer wavelength and became sharper after heating. In particular, the absorption band around 340 nm was a shoulder before heating, while a more distinct band was seen at 340 nm after heating, which is characteristic of the parent C60 LB films.<sup>9</sup>

The important question is whether the anthracene carboxylic acid remained in the LB films after the dissociation of C60-AN. We conclude that the anthracene moiety is eliminated from the films after the dissociation due to the following reasons:



**Figure 7.** Infrared reflection-absorption (RA) spectra of 20-layer C60-AN LB films after the heat treatment at the given temperatures for 3 h under reduced pressure.

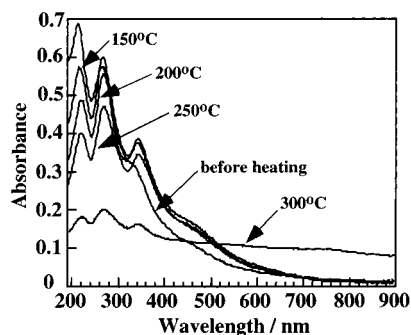
(1) The characteristic bands at 884 and 726 cm<sup>-1</sup> due to the anthracene moiety were not observed in the RA spectra of the LB films after the heat treatment. The intensities of these bands were comparable with that of the carbonyl stretching band at 1706 cm<sup>-1</sup> for the anthracene carboxylic acid in the form of powder. The absence of these bands indicates that the anthracene moiety, either as the anthracene carboxylic acid or as its decomposed form, does not exist in the LB films. This is further supported by the nearly complete disappearance of the absorption bands in the 3100-3000 cm<sup>-1</sup> region assigned to the stretching vibration modes of aromatic C-H.

(2) With increasing heating times, the intensities of the 220- and 270-nm bands in the UV-visible absorption spectrum of the LB film decreased, whereas the absorption around 340 nm increased. The decrease in the intensities of the former bands should be ascribed to the exclusion of the aromatic groups due to anthracene from the LB films. Further, a strong absorption band was observed at 236 nm in the absorption spectrum of the LB film of another amphiphilic anthracene carboxylic acid without the C60 core. The absence of this band indicates that the anthracene carboxylic acid molecule does not exist in the LB films.

Next, the LB films were subjected to heat treatments at various temperatures for 3 h. Figure 7 shows the variation of the RA spectrum of the LB film on changing the heating temperature. The intensities of the 1429- and 1183-cm<sup>-1</sup> bands increased above 100 °C, which is related to the dissociation of C60-AN. The dissociation reaction proceeded more at higher temperatures.

The behaviors of the CH<sub>2</sub> and the carbonyl stretching bands provided important information on the structure of the LB film. Up to 100 °C, the behaviors of these bands are explained by the inclination of the hydrocarbon chain of C60-AN and the exclusion of a small portion of the anthracene moiety. Above 100 °C, the intensities of these bands decreased rapidly. This means that the dissociated anthracene carboxylic acid was excluded from the LB films effectively. The spectrum at 200 °C suggests that the anthracene carboxylic acid was decomposed at this temperature and that a certain form of hydrocarbon remained in the LB films. All the absorption bands disappeared at 350 °C, indicating that all the materials have been evaporated.

The change in the UV-visible absorption spectrum of the C60-AN adduct LB film with an increase in the heating temperature is shown in Figure 8. Above 100 °C, the narrowing



**Figure 8.** UV-visible absorption spectra of 20-layer C60-AN LB films after the heat treatment at the given temperatures for 3 h under reduced pressure.

of the 220- and 265-nm bands occurred and the shoulder at 340 nm becomes clearer, which indicates that C60-AN dissociated to the parent C60. Above 200 °C, the intensities of the absorption bands become smaller, indicating the sublimation of parent C60. This is more conspicuous above 300 °C. At 350 °C, no bands were observed, indicating the evaporation of all the materials.

#### 4. Conclusions

We have demonstrated that the LB films of parent C60 can be fabricated by using the precursor method. Most of the C60-AN molecules are dissociated to the parent C60 and the amphiphilic anthracene at 100 °C, followed by the exclusion of the anthracene moiety from the LB films. The thermal dissociation proceeded more at higher heating temperatures. At 200 °C, the thermal dissociation proceeded completely, although a certain form of hydrocarbon remained in the LB films. All the materials disappeared when the films were heated above 350 °C. This method provides a new way of fabricating the LB films of parent C60. With an appropriate choice of the C60 adduct, the heating temperature for the thermal conversion can be lowered.

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