

Formation and structural characteristics of Langmuir–Blodgett films of C_{60} and C_{70}

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Abstract

The fullerenes, C_{60} and C_{70} , were prepared with high purity by high performance liquid chromatography. These materials could form condensed layers at the air–water interface. Under appropriate experimental conditions, we have fabricated four species of films, consisting of C_{60} , C_{70} and their mixtures with arachidic acid, onto various substrates by the Langmuir–Blodgett technique. The structural characteristics of these films were studied by UV–visible and Fourier transform IR spectroscopies, scanning tunneling microscopy, transmission electron microscopy and low-angle X-ray diffraction measurements.

1. Introduction

The discovery of C_{60} and C_{70} clusters has received a considerable amount of attention due to their attractive prospects for fundamental research and future applications. After the successful efficient synthesis of macroscopic quantities of the fullerenes, studies on the structure and properties of these species have appeared in the international community [1]. Moreover, the observation of superconducting transitions for alkali-metal doped fullerenes has accelerated the investigations in this field [2, 3].

Although fullerene is not typically used to form Langmuir–Blodgett (LB) films, according to the literature a few hydrophobic sphere-like molecules can also form rigid films at the air–water interface and can be transferred to solid supports by the LB method [4, 5]. Recently, there has been growing interest in a study based on C_{60} LB films [6–8], which will be precursors of the molecular systems using the functional properties of the fullerenes. We have described scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) observations for pure C_{60} LB films [9, 10]. In this paper, we report some new results concerning the formation and structural characterization of four LB films composed of pure C_{60} , C_{70} , and their mixtures with arachidic acid (AA).

2. Experimental details

The preparation of C_{60} and C_{70} used in this work is similar to the Kratschmer–Huffman method [11]. After separation by high performance liquid chromatography

(HPLC), the purity of C_{60} and C_{70} was confirmed to be 99.9% and 99.1% respectively.

Surface pressure–area isotherm measurements and deposition experiments were carried out on a full automatic KSV instrument (Finland) at 18–19 °C. The fullerenes or their mixtures with AA (molar ratio 1:1) dissolved in benzene (4×10^{-4} – 1×10^{-3} M) were spread onto double-distilled water, or 1×10^{-2} M KCl solution, or onto an aqueous subphase containing 5×10^{-4} M $CdCl_2$. After complete evaporation of the solvent, the floating layers on the subphase were compressed by a mobile Teflon barrier at a speed of 20 mm min^{-1} and were then transferred to various substrates at a constant pressure (18 – 20 mN m^{-1}) using the vertical dipping or the horizontal lifting method. The choice of experimental conditions depends on the sample used and the requirements for the measurements.

UV–visible and Fourier transform (FT) IR spectra of the LB films were recorded on an HP 8451A spectrometer and a Bruker IFS 113V spectrometer. The STM images of C_{60} and C_{70} LB films were obtained on an Au (100) surface using a CSTM-9000 scanning tunneling microscope in the constant current mode. The films deposited on electron microscope copper grids were examined in an Hitachi H-800 electron microscope at an operating voltage of 100 kV. Low angle X-ray diffraction (XRD) measurement was performed on a D/max-rB X-ray diffractometer using $Cu \text{ K}\alpha$ radiation.

3. Results and discussion

Figure 1((a)–(c)) shows the surface pressure–area isotherms of pure C_{60} and C_{70} on different subphases at

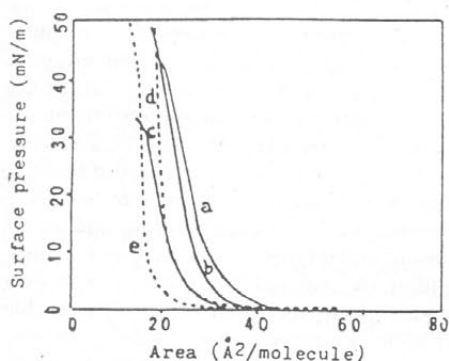


Fig. 1. Surface pressure-area isotherms of (a) C_{60} on pure water, (b) C_{60} on 1×10^{-2} M KCl solution, (c) C_{70} on pure water, (d) C_{60} mixed with AA (1:1) on 5×10^{-4} M $CdCl_2$ solution, (e) C_{70} mixed with AA (1:1) on 5×10^{-4} M $CdCl_2$ solution at 19 °C.

19 °C. Although the fullerenes are not self-assembling amphiphilic molecules, it can be seen that insoluble condensed films of C_{60} and C_{70} were formed at the air-water interface and did not collapse until 30–40 $mN m^{-1}$. The limiting molecular area of C_{60} is from about 28.5 to 31.0 \AA^2 , depending on the subphase used. Neither the dilution of the C_{60} solution nor the slowing down of the compression by a factor of 10 was found to produce an isotherm with an area per molecule larger than 34.7 \AA^2 . The limiting molecular area of C_{70} is around 25 \AA^2 . All these values obtained from the isotherms of the fullerenes are obviously smaller than the ideal areas per molecule of C_{60} and C_{70} , calculated from the sum of XRD data plus the van der Waals diameter of carbon [12, 13]. This suggests that the floating films of pure C_{60} or C_{70} are more than a single monolayer in thickness. In most cases, C_{60} and C_{70} molecules exist in the form of bilayers or multilayers at the air-water interface. Figure 1((d), (e)) shows the surface pressure-area isotherms of the fullerenes mixed with AA (1:1) on a 5×10^{-4} M $CdCl_2$ aqueous solution at 19 °C. All mixed systems exhibit steep isotherms. The average limiting molecular area is 20.0 \AA^2 for mixed films of C_{60} with AA and 17.0 \AA^2 for mixed films of C_{70} with AA respectively. Taking the area of AA (20 \AA^2) into account, this implies that most of the fullerene molecules were squeezed out of the water surface into the AA film at high pressure as described by Obeng and Bard [6].

Because of limitations of the molecular structure features, it is difficult to fabricate high quality LB films of pure fullerenes by the vertical dipping method. Particularly when pure water was used as subphase, the transfer of pure C_{60} was poor. Under appropriate conditions the transfer ratio of pure C_{60} or C_{70} was 0.4–0.6 through Z-type deposition. However, the mixed films of the fullerenes with AA could easily be transferred onto

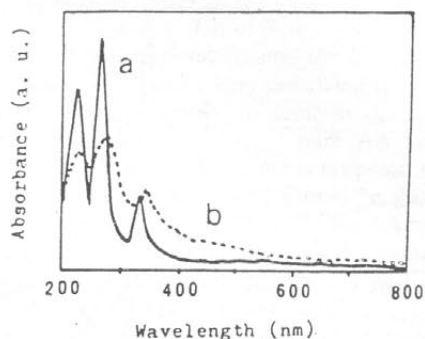


Fig. 2. UV-visible absorption spectra of C_{60} : (a) in hexane; (b) in the LB films.

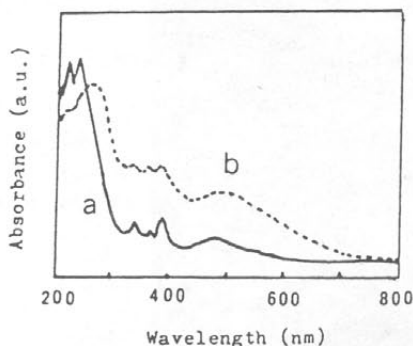


Fig. 3. UV-visible absorption spectra of C_{70} : (a) in hexane; (b) in the LB films.

solid substrates with a deposition ratio of 1 for C_{60}/AA and 0.8 for C_{70}/AA , forming Y-type films.

The UV-visible absorption spectra of pure C_{60} and C_{70} respectively in the LB films and in hexane solutions [14] are shown in Figs. 2 and 3. The spectra of the fullerenes' LB films show a slight broadening of the bands and a red-shift of the absorption peaks compared with those of the corresponding solutions. This is probably due to the different molecular environment in each state and the interaction of the molecules in the LB films.

The FTIR absorption spectrum of C_{60} LB films has been measured [15]. In this spectrum, two bands at 1182 and 1428 cm^{-1} belonging to C_{60} appeared. Here we obtained the FTIR spectrum of pure C_{70} LB films on a CaF_2 substrate, as shown in Fig. 4. A strong peak at 1431 cm^{-1} , characteristic of C_{70} solid, was observed. It was confirmed that the transferred films consisted of C_{70} molecules.

The STM images of pure C_{60} LB film drawn from 1×10^{-2} M KCl subphase on an Au (100) surface show that different structural regions exist. In a small area, such as the middle region of Fig. 5(a), several rows of

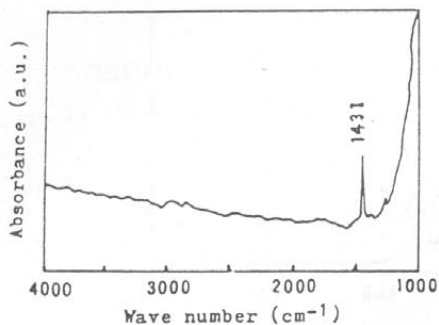
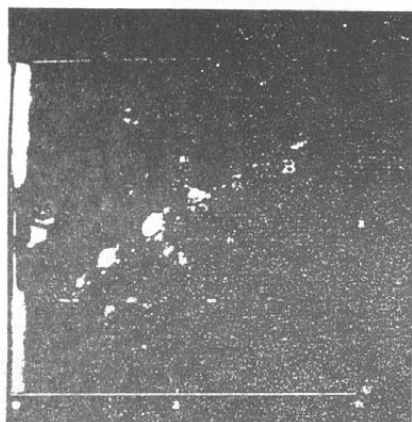
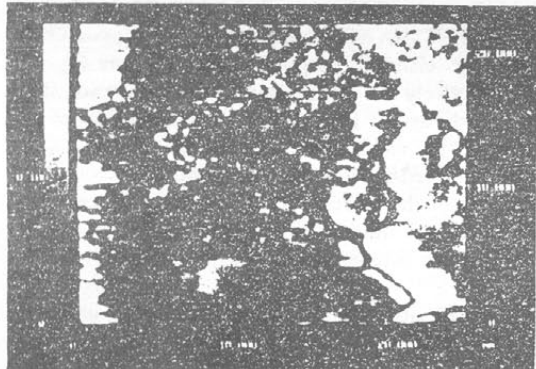


Fig. 4. FTIR spectrum of a 24-layer LB film of C_{70} deposited on a CaF_2 substrate.



(a)



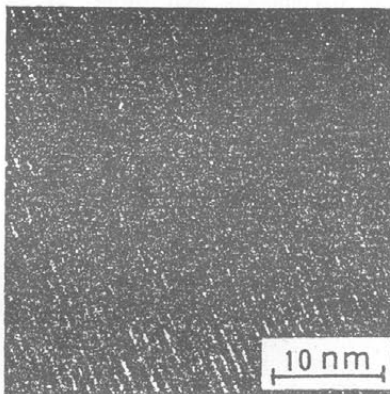
(b)

Fig. 5. (a) STM image of C_{60} LB film on Au (100) surface (scanning area $4.78 \times 4.84 \text{ nm}^2$); (b) STM image of C_{70} LB film on Au (100) surface (scanning area $24.9 \times 21.8 \text{ nm}^2$).

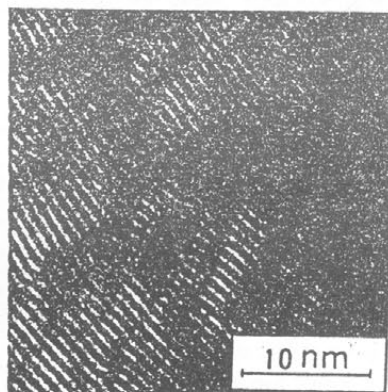
individual, sphere-like C_{60} molecules in ordered arrays can be seen, but the STM image obtained from other areas of the LB film shows aggregation of close-packed C_{60} molecules [9]. Figure 5(b) is the STM image of a

transferred film of pure C_{70} . On scanning the whole area of the substrate surface, only disorganized granular structural features were observed, and ordered arrays of C_{70} molecules such as those shown in Fig. 5(a) for C_{60} were not found under our experimental conditions.

The TEM results of the films' growth on Cu electron microscope grids by horizontal lifting revealed that C_{60} and C_{70} films have polydomain structures including regular lattice fringes, defects, dislocations, and amorphous-like disordered arrangements. In more crystalline parts of the films, the spacings of the lattice fringes were measured directly from the images to be 0.86 nm for C_{60} LB film (Fig. 6(a)) and 0.80 nm for C_{70} LB film (Fig. 6(b)). These regions of the film were found to have hexagonal and distorted hexagonal structures. However, it should be noted that the average size of crystalline regions in the C_{70} LB film is obviously smaller than that in C_{60} LB film, and distorted fringes and stacking faults can often be found in the C_{70} LB



(a)



(b)

Fig. 6. (a) High resolution electron micrograph of lattice image in C_{60} LB film; (b) High resolution electron micrograph of C_{70} LB film.

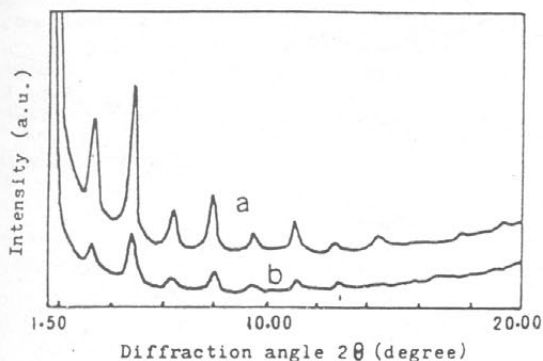


Fig. 7. X-ray diffraction patterns of (a) 40-layer LB films of C_{60} mixed with AA (1:1), (b) 34-layer LB films of C_{70} mixed with AA (1:1).

film. The microstructural differences between C_{60} and C_{70} LB films may originate from their different molecular natures. Compared with sphere-like C_{60} , the ellipsoid-shaped C_{70} molecule is anisotropic and has little spatial symmetry; this is liable to cause a lack of complete molecular orientations when the C_{70} floating layer is compressed and transferred onto a substrate.

XRD in a low angle range was employed to detect the periodic structure of LB films. No characteristic peaks were found for pure C_{60} and C_{70} multilayers. Figure 7 shows the XRD patterns obtained from the multilayer films fabricated from mixed systems of C_{60} and C_{70} with AA. In all cases, several Bragg reflections were observed; this demonstrates the formation of a well-defined layered structure for both mixed films. It is known that the diameter of C_{60} molecule is about 10 Å. If domains of C_{60} are not confined within a multilayer matrix created by highly ordered AA molecules, the

thickness per layer of the mixed films should be apparently larger than that of pure AA films. But, according to the experimental results, the bilayer d -spacings of both mixed systems were calculated to be about 55.7 Å. This value is almost the same as the bilayer distance measured for LB films of pure AA (about 56.2 Å). Therefore, a possible model is proposed in which most of the fullerene molecules should be dispersed among the hydrophobic alkyl chains of the AA molecules. This hypothesis was supported by STM observations. Figure 8 is an STM image of the LB film of C_{60} mixed with AA (1:1). Compared to the pure C_{60} LB film, the mixed film had a flatter surface, with some small bumps that are faintly seen. This also means that most of the C_{60} molecules were concealed in the AA film and located near the hydrocarbon tails of AA molecules.

4. Conclusions

We have fabricated four films of fullerenes and their mixtures with AA by the LB method, and evaluated the structural features of these films. It is difficult to get uniform and excellent multilayers of pure fullerenes (C_{60} and C_{70}) on a large scale, whereas the mixed films of the fullerenes with AA have a well-defined layered structure. In order to provide functionalized films for future applications, we intend to modify C_{60} molecules by chemical methods so as to obtain a new material that possesses both the special properties of fullerenes and good film-forming ability. These further efforts are in progress.

Acknowledgments

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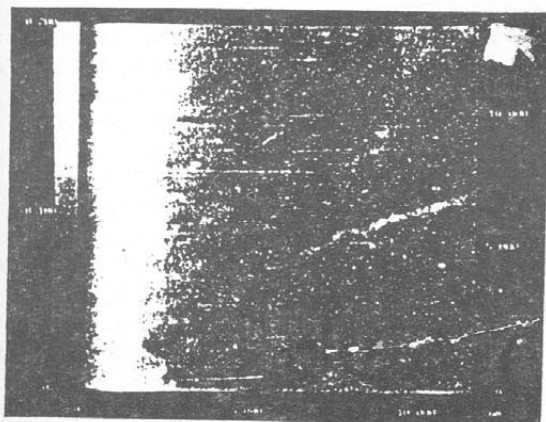


Fig. 8. STM image of LB film of C_{60} mixed with AA (1:1) on Au (100) surface (scanning area $12.4 \times 13.3 \text{ nm}^2$).

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