

Langmuir–Blodgett films and optical second-harmonic generation of a crowned [60]fulleropyrrolidine

Z. Guo¹, Y. Li^{1,*}, Z. Ge¹, J. Yan¹, D. Zhu¹, J. Si², P. Ye²

¹Center for Molecule Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P.R. China

²Institute of Physics, Chinese Academy of Sciences, Beijing 100080, P.R. China

Received: 21 October 1999/Revised version: 30 March 2000/Published online: 2 August 2000 – © Springer-Verlag 2000

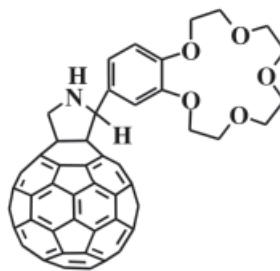
Abstract. The Langmuir and Langmuir–Blodgett (LB) films of a novel crowned [60]fulleropyrrolidine (CFP) were produced in different conditions. Macroscopic second-harmonic generation of the LB film was investigated by means of AM1 Hamiltonian as well as experiments. The monolayer LB film displayed a periodic fringe pattern. A linear dependence of second-harmonic intensity on the number of layers was observed. The second-order molecular susceptibility $\chi^{(2)}$ and hyperpolarizability β were evaluated to be 3.2×10^{-8} and 8.3×10^{-29} esu.

PACS: 74.70.Wz; 42.70.Nq

The covalent functionalization of [60]fullerene has developed dramatically since [60]fullerene was available in macroscopic quantities. Various derivatives of [60]fullerene have been synthesized and exhibited potential application ranging from drug delivery to advanced nanostructured devices [1, 2]. Among manifold [60]fullerene derivatives, [60]fulleropyrrolidine, which can be readily obtained from [60]fullerene and the azomethine ylide formed by the coupling of ketone/aldehyde and amino acid via 1,3-dipolar cycloaddition reactions, proved to be one kind of important compound [3–5]. Several phenyl-substituted [60]fulleropyrrolidines [6–8] were synthesized very recently. The photophysical studies show that these compounds possess intramolecular electron transfer efforts, whereas [60]fullerene moiety acts as the electron acceptor. This unique property makes such compounds more competitive among various [60]fullerene derivatives in the development of advanced materials with new optical optomagnetic properties.

Being a kind of typical functional molecule possessing unique supramolecular properties such as molecular recognition and molecular regulation, crown ether [9] plays an important role in both biological and material sciences. The crown-ether-modified [60]fullerenes will be typical

supramolecules which combine the unique properties of both [60]fullerene and crown ethers together. Meanwhile, the solubility and amphipathy of [60]fullerene will be improved due to the good hydrophilic properties of the crown ether moiety. This makes crowned [60]fullerenes a kind of competitive compound to form structurally ordered fullerene thin films, and may find practical applications such as active surface layers in microsensors or optoelectronic devices. Several kinds of crowned [60]fullerene derivatives have been synthesized [10–16]. A few works have been done on the formation of Langmuir and Langmuir–Blodgett films based on these compounds [13, 14, 17, 18]. However, little work has been done concerning the photophysical properties especially the second-harmonic properties of such species [19, 20]. Leigh et al. [17] reported the second-order nonlinear susceptibilities $\chi_{pp}^{(2)}$ were within the range of 2.3–3.6 pm/V, but no further detailed research was performed.



Scheme 1

Recently, we took advantage of the intramolecular electron transfer of phenyl-substituted [60]fulleropyrrolidine, successfully combined a benzo-15-crown-5 moiety onto [60]fullerene via 1,3-dipolar cycloaddition reaction, and obtained the first crown-ether-bearing [60]fulleropyrrolidine (CFP) [21] (Scheme). This compound should be an electron donor–acceptor system and will possess intramolecular electron transfer according to the previous studies [6–8]. CFP will also be a molecule with relatively good hydrophilicity and can easily form Langmuir and Langmuir–Blodgett film. As intramolecular electron transfer is a necessary term for

*Corresponding author.

(Fax: +86-10/6255-9373, E-mail: ylli@infoc3.icas.ac.cn)

a molecule possessing second-harmonic properties, we assume CFP will have good second-harmonic properties. Here we report the results.

1 Experimental

C₆₀ (purity > 99.5%) was obtained from Beijing University and was used without further purification. All other chemicals used are analytical pure grade. Solvents are purified according to standard procedures. CFP was prepared by the method reported before [21]. Pure product was obtained via HPLC (JAIGEL – 1H + 2H preparative gel permeation chromatography columns eluted with chloroform) and characterized by FT-IR, FD-MS, ¹HNMR, and ¹³CNMR.

Preparation of LB film of CFP was performed by utilizing a computerized Langmuir Trough 4 (Joyce Loeb). Quartz plates were used as substrates, which were washed by conventional method. CFP was dissolved in fresh distilled chloroform to form a solution of 5.0×10^{-4} M. Either deionized double-distilled water or alkali chlorides in deionized double-distilled water was used as subphase. Onto a stable subphase surface, 200 μ l of the chloroform solution was carefully spread at a temperature of 23 °C. After “resting” more than 20 min, the dispersed molecules were compressed at $0.8 \text{ cm}^2 \text{ min}^{-1}$, in order to measure the isotherm or to form a LB film. The film was transferred at a film pressure of 30 mN m^{-1} after the pressure was held constant for 20 min.

Absorption spectra were obtained using a computer-controlled diode array spectrophotometer (HP8452A, Hewlett-Packard). Second-harmonic generation (SHG) was measured in the transmission, using 1.064- μ m output from an Nd:YAG mode-locked laser, and the experimental setup was similar to that described in the previous paper [22]. Linearly polarized light that was parallel to the plane of incidence was directed at a variable incident angle θ or a fixed angle of 45° onto the vertically mounted samples. An infrared blocking filter and a 532-nm interference filter were used to ensure that only SH irradiation was detected. The SHG signal was measured with a photomultiplier and a boxcar integrator.

Computation was performed via MOPAC6.0 (Ergo Computing, Inc.) on an IBM-PC computer.

2 Results and discussion

Figure 1 shows the surface pressure – area ($\Pi - A$) isotherm of CFP on the Langmuir Trough 4 under different subphases. In every case, the concentrations of the dispersed solution were kept the same. The zero-pressure limiting areas per molecule, A_0 , of the isotherms were evaluated by extrapolating the linear region of the isotherm to the X axis ($\pi = 0 \text{ mN/m}$). The A_0 value is 60 \AA^2 with a collapse pressure over 40 mN/m for a pure water subphase. As for a 0.1-M NaCl subphase, the A_0 value is 63 \AA^2 with a collapse pressure over 35 mN/m . Compared with that of pure C₆₀ films (20 \AA^2), the molecular area of CFP is greatly increased, mainly because of the huge hydrophilicity of the polar crown-ether group, which favors the formation of the monolayer instead of an aggregated multilayer.

Monolayers prepared from CFP were transferred to solid substrates by the LB technique, and the transfer was moni-

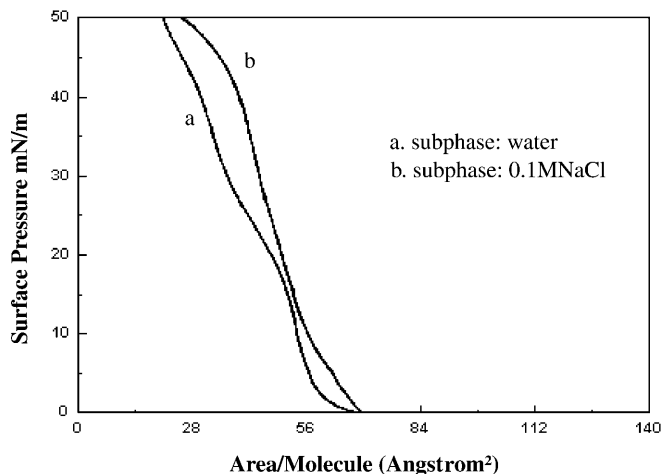


Fig. 1. Pressure–area ($\Pi - A$) isotherm film of CFP on the Langmuir trough 4

tored by absorption spectrophotometry. The absorption spectrum of CFP in solution shows three major bands at 280, 308, and 432 nm. The onset absorption lies at about 730 nm, with the first small evident peak at 706 nm. The five-layer LB film in pure water subphase shows two major bands at 204 and 270 nm, with a shoulder around 320 nm. The absorption peak at 432 nm and the well-defined weak bands in the range of 730–400 nm cannot be distinguished, instead a flat curve is observed (Fig. 2). The absorption spectrum of five-layer LB film in 0.1-mol NaCl subphase is very similar to that of the LB film using pure water as subphase, showing two peaks at 204 and 264 nm with a shoulder around 320 nm (Fig. 2). In the plot of the absorbance of the LB film in 0.1-mol NaCl subphase at 268 nm against the layer number, a linear line is obtained (Fig. 3 inset), indicating that the Langmuir film is effectively transferred onto the quartz substrates. However, the same plot of the LB film in pure water subphase shows a relatively bad linear relationship. These imply that the addition of metal ions in the subphase can improve the transference of the Langmuir film to the quartz substrates.

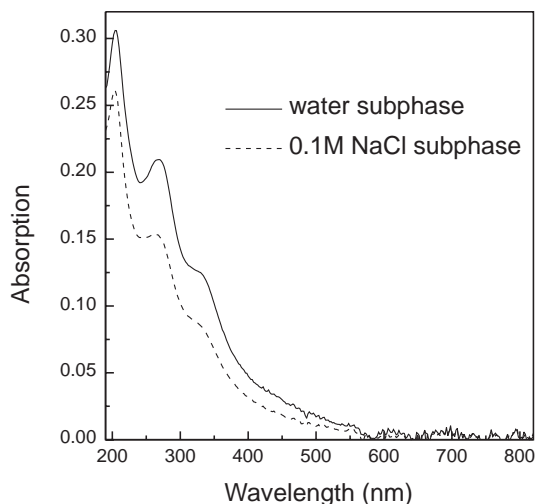


Fig. 2. Absorption spectra of five-layer LB films in different subphases

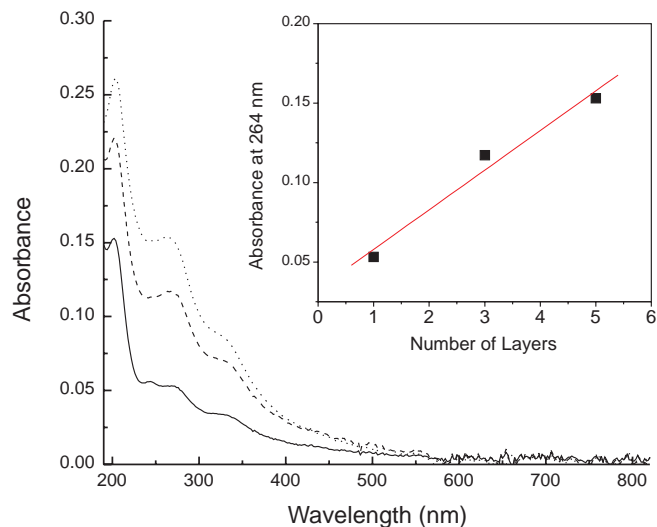


Fig. 3. Absorption spectra of LB films from CFP. The inset shows plots of absorbances at 268 nm vs. numbers transferred for the LB films

CFP is a typical phenyl-substituted [60]fulleropyrrolidine possessing intramolecular electron transfer with methyleneoxy groups as electron-donors and [60]fullerene as the electron-acceptor. In the meantime, CFP has abundant π electrons and has no central symmetry due to the functionality of the crown-ether group. Thus it should have macroscopic SHG response in the LB films.

To confirm the SHG properties of CFP, the computation of the SHG properties of CFP were performed. Based on the optimized geometries [23], the AM1 Hamiltonian was employed to calculate the hyperpolarizability (β) of CFP following the change of dihedral angle of benzo crown-ether plane and pyrrolidine plane (Fig. 4). It can be seen clearly that when the dihedral angle changes from about 50° to 130° , which is quite reasonable due to the very small changes of heat of formation, the β value is between 4×10^{-30} esu and

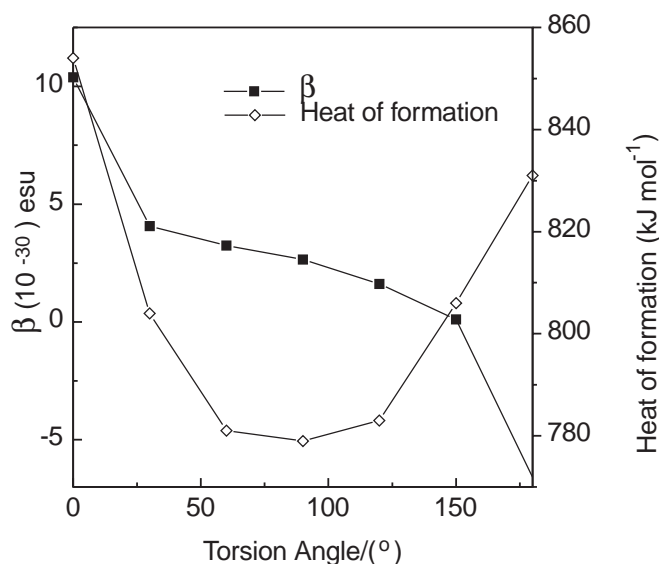


Fig. 4. The relationship between the changing of dihedral angle of benzo crown-ether plane and pyrrolidine plane with hyperpolarizability (β) and heat of formation of CFP calculated using AM1 Hamiltonian

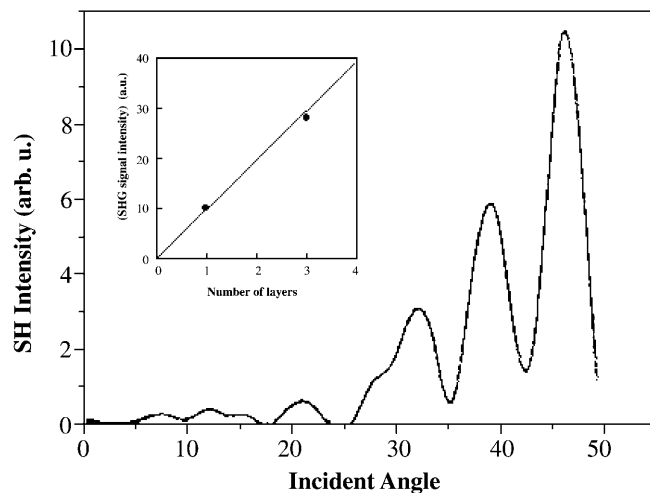


Fig. 5. SH intensities as a function of incident angle of *p*-polarized fundamental light for monolayer of CFP. The inset shows the dependence of SH intensity from CFP LB films on the number of layers

1×10^{-30} esu, which is comparable with that of the typical NLO molecule *p*-nitroaniline.

In the SHG experiment, we assume that the refractive index is 1.70 [24], the film thickness was calculated as 1.50 nm, and the limiting area of LB film was determined as $1.67 \times 10^{-14} \text{ cm}^{-2}$. Using the methods developed by Ashwell et al. [25], the second molecular hyperpolarizability β and susceptibility $\chi^{(2)}$ can be evaluated as 8.3×10^{-29} esu and 3.2×10^{-8} esu, respectively. These values are comparable with those of the [60]fullerene derivatives reported before [17, 24, 26, 27].

Figure 5 shows fringing patterns for the mono-LB film of CFP. A periodic fringe pattern was observed. However, the periodic fringe pattern seems different from the Makers fringe for a 1.50-nm-thick film, normally observed for the SHG data in Fig. 5. It is possible that the LB film does not level on the substrate perfectly, and the results lead to different structural regions in some area in the LB film of CFP. To our knowledge, this phenomenon has never been reported before for a LB film of [60]fullerene derivatives. The measured data for the square root of the SHG intensity versus the number of LB film layers are shown (Fig. 5 inset). It can be seen clearly that the SHG intensity increased quadratically with increasing number of LB films. This implies that the LB films of CFP are a promising material for SHG.

3 Conclusion

The Langmuir and Langmuir–Blodgett films of CFP can be produced in pure water and alkali chloride subphases. Second-harmonic-generation study shows that the monolayer film exhibits strong SH responds. The second-order molecular susceptibility $\chi^{(2)}$ and hyperpolarizability β were evaluated to be 3.2×10^{-8} and 8.3×10^{-29} esu. The monolayer LB film displayed a periodic fringe pattern. A linear dependence of second-harmonic intensity on the number of layers was also observed.

Acknowledgements. The financial support from the National Natural Science Foundation of China and Chinese Postdoctoral Foundation is greatly acknowledged.

References

- M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund: *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego 1996)
- F. Diederich, C. Thilgen: *Science* **271**, 317 (1996)
- M. Prato, M. Maggini: *Acc. Chem. Res.* **31**, 519 (1998)
- M. Maggini, G. Scorrano, M. Prato: *J. Am. Chem. Soc.* **115**, 9798 (1993)
- Y. Li, Z. Mao, J. Xu, J. Yang, Z. Guo, D. Zhu: *Chem. Phys. Lett.* **265**, 361 (1997)
- R.W. Williams, J.M. Zwieter, J.W. Verhoeven: *J. Am. Chem. Soc.* **117**, 4093 (1995)
- D.M. Guldi, M. Maggini, G. Scorrano, M. Prato: *J. Am. Chem. Soc.* **119**, 974 (1997)
- P.A. Liddell, D. Kuciauskas, J.P. Sumida, B. Nash, D. Nguyen, A.L. Moore, T.A. Moore, D. Gust: *J. Am. Chem. Soc.* **119**, 1400 (1997)
- M. Hiraoka (Ed.): *Crown Ethers and Analogous Compounds* (Elsevier, Amsterdam 1992)
- J. Osterodt, M. Nieger, P.-M. Windscheif, F. Vögtle: *Chem. Ber.* **126**, 2331 (1993)
- S.R. Wilson, Y. Wu: *J. Chem. Soc., Chem. Commun.* **784** (1993)
- S.N. Davey, D.A. Leigh, A.E. Moody, L.W. Tetler, F.A. Wade: *J. Chem. Soc., Chem. Commun.* **397** (1994)
- F. Diederich, U. Jonas, V. Granlich, A. Herrmann, H. Ringsdorf, C. Thilgen: *Helv. Chim. Acta.* **76**, 2445 (1993)
- U. Jonas, F. Cardullo, P. Belik, F. Diederich, A. Gügel, E. Harth, A. Herrmann, L. Isaacs, K. Müllen, H. Ringsdorf, C. Thilgen, P. Uhlmann, A. Vasella, C.A.A. Waldraff, M. Walter: *Chem. Eur. J.* **1**, 243 (1995)
- A. Ikeda, C. Fukuhara, S. Shinkai: *Chem. Lett.* **407** (1997)
- P.S. Baran, R.R. Monaco, A.U. Khan, D.I. Schuster, S.R. Wilson: *J. Am. Chem. Soc.* **119**, 8363 (1997)
- D.A. Leigh, A.E. Moody, F.A. Wade, T.A. King, D. West, G.S. Bahra: *Langmuir* **11**, 2334 (1995)
- S. Wang, R.M. Leblanc, F. Arias, L. Echegoyen: *Langmuir* **13**, 1672 (1997)
- H.S. Nalwa, S. Miyatta (Eds.): *Nonlinear Optics of Organic molecules and Polymers* (CRC, Boca Raton, Florida 1997)
- J. Zyss (Ed.): *Molecular Nonlinear Optics* (Academic Press, New York 1994)
- Z. Guo, Y. Li, J. Xu, Z. Mao, Y. Wu, D. Zhu: *Synth. Commun.* **28**, 1672 (1998)
- Y. Liu, Y. Xu, D. Zhu, T. Wada, H. Sasabe, X. Zhao, X. Xie: *J. Phys. Chem.* **99**, 6957 (1995)
- Z. Guo, J. Yan, Y. Li, D. Zhu: *Science in China (Ser. C)* **42**(1), 27 (1999)
- D. Zhou, L. Gan, C. Luo, H. Tan, C. Huang, G. Yao, X. Zhao, Z. Liu, X. Xia, B. Zhang: *J. Phys. Chem.* **100**, 3150 (1996)
- G.J. Ashwell, R.C. Hargreaves, C.E. Baldwin, G.S. Bahra, C.R. Brown: *Nature* **357**, 393 (1992)
- L. Gan, D. Zhou, C. Luo, C. Huang, T. Li, J. Bai, X. Zhao, X. Xia: *J. Phys. Chem.* **98**, 12459 (1994)
- D. Zhou, L. Gan, C. Luo, H. Tan, C. Huang, Z. Liu, Z. Wu, X. Zhao, X. Xia, F. Sun, S. Zhang, Z. Xia, Y. Zou: *Chem. Phys. Lett.* **235**, 548 (1995)