Scanning tunneling microscope studies of Langmuir-Blodgett films

of fullerenes

J. Guo[+], Y. Xu, Y. Li, Y. Yao, D. Zhu and C. Bai

Institute of Chemistry, Chinese Academy of Sciences,

Beijing   100080, P. R. China

Abstract

Four species of films of C_{60} and C_{70} formed by Langmuir-Blodgett (LB) technique were studied with a scanning tunneling microscope (STM) on a Au(100) surface in air and at room temperature. The STM images of pure C_{60} film showed a small area of ordered C_{60} arrays and the close-packed aggregation of C_{60} molecules. The monolayer of C_{60} mixed (1:1) with arachidic acid (AA) has a flat surface formed mainly by the hydrophobic groups of AA molecules and a part of C_{60} molecules should be present near the hydrocarbon tails of AA molecules under the surface. The surface topography of the transferred film of pure C_{70} showed disorganized granular features, while the STM images of a single-layered sample of C_{70} mixed (1:1) with AA consisted of three sections, i.e. film areas of pure C_{70}, pure AA and the mixture of the two materials. Some structural parameters and further information were provided.

+ Current address: Department of Chemistry, The University of New Mexico, Albuquerque,

NM 87131, USA

* To whom correspondence should be addressed

I Introduction

Owing to the recently developed methodology for the macroscale syntheses of fullerenes (C_{60} and C_{70}), the progress has led to a number of studies of their physical and chemical properties as well as the interest in the possible applications of these molecules [1].

The Langmuir-Blodgett (LB) technique is one of the most powerful methods to construct ordered thin films whose structure are controlled at the molecular level. At present this method is not only confined within the conventional amphiphilic molecules, in some cases, a few hydrophobic, sphere-like molecules such as a kind of metallorganic molecule $Ru(dp-bpy)_3^{2+}$ can also form stable Langmuir film at the air/aqueous subphase interface and can be transferred to solid supports by the LB method [2]. In other cases, some functional molecules which do not have film-forming ability at the air-water interface can be incorporated into the LB films by mixing with film-forming materials. For example, the LB films with metallic conductivity were constructed using a mixture of a metal-dmit complex and arachidic acid [3].

As mentioned above, although fullerenes (C_{60} and C_{70}) are not self-assembling amphiphilic molecules of the type usually used to form LB films, however, since the initial investigation of Langmuir films of C_{60} was performed by Obeng and Bard [4], formation and surface structure of LB films composed of pure C_{60} or C_{60} mixed with other organic molecules have been studied [5,6]. We have reported some results of pure C_{60} LB film

[7,8]. In this paper we reveal again our direct observation of the surface topographies of four LB films which consisted of pure C_{60}, pure C_{70} and their mixtures with arachidic acid, respectively, on a single crystal surface of gold using a scanning tunneling microscope.

II Experiment

The fullerenes, C_{60} and C_{70} were obtained from carbon soots as described in the literature [9,10]. We set up our own installation to produce the samples and the production technique is similar to the widely used Kratschmer-Huffman method [11]. After obtaining the carbon soots, a HPLC was employed to separate the solid residue and the fractions of C_{60} and C_{70} were found to have satisfactory purity of 99.90% and 99.10%, respectively. The measurement of pressure-area isotherms (Π-A curve) and deposition experiments were totally performed on a computer controlled KSV 5000 instrument (Finland).

The processes of film formation of the four samples were almost the same. Firstly, the purified sample was dissolved in benzene (G.R.) using ultrasonic wave to form a solution with a concentration of $0.7 \sim 1.0$ mM. Then approximately 200 μl of the solution was carefully spread onto different subphases in a LB trough (area 707 cm^2) at room temperature (around 19 °C). After evaporation of the solvent, the floating layer at the air-water interface was compressed by a mobile teflon barrier at a speed of 20 mm/min, and the surface pressure was simultaneously monitored by a Wilhelmy balance. In the meantime the surface pressure-area isotherm of the sample was recorded on the computer terminal.

The Langmuir film thus formed was maintained at a surface pressure of 15 ~ 20 mN/m for about 1 hr, after which stability was reached. The film was then transferred onto a single crystal surface of Au(100) by vertical dipping at a speed of 1 ~ 2 mm/min, with Z-type deposition formed finally.

We used a CSTM-9000 scanning tunneling microscope developed by our institute to image the surface topographies of the film on gold substrate in the constant-current mode. The measurement was performed under ambient temperature and air pressure. The reference value of the tunneling current was set to be -0.7 nA or so, and the bias voltage was typically from -20 mV to +35 mV.

After enough STM images were obtained, we used several softwares for image process to select good-qualified topographic images, then calculated some structural parameters with the aid of standard graphite images. The cross-line technique in our computer program was employed to reveal some structural information in the STM images.

III Results and discussion

The surface pressure-area isotherms (II-A curve) of the four samples are shown in Fig.1. In each curve, it can be judged that a stable Langmuir film was formed at the air-water interface and did not collapse until a certain value of pressure. Table 1 shows all experimental data of the four samples during the film formation processes, including subphase, transfer ratio and the limiting molecular area.
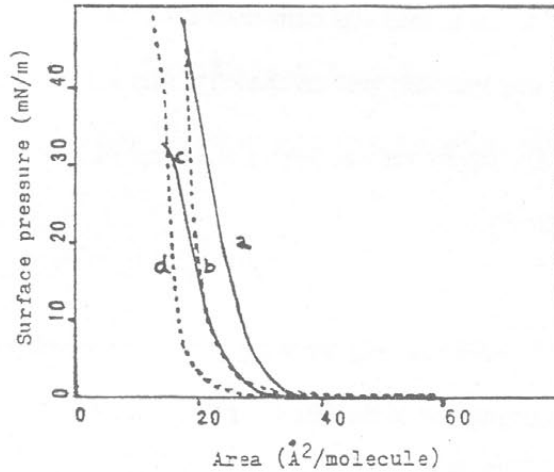
Fig.1 Surface pressure-area isotherms of (a) C_{60} on 1×10^{-2} M KCl solution, (b) C_{60} mixed with AA (1:1) on 5×10^{-4} M $CdCl_2$ solution,   (c) C_{70} on pure water and (d) C_{70} mixed with AA (1:1) on 5×10^{-4} M $CdCl_2$ solution at 19 °C.

TABLE 1 Experimental data for film formation

Sample	C_{60}	C_{70}	C_{60}+AA	C_{70}+AA
Subphase	0.01M KCl	dist. water	5×10^{-4}M $CdCl_2$	5×10^{-4}M$CdCl_2$
Transfer ratio	0.4~0.5	0.5~0.6	1.1	0.8
Molecular area(nm^2)	0.285	0.25	0.20	0.17

Two STM images of C_{60} LB film in different areas on the Au(100) surface are shown in Fig.2 and Fig.3 where 0.01M KCl solution was used as the subphase, with the transfer ratio twice as much as that of pure water subphase. In the middle area of Fig.2, two rows of C_{60} molecules in ordered arrays are shown. In the upper-right rectangle a cross line is

drawn along the direction of line AB in the figure. The five peaks of the cross line indicate five C_{60} molecules existing in the cross section along line AB, consistent with the directly perceived result in Fig.2. The statistically calculated results of the molecular diameters in Fig.2 gave different values in two directions when a standard STM image of the cleaved graphite with a scanning area of 4x4 nm^2 was used for geometric calibration. The diameter along the AB direction is 0.635 ± 0.013 nm long, while the other one along the perpendicular direction is 0.572 ± 0.025 nm. The average area occupied by a single molecule on the image is calculated to be 0.285 nm^2, which accords with the area value obtained from the II-A curve very well. The limiting molecular area in our II-A curve was in agreement with the result of Williams et al. during their film compression process [6].
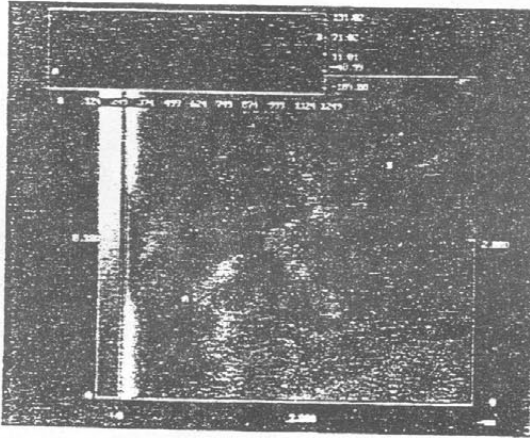

Fig.2 STM image of the C_{60} LB film on an Au(100) surface
(Tunneling current 0.84 nA, Sample bias 29 mV, scanning area   4.78x4.84 nm^2)

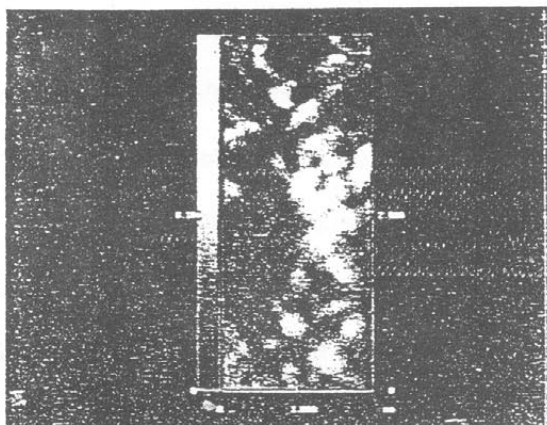Fig.3 STM image of another area of the C_{60} LB film, showing   molecular aggregation of close-packed C_{60}

(Tunneling current 0.84 nA, Sample bias 29 mV, scanning area   1.70x4.27 nm^2)

Fig.3 is another image obtained simultaneously with Fig.2, which shows the aggregation of close-packed C_{60} molecules. This image indicates that spherical hydrophobic molecules of C_{60} are easy to aggregate when spread and compressed to form the Langmuir film. The speculation that there exist different structural areas in the C_{60} LB film was proved by a transmission electron microscope observation of Long et al.[7].
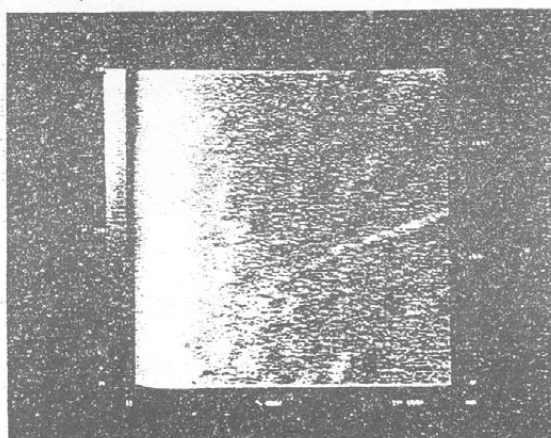

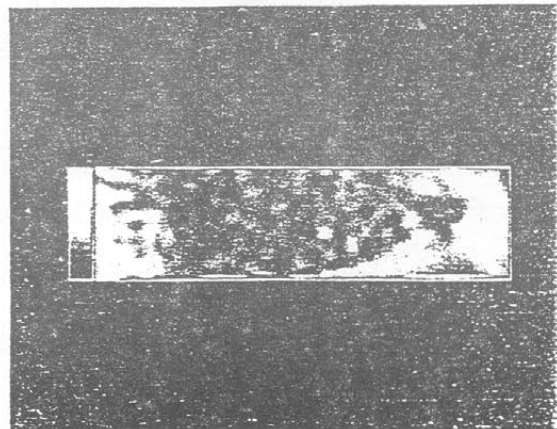Fig.4 STM image of the LB film of C_{60} mixed with AA (1:1)
(Tunneling current 0.86 nA, Sample bias 25 mV, scanning area   12.4x13.3 nm^2)

When the mixture of C_{60} and arachidic acid (molecular ratio 1:1) was used to form a monolayer, the transfer ratio could be much higher. Fig.4 is a typical image obtained from this type of LB film on the gold substrate. Compared with the pure C_{60} LB film, the mixed film had a flatter surface with some small bumps that are faintly seen. Taking the limiting molecular areas of pure C_{60}, pure AA and the mixture into account, we consider that C_{60} molecules should be squeezed into the AA film. From the perceived result of Fig.4, it can be induced that most of C_{60} molecules were concealed among the hydrophobic alkyl chains of the AA molecules and located near the hydrocarbon tails of AA. This conclusion was supported by a latest low angle X-ray diffraction experiment of the same sample [12].
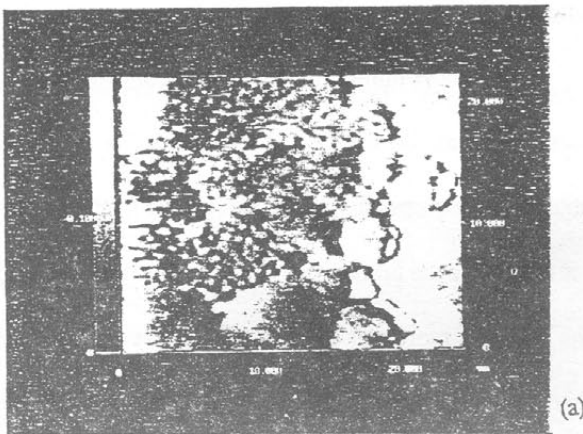
(a)

Fig.5 (a) STM image of the C_{70} transferred film on an Au(100) surface (Tunneling current 0.86 nA, Sample bias -15 mV, scanning area 24.9×21.8 nm^2) (b) An enlarged area selected from the lower part of (a)

(b)

The STM images of the transferred film of C_{70} or C_{70} mixed with AA (1:1) revealed different structural features from those of C_{60} or C_{60} mixed with AA (1:1). Fig.5 (a) is a STM image of pure C_{70} film. The upper area of this image shows irregularly granular surface topography. Compared to the flat gold surface in the lower area, it can be judged that the upper area just reflects the surface structure of C_{70} transferred film. Through the scanning of the whole area of the substrate surface, only surface topographies as shown in Fig.5 (a) were observed, and ordered arrays of C_{70} molecules as that of Fig.2 were not found under the experimental conditions as described above. This phenomena can be explained as follows: The ellipsoid-shaped C_{70} molecule is anisotropic. When the floating layer was compressed and transferred onto a substrate, the surface topography of the film will show these disorganized granular structural features due to the incompatibility of molecular orientations and arrangements. Whereas the situation of C_{60} is just the opposite. Fig.5(b) is an enlarged image selected from the middle area of Fig.5(a), and in the lower-right position an ellipse-shaped speck with even brightness is clearly shown, indicating that this is a lie-down C_{70} molecule. The long and short axes of this molecule were calculated to be 0.84 nm and 0.49 nm, giving the molecular area of 0.323 nm^2, which is somewhat larger than the limiting molecular area (0.25 nm^2) obtained from the II-A curve. It is comprehensible that a lie-down molecule occupies the largest area.

The STM image of a single-layered sample of C_{70} mixed (1:1) with AA showed some "separation" structural features. Fig.6 is a STM image obtained from one local area of the mixed film, showing disorganized, granular surface features. Thus it is believable that this area was occupied by pure C_{70} molecules. The average long diameter of these small particles was calculated to be ~ 0.9 nm, which approaches the longer one in Fig.5(b) well.

The STM images of the transferred film of C_{70} or C_{70} mixed with AA (1:1) revealed different structural features from those of C_{60} or C_{60} mixed with AA (1:1). Fig.5 (a) is a STM image of pure C_{70} film. The upper area of this image shows irregularly granular surface topography. Compared to the flat gold surface in the lower area, it can be judged that the upper area just reflects the surface structure of C_{70} transferred film. Through the scanning of the whole area of the substrate surface, only surface topographies as shown in Fig.5 (a) were observed, and ordered arrays of C_{70} molecules as that of Fig.2 were not found under the experimental conditions as described above. This phenomena can be explained as follows: The ellipsoid-shaped C_{70} molecule is anisotropic. When the floating layer was compressed and transferred onto a substrate, the surface topography of the film will show these disorganized granular structural features due to the incompatibility of molecular orientations and arrangements. Whereas the situation of C_{60} is just the opposite. Fig.5(b) is an enlarged image selected from the middle area of Fig.5(a), and in the lower-right position an ellipse-shaped speck with even brightness is clearly shown, indicating that this is a lie-down C_{70} molecule. The long and short axes of this molecule were calculated to be 0.84 nm and 0.49 nm, giving the molecular area of 0.323 nm^2, which is somewhat larger than the limiting molecular area (0.25 nm^2) obtained from the II-A curve. It is comprehensible that a lie-down molecule occupies the largest area.

The STM image of a single-layered sample of C_{70} mixed (1:1) with AA showed some "separation" structural features. Fig.6 is a STM image obtained from one local area of the mixed film, showing disorganized, granular surface features. Thus it is believable that this area was occupied by pure C_{70} molecules. The average long diameter of these small particles was calculated to be ~ 0.9 nm, which approaches the longer one in Fig.5(b) well.

Fig. 7 is another STM image obtained simultaneously with Fig. 6. An ellipse-shaped big speck is clearly shown, together with a small round-like one. Compared with another result observed by STM . [13], this image can be considered as the surface topography of the hydrophobic group aggregations of AA molecules. Detailed structural features were not resolved due to large scanning area. Since there existed some areas of pure C_{70} molecules the areas composed of AA must also exist in the meantime, because the mixed molar ratio of C_{70} and AA was 1:1.
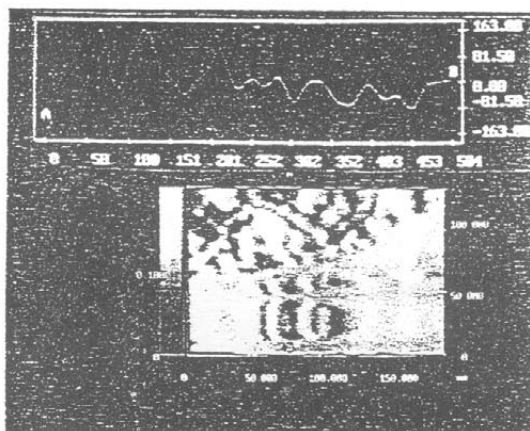

Fig.8 STM image of the mixed film of C_{70} and AA (1:1) obtained in a large scanning area (Tunneling current 0.87 nA, Sample bias 33 mV, scanning area   192x132 nm^2)

On the basis of the above results, Fig.8 can be explained more easily. This figure is a STM image of the mixed film of C_{70} and AA obtained in a much larger scanning area. In the lower area of the image, several ellipse-shaped specks should be the topographies of the film area of pure AA, and their long and short axes were 41.0 nm and 23.0 nm or so according to calculation. In the upper area, some stacking structural features of large size particles are resolvablely shown. From the point of view of the cross line along "AB" direction, the perpendicular height of this area is apprantly higher than that of the AA film area, and it can be concluded that the upper area is just the surface topography of the mixed film of C_{70} and AA. Those disorganized big particles should be the aggregations of C_{70} molecules, sitting closely on the top of the hydrophobic groups of AA molecules. In such a large scanning area of 202x157 nm^2, these granular structural features can only be the reflection of the molecular aggregations of C_{70} and the granular size of these aggregations varies from 10 nm to 20 nm. These structural features existed mainly in many areas of the mixed film.

IV Conclusions

In summary, according to our STM investigations, on the surface of C_{60} LB-film there existed small monolayer area of ordered C_{60} arrays, as well as close-packed aggregations of C_{60} molecules. The surface topography of C_{70} transferred film showed disorganized granular structural features.

In the LB film of C_{60} mixed (1:1) with AA, most of C_{60} molecules were squeezed into the AA film and the surface topography only reflected the flat surface of the mixed film with some small bumps formed by groups of C_{60} molecules sitting near the ends of AA hydrophobic tails. The single-layered sample of C_{70} mixed (1:1) with AA showed some "separation" features. As observed from STM images, the film areas of pure AA and pure C_{70} coexisted independently, while in the mixed film area of the two species, C_{70} molecules formed many molecular aggregations of slightly different sizes and sit closely on the top of the hydrophobic tails of AA molecules.

ACKNOWLEDGEMENT

REFERENCES

1. H. Kroto et al.: Chem. Rev. 91, 1213 (1991)

2. C. Miller et al.: Langmuir 7, 2781 (1991)

3. T. Nakamura et al.: Chem. Lett. 367,   (1989)

4. Y. Obeng, A. Bard: J. Am. Chem. Soc. 113, 6279 (1991)

5. T. Nakamura et al.: Langmuir 8, 4 (1992)

6. G. Williams et al.: Thin Solid Films 209, 150 (1992)

7. C. Long et al.: Solid State Communications 82(5), 381 (1992)

8. J. Guo et al.: Chem. Phys. Lett. 195, 625 (1992)

9. W. Kratschmer et al.: Chem. Phys. Lett. 170, 167 (1990)

10. W. Kratschmer et al.: Nature 347, 354 (1990)

11. Y. Li et al.: Chin. Sci. Bull. 37(19), 1823 (1992)

12. Y. Xu et al.: Synthetic Metals, to be published, 1993

13. W. Mizutani et al.: Japan. J. Appl. Phys. Part I 27(10), 1803 (1988)