Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Study on LB Films of Novel Fullerene Derivatives

Yu Xu [a], Changcheng Zhu [a], Chengfen Long [a], Yunqi Liu [a], Daoben Zhu [a], Xinshen Zhao [b] & Anchi Yu [b]

[a] Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, P. R. China

[b] Department of Chemistry, Peking University, Beijing, 100871, P. R. China

Version of record first published: 24 Sep 2006

To cite this article: Yu Xu, Changcheng Zhu, Chengfen Long, Yunqi Liu, Daoben Zhu, Xinshen Zhao & Anchi Yu (1997): Study on LB Films of Novel Fullerene Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 294:1, 7-10

To link to this article: http://dx.doi.org/10.1080/10587259708032235

Mol. Cryst. Liq. Cryst., 1997, Vol. 294, pp. 7–10
Reprints available directly from the publisher
Photocopying permitted by license only

STUDY ON LB FILMS OF NOVEL FULLERENE DERIVATIVES

YU XU, CHANGCHENG ZHU, CHENGFEN LONG, YUNQI LIU,
DAOBEN ZHU, XINSHEN ZHAO† and ANCHI YU†
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P.R. China
†Department of Chemistry, Peking University, Beijing 100871, P.R. China

Abstract: The LB films of two C_{60} derivatives, ethoxycarbonyldecylenefullerene and bis(ethoxycarbonyldecylene)fullerene, were prepared and characterized. The second harmonic generation from these LB films were measured.

INTRODUCTION

Recently, the fullerene Langmuir-Blodgett (LB) films have attracted much attention due to their fascinating properties in the ordered thin films for future application. However, it is difficult to fabricate high quality LB films of pure C_{60} because of its hydrophobic spherical structure. To solve this problem, an effective method is to render C_{60} molecule amphiphilic by suitable modification, aiming at obtaining a new compound which possesses both the specialities of C_{60} and good film-forming ability. In this field, scientists have made much effort and achieved encouraging progress.[1] We have reported several amphiphilic C_{60} derivatives containing -CN, -NH- and -OH groups respectively.[2] This paper describes the first investigation of the LB films of two novel C_{60} derivatives, ethoxycarbonyldecylenefullerene (ECDF) and bis(ethoxycarbonyl-decylene)fullerene (BECDF), as well as their second harmonic generation (SHG) response.

EXPERIMENTAL

The preparation of ECDF and BECDF will be reported elsewhere.[3] Their structures are as shown in Figure 1

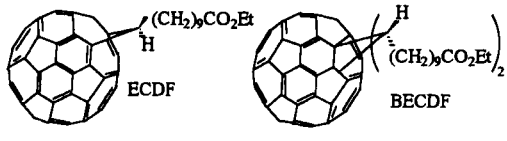

FIGURE 1 Chemical structures of ECDF and BECDF.

Surface pressure-area isotherm measurements and deposition experiments were carried out on a KSV 5000 instrument at 20±1°C. A known amount of the compounds dissolved in chloroform (~0.6 mM) was spread onto double-distilled water. The floating layers on the subphase were compressed with a speed of 20 mm/min and transferred to various substrates by the vertical dipping or horizontal lifting method at a constant pressure of 20-24 mN/m.

UV-vis spectra of the LB films were recorded on an HP 8451A spectrometer. Transmission electron microscopy (TEM) imaging was performed using a Hitachi H-800 transmission electron microscope. Atomic force microscopy (AFM) images of the LB films were obtained on a mica surface with a Nanoscope III (Digital Instruments Inc.). SHG was measured in transmission with a Y-cut quartz plate as reference and with a Nd:YAG laser beam (λ= 1064 nm) at an angle of 45° to the film surface.

RESULTS AND DISCUSSION

Figure 2 shows the surface pressure-area isotherms of ECDF and BECDF. The limiting molecular area of ECDF is 0.52 nm^2, which is obviously larger than the reported value of 0.31 nm^2 for C_{60},[4] suggesting that the introduction of polar group indeed enhances amphiphilicity of C_{60} and reduces the molecular aggregation at the air-water interface. However, this value is still smaller than the ideal area per molecule of C_{60} (~0.87 nm^2) formed a monolayer, which is probably due to the weaker hydrophilicity of the ester group. It was found from Figure2(b) that the isotherm of BECDF is different from that of ECDF. Detectable increases in the surface pressure started at an area per molecule larger than 1.40 nm^2. From the π~A curve, we infer that when π is below 8 mN/m, BECDF molecules may form a monolayer at the air-

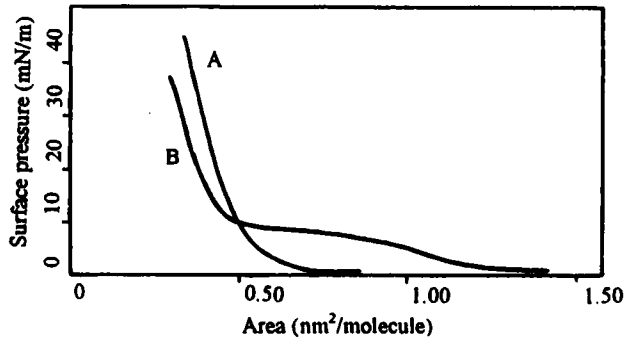

FIGURE 2 π~A isotherms of (a) ECDF and (b) BECDF

water interface with a limiting molecular area of 1.25 nm^2. In the pressure range of 8~10 mN/m, the π~A curve exhibited flatter aspect, whereas a distinct change of slope in the isotherm was observed above 10 mN/m with a limiting molecular area around 0.47 nm^2. The result implies that with increasing pressure, the BECDF molecules in the monolayer will rearrange and finally form the film consisting of a bilayer.

As expected, the floating layers at the air-water interface of both ECDF and BECDF could be transferred onto various substrates with a transfer ratio of 0.8, forming Z-type films. The polar ester group should be responsible for the higher transferability.

There exist three major bands at 225, 275, 346 nm in the UV-vis spectrum of ECDF LB films, which is very similar to that of C_{60} LB films at 222, 268, 342 nm, implying that the intrinsic character of C_{60} is still maintained in ECDF molecules.

From the AFM images of ECDF LB film on mica, the uniform surface morphology was observed in larger scanning area (400×400 nm^2). In a selected region (20×20 nm^2) as shown in Figure 3, many rows of the individual molecules in ordered arrays can be seen and the surface was much smoother than the one obtained for the C_{60} LB film.[4]

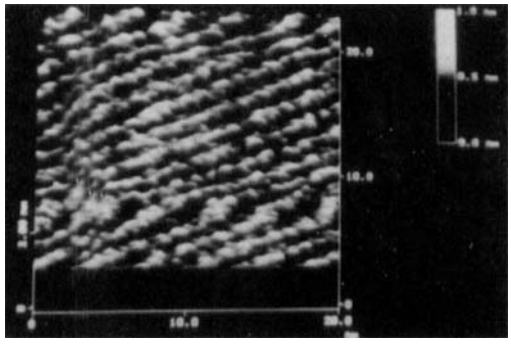

FIGURE 3 AFM image of the LB film of ECDF

TEM images can reveal directly the stacking of close-packed molecules. Figure 4 shows well-defined lattice fringes in most areas of the ECDF LB film. The spacing of the regular lattice fringes of 0.82±0.01 nm was measured directly from the image. Though disordered lattice fringes and stacking faults were also found in some regions of the LB film due to the entanglement between neighboring alkyl chains and the molecular aggregation, the ECDF LB film has higher ordered microstructure than C_{60}.

The modified C_{60} derivatives have no central symmetry and should show macroscopic

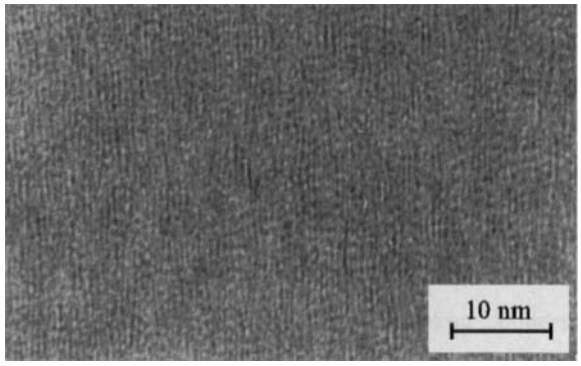

FIGURE 4 TEM image of the LB film of ECDF

SHG response in ordered Z-type films. It is worthwhile mentioning that improved transfer ability of the compounds makes the detection of SHG possible. We assume that the refractive indices of the derivatives are similar to those of C_{60}[5](n_ω=1.95, $n_{2\omega}$= 2.43). Comparing the signals of the sample films with the quartz reference (d_{11} = 1.2 × 10^{-9} esu) and using the reported method,[6] the second-ordered susceptibility $\chi^{(2)}$ and molecular hyperpolarizability (β) were determined to be 2.3×10^{-6} esu and 1.0×10^{-28} esu for ECDF as well as 4.9×10^{-6} esu and 2.0×10^{-28} esu for BECDF respectively.

In summary, the LB films of ECDF and BECDF, two C_{60} derivatives with alkyl chain and ester group, have been prepared. The derivatives have better film-forming ability and transferability than C_{60}. The SHG response of their LB films was measured. The results of AFM and TEM indicate that the monofunctionalized ECDF molecules in the LB film have well-oriented structures. The attempts to obtain the new C_{60} derivatives with stronger hydrophilic groups are in progress.

REFERENCES

1. M. Matsumoto, H. Tachibana, R. Azumi, M. Tanaka, T. Nakamura, G. Yunome, M. Abe, S. Yamago, E. Nakamura, Langmuir, 11, 660 (1995).
2. D.B. Zhu, C.C. Zhu, Y. Xu, C. F. Long, Y. Q. Liu, M. Y. Han, Y. X. Yao, X. S. Zhao, X. H. Xia, Thin Solid Films, in press.
3. C.C. Zhu, Y. Xu, Y. Q. Liu, D.B. Zhu, J. Org. Chem., in submission
4. J. Guo, Y. Xu, Y. L. Li, C. Yang, Y. X. Yao, D. B. Zhu, C. L. Bai, Chem. Phys. Lett., 195(5-6), 625 (1992)
5. R. L. Ren, Y. Wang, A. M. Rao, E. McRae, J. M. Holden, T. Hager, K. A. Wang, W. T. Lee, H. F. Ni, J. Selegue, P. C. Eklund, Appl. Phys. Lett., 59, 2678 (1991)
6. G. J. Ashwell, R. C. Hargreaves, C. E. Baldwin, G. S. Bahra, C. R. Brown, Nature, 357, 393 (1992)