

Langmuir–Blodgett film formation and photocurrent generation of a C₆₀ pyrrolidine derivative C₆₀(C₈H₁₅NO₂)

Yanyi Huang, Liangbing Gan*, Chun-Hui Huang and Fanyu Meng

State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, People's Republic of China

A novel C₆₀ pyrrolidine derivative, C₆₀(C₈H₁₅NO₂) (1), has been synthesized and its Langmuir and LB films were investigated. The monolayer of 1 can be transferred on to hydrophilic substrates. Photocurrent generation of the LB film modified ITO electrode has been measured. The anodic photocurrent can be suppressed by oxygen and enhanced by the electron donor Vc (ascorbic acid). The quantum yield is 1.9% with the concentration of Vc at 0.5 mg ml⁻¹ in the KCl solution. © 1998 Elsevier Science Limited. All rights reserved.

(Keywords: fullerenes; LB film; photocurrent)

INTRODUCTION

Preparation of fullerene films is a very important method in the exploration of their practical applications^{1–3}. Various methods such as solvent casting, spin coating and thermal evaporation have been used¹. LB technology is one of the best methods to prepare highly ordered thin films, but pure C₆₀ is completely hydrophobic and it is very difficult to form a stable monolayer on a water surface^{4–6}. Mixing C₆₀ with stearic acid and other conventional LB compounds has been used successfully to produce C₆₀ containing LB films^{7,8}. Functionalization of C₆₀^{9–11} is another method to prepare fullerene LB films. We have found that attachment of N and/or O containing polar groups on to C₆₀ greatly enhance the film stability and transferability. High-quality LB films can be formed using C₆₀ derivatives^{12–17}. In this paper, a C₆₀ pyrrolidine derivative C₆₀(C₈H₁₅NO₂), 1, has been synthesized and its Langmuir film, LB films and photoelectric properties are investigated.

METHODS

Materials

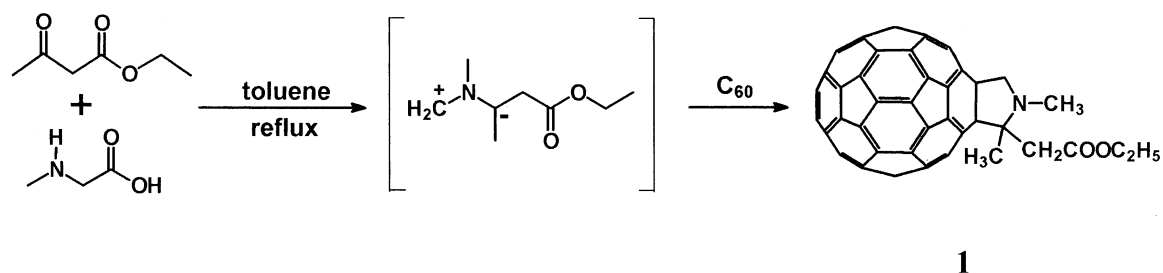
C₆₀ (> 99%) was prepared by contact arc and purified on a charcoal column. Sarcosine (> 98%) was purchased from Fluka. Ethyl acetoacetate and all other solvents were A.R. grade reagents from Beijing Chemical Factory. All reagents mentioned above were directly used without any further purification.

Compound 1 was prepared by the method similar to that of Prato *et al.*^{18–20}. A brief synthetic procedure follows (*Scheme 1*): 60 mg (0.083 mmol) of C₆₀ was dissolved in 150 ml toluene to get a clear solution and then 88 mg (0.99 mmol) of sarcosine and 1 ml (8 mmol) ethyl acetoacetate were added under constant stirring. The resulting solution refluxed for 25 min, turned a dark red solution. The solvent was removed under vacuum and the residue was chromatographed on a silica gel column. Toluene eluted the unreacted C₆₀ first, followed by the main product (brown). The product was recrystallized from the CS₂/petroleum ester mixture to yield 10 mg of a black crystalline solid, 1. Spectroscopic data for 1: δ_{H} (400 MHz, CS₂/CDCl₃): 4.73 (d of q, 1H, $J = 10.2$ Hz), 4.66 (d of q, 1H, $J = 10.2$ Hz), 4.16 (q, 2H, $J = 6.4$ Hz), 3.51 (d of q, 1H, $J = 14.8$ Hz), 3.36 (d of q, 1H, $J = 14.8$ Hz), 3.01 (s, 3H), 2.26 (s, 3H), 1.30 (t, 3H, $J = 7.2$ Hz). m/z (FDMS): 877 (M⁺, 100%), 720 (C₆₀⁺, 15%). FT-IR (KBr pellet): 479, 527, 554, 562, 575, 1029, 1081, 1097, 1109, 1122, 1151, 1183, 1245, 1329, 1365, 1373, 1384, 1428, 1440, 1448, 1462, 1513, 1733 cm⁻¹. UV-Vis λ_{max} (CHCl₃) 256, 316, 429 nm. Anal. Calcd. for C₆₀(C₈H₁₅NO₂)·H₂O: C 91.17%, H 1.91%, N 1.56%; found C 91.74%, H 2.21%, N 1.30%.

LB films formation

Crystalline solid of 1 in chloroform was used as the spreading solution (0.0146 mg ml⁻¹, 1.66 × 10⁻⁵ mol l⁻¹). ITO coated glass slides (20 × 50 mm) and quartz slides (10 × 30 mm) were used as substrates. All substrates were hydrophilically pretreated as follows: for ITO glass, it was immersed into a saturated methanol solution of sodium methylate, then ultrasonically washed with acetone, ethanol and ultrapure water sequentially; the

* Author to whom correspondence should be addressed



Scheme 1 The synthetic procedure of **1**

quartz slide was ultrasonically washed with concentrated sulfuric acid, acetone, ethanol and ultrapure water. The NIMA 622 computer-controlled alternate Langmuir–Blodgett trough was used for this experiment. An EASYpure RF compact ultrapure water system (Barnstead Co., USA) was used to prepare fresh ultrapure water ($18.0 \pm 0.1 \text{ M}\Omega \text{ cm}$, $\text{pH } 5.6 \pm 0.1$). About 10 ml spreading solution was carefully spread on to the subphase in ca. 10 μl droplets, then left for at least 30 min to allow the solvent to evaporate. The films were compressed at a rate of $20 \text{ cm}^2 \text{ min}^{-1}$ and the surface pressure vs. area (π - A) isotherms were recorded. The Langmuir film was transferred on to the hydrophilic substrates at a rate of 2.0 mm min^{-1} (vertical dipping) at a constant surface pressure of $30.0 \pm 0.1 \text{ mN m}^{-1}$. Transfer ratios of 1.0 ± 0.1 for the upstroke were maintained.

Spectroscopic and photoelectrochemical measurement

The absorption spectra of the films and the solution in chloroform ($1.66 \times 10^{-5} \text{ mol l}^{-1}$) were measured using a Shimadzu UV-3100 spectrophotometer. The FT-IR spectrum of **1** was recorded on a Nicolet Magna-IR 750 spectrometer. The photoelectrochemical studies were performed by using a model 600 voltammetric analyzer (CH Instruments Inc., USA) and a 500 W xenon lamp (USHIO Electric, Japan). A IRA-25S filter (TOSHIBA, Japan) which can cut off the IR radiation was used to avoid the thermoeffect. A three-electrode configuration was used throughout and a platinum electrode or a saturated calomel electrode (SCE) was used as the counter or reference electrode, respectively. The LB-film-modified ITO electrode was used as the working electrode while 0.1 mol l^{-1} KCl solution was used as the electrolyte solution.

RESULTS AND DISCUSSION

Surface pressure–area isotherms

The surface pressure–area (π - A) isotherms of Langmuir films of **1** (compressing rate $20 \text{ cm}^2 \text{ min}^{-1}$) were recorded as shown in *Figure 1*. Three regions are evident in the isotherm: I, II and III. The limiting areas of regions I and III obtained by extrapolation to $\pi = 0$ are 1.21 and 0.98 nm^2 , respectively. They are close to that of pure C_{60} [4] and its derivatives^{9,12–17}, suggesting that

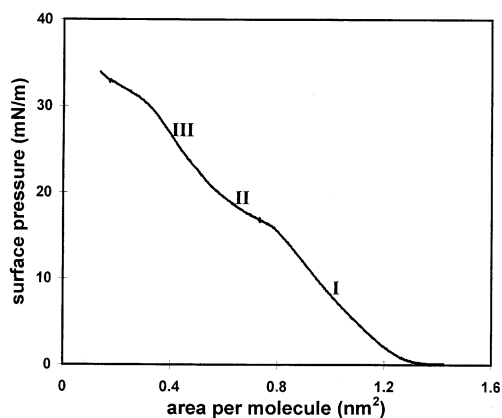


Figure 1 Surface pressure–area (π - A) isotherm of **1** at a compression rate of $20 \text{ cm}^2 \text{ min}^{-1}$

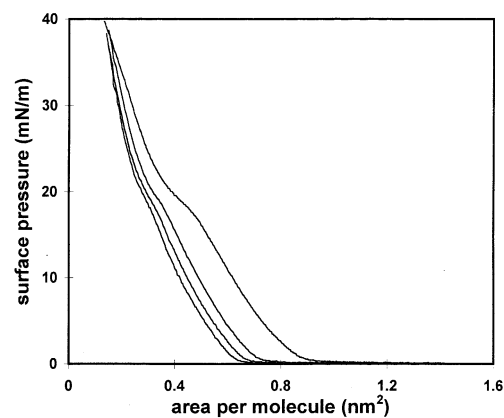


Figure 2 Surface pressure–area (π - A) isotherm of **1** at a compression rate of (from left to right, 250 , 140 , 100 and $60 \text{ cm}^2 \text{ min}^{-1}$)

the film of **1** is a monolayer. In region I, the orientation of **1** on the water subphase is not so rigid and there exists some space among the spheres of C_{60} molecules; in region III, the molecules are more closely packed and the whole hydrophilic group dips into the subphase, so the limiting molecular area is mainly due to the spherical part of the molecule.

The isotherms were slightly different when a different compressing rate was applied. The limiting area decreased when the compressing rate was higher than $60 \text{ cm}^2 \text{ min}^{-1}$. The isotherms obtained under different compressing rates are shown in *Figure 2*.

Formation of LB films

Monolayers of 1 can be transferred on to hydrophilic substrate (quartz and ITO-coated glass) by the vertical dipping method. The monolayer was transferred at $30.0 \pm 0.1 \text{ mN m}^{-1}$ under an increasing speed of 2.0 mm min^{-1} , the transfer ratio in most cases is 1.0 ± 0.1 when the first layer was transferred. After that the transfer ratios are usually 0.8 ± 0.1 on upstroke and 0.6 ± 0.1 on downstroke.

The UV-Vis absorption spectra of 1 in chloroform ($1.66 \times 10^{-5} \text{ mol l}^{-1}$) and that of the LB films on quartz slides are shown in Figure 3. There are two major bands at 256 and 316 nm in chloroform. A little sharp absorption peak at 429 nm, typical of the fullerene monoadduct, is also clearly observed. For the LB films, the two major bands are red-shifted to 272 and 338 nm, respectively. The absorbance at 244, 272 and 338 nm vs. the number of layers are plotted in Figure 4 and it shows an approximate linear relationship.

Photocurrent generation of the LB-films-modified ITO electrode

The working band of the incident light is ca. 320–800 nm with an intensity of 70 mW cm^{-2} and an effective working area of 0.80 cm^2 on the ITO electrode. The photocurrent from the monolayer LB-film-modified ITO electrode was in the range of 35–50 nA under the conditions described above and nitrogen atmosphere. The effect of bias was investigated in the range from -100 to 300 mV. The results show that positive bias improves the photocurrent but a negative bias depresses it with a slope

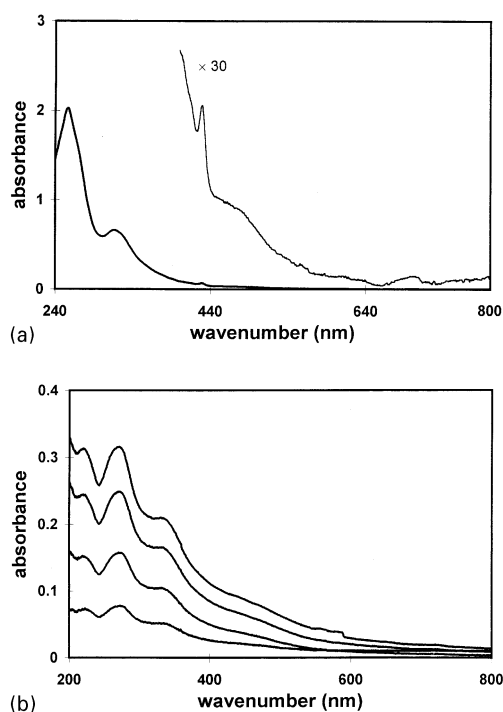


Figure 3 The UV-Vis spectra of 1. (a) In chloroform solution ($1.66 \times 10^{-5} \text{ mol l}^{-1}$); (b) in LB films (from top to bottom, 7-layer, 5-layer, 3-layer and 1-layer)

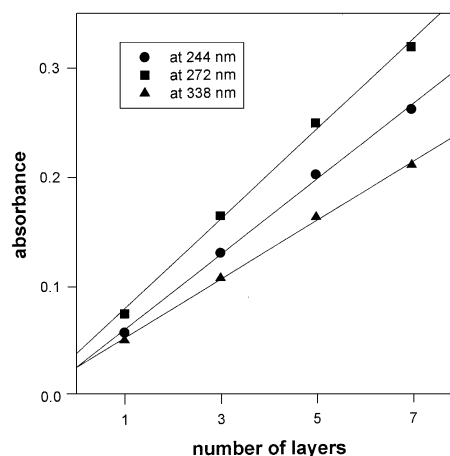


Figure 4 The relationship between the UV absorbance and the number of layers of LB films at 244, 272 and 338 nm

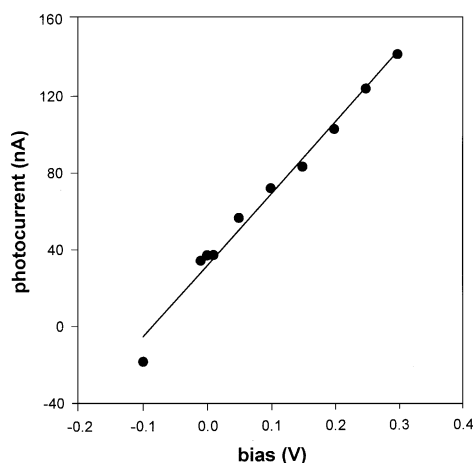


Figure 5 Photocurrent from the LB film modified ITO electrode vs. the bias

of $3.7 \times 10^2 \text{ nA V}^{-1}$. This suggests that the photocurrent is anodic (Figure 5) and the electrons flow from the electrolyte through the LB film to the electrode. The photocurrent is also decreased when oxygen was introduced into the electrolyte solution. This may be due to the fact that oxygen can quench the triplet state of fullerenes^{17,21–22}. When Vc (ascorbic acid) was added into the electrolyte solution as an electron donor, the photocurrent was enhanced remarkably. The photocurrent can reach 320 nA (under the irradiation of white light, no bias) if the concentration of Vc in electrolyte solution is 0.5 mg ml^{-1} , corresponding to an external quantum yield around 1.9% (400 nm). Without Vc the quantum yield is 0.2% under the same conditions.

ACKNOWLEDGEMENTS

This project was supported by the Natural Science Foundation of China (29571004 and 29671001) and the Climbing Program A (A National Fundamental Research Key Project).

REFERENCES

- 1 Mirkin, C.A. and Caldwell, W.B. *Tetrahedron*, 1996, **52**, 5113
- 2 Yu, G., Gao, J., Hummelen, J.C., Wudl, F. and Heeger, A.J. *Science* 1995, **270**, 1789
- 3 Miller, B., Rosamilia, J.M., Dabbagh, G., Tycko, R., Haddon, R.C., Muller, A.J., Wilson, W., Murphy, D.W. and Hebard, A.F. *J. Am. Chem. Soc.* 1991, **113**, 6291; Haddon, R.C. *J. Am. Chem. Soc.* 1996, **118**, 3041
- 4 Obeng, Y.S. and Bard, A.J. *J. Am. Chem. Soc.* 1991, **113**, 6279
- 5 Kharlamov, A.A., Chernozatonskii, L.A. and Dityat'ev, A.A. *Chem. Phys. Lett.* 1994, **219**, 457
- 6 Back, R. and Lennox, R.B. *J. Phys. Chem.* 1992, **96**, 8149
- 7 Milliken, J., Dominguez, D.D., Nelson, H.H. and Barger, W.R. *Chem. Mater.* 1992, **3**, 252
- 8 Xiao, Y., Yao, Z. and Jin, D. *J. Phys. Chem.* 1994, **98**, 5557; Xiao, Y., Yao, Z., Jin, D., Yan, F. and Xue, Q. *J. Phys. Chem.* 1993, **97**, 7072
- 9 Maliszewskij, N.C., Heiney, P.A., Jones, D.R., Strongin, R.M., Cichy, M.A. and Smith, A.B. *Langmuir* 1993, **9**, 1439
- 10 Gan, L., Zhou, D., Luo, C., Tan, H., Huang, C., Lu, M. Pan, J. and Wu, Y., *Org. J. Chem.* 1996, **61**, 1954
- 11 Zhang, W., Su, Y., Gan, L., Jiang, J., Huang, C. *Chem. Lett.* 1997, **10**, 1007
- 12 Luo, C., Gan, L., Zhou, D. and Huang, C. *J. Chem. Soc. Faraday Trans.* 1997, **93**, 3115
- 13 Zhou, D., Ashwell, G.J., Rajan, R., Gan, L., Luo, C. and Huang, C. *J. Chem. Soc. Faraday Trans.* 1997, **93**, 2077
- 14 Gan, L.B., Zhou, D.J., Luo, C.P., Huang, C.H., Li, T.K., Bai, J., Zhao, X. S. and Xia, X.H. *J. Phys. Chem.* 1994, **98**, 12459
- 15 Zhou, D., Gan, L., Luo, C., Tan, H., Huang, C., Yao, G., Zhao, X., Liu, Z., Xia, X. and Zhang, B. *J. Phys. Chem.* 1996, **100**, 3150
- 16 Zhou, D., Gan, L., Luo, C., Tan, H., Huang, C., Liu, Z., Wu, Z., Zhao, X., Xia, X., Zhang, S., Sun, F., Xia, Z. and Zou, Y., *Chem. Phys. Lett.* 1995, **235**, 548
- 17 Luo, C., Huang, C., Gan, L., Zhou, D., Xia, W., Zhuang, Q., Zhao, Y. and Huang, Y. *J. Phys. Chem.* 1996, **100**, 16685
- 18 Prato, M., Bianco, A., Maggini, M., Scorrano, G., Toniolo, C. and Wudl, F. *J. Org. Chem.* 1993, **58**, 5578
- 19 Maggini, M., Karlsson, A., Scorrano, G., Sandona, G., Farnia, G. and Prato, M., *J. Chem. Soc. Chem. Commun.* 1994, 589
- 20 Prato, M., Maggini, M., Giacometti, C., Scorrano, G., Sandona, G. and Farnia, G. *Tetrahedron*, 1996, **53**, 5221
- 21 Arbogast, J.W., Darmany, A.D., Foote, C.S., Rubin, Y., Diederich, F.N., Alvarez, M.M. and Whetten, R.B. *J. Phys. Chem.* 1991, **93**, 11
- 22 Hung, R.R. and Grabowski, J.J. *J. Phys. Chem.* 1991, **99**, 6073