Hydrogen-Bonding Fabrication of NLO Langmuir−Blodgett Films with Nontraditional Molecular Architecture and Unique Thermal Stability

Yao Wang,† Chengshan Wang,† Xinjiao Wang,†
Ying Guo,† Bin Xie,† Zhanchen Cui,*,† Liying Liu,‡
Lei Xu,‡ Daming Zhang,§ and Bai Yang*,†

Key Lab of Supramolecular Structure & Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China, State Key Lab for Advanced Photonic Materials and Devices, Department of Optical Science and Engineering, Fudan University, Shanghai 200433, P. R. China, and State Key Lab on Integrated Opto-electronics, Jilin University Region, Changchun 130023, P. R. China

Received September 6, 2004
Revised Manuscript Received January 28, 2005

Using the Langmuir−Blodgett (LB) technique, chromophoric amphiphilic molecules consisting of a donor-(π-bridge)-acceptor could be oriented at the air−water interface and deposited onto the substrates easily to construct macroscopically non-centrosymmetric LB films. Because of this advantage of the LB technique, study of the preparation of nonlinear optical (NLO) LB film materials has continued to attract keen interest from chemists.[1] As we have known,[2] most of these NLO Langmuir films were obtained with the hydrophobic alkyl chains oriented toward the air and the polar moieties embedded in the water, according to the traditional concept. Only a few unconventional NLO LB films were fabricated based on the molecular electrostatic interaction. More recently, with the development of supramolecular structures fabricated via hydrogen bonding,[3] a stable nontraditional Langmuir monolayer formed from a disubstituted urea lipid molecule was first fabricated by the Leblanc group.[4] The polar moiety of the lipid molecule was suspended in the air phase while one of the hydrophobic tails contacted water. This instructive effort, which is just attributed to the strong hydrogen-bonding network formation between the urea functional groups in the air phase, not only broke the traditional concept for LB structure and then broadened the research field of LB film structures but also provided a promising approach to fabricate novel and stable LB film materials with some functions such as for NLO application. However, to our knowledge, few reports concerning fabricating functional nontraditional LB films based on this kind of strong molecular interactions of hydrogen bonding has been demonstrated so far.

In this paper, we have, based on the molecular interactions of hydrogen bonding, designed and fabricated a nontraditional non-centrosymmetric Langmuir monolayer and obtained SHG active LB monolayer and multilayer films which contain a photopolymerizable group of diacetylene. The molecular architecture and the SHG activity of the films were characterized and investigated using surface pressure−area (π−A) isotherm, atomic force microscopy (AFM), UV−vis absorption spectroscopy, contact angle, and SHG equipment.

The experimental molecule 1-(10-{[(10-nitro)-6,7-azobenzenl]-ether}-decyl)-3-(tetracosa-12,14-diynyl)urea (NAEDTDU) was first synthesized in analogy to the previous procedure.[5] An unusual π−A isotherm of Langmuir film of NAEDTDU was obtained with the normal method. Figure 1 illustrated a characteristic molecular area of 35 Å^2/molecule, which is smaller than the limiting molecular area (50 Å^2/molecule) of the traditional urea Langmuir film model. According to the traditional concept of a Langmuir film, it is easily assumed that the NAEDTDU molecule will form a monolayer with the embedment of its urea polar moiety in the water and the intrusion of both alkyl tail and nitro-azobenzene moiety to the air, which will result in larger than 50 Å^2/molecule of the limiting molecular area instead of the observed 35 Å^2/molecule.[4,6] From this abnormal result, it is presumed that the nitro group of molecule NAEDTDU lie on the air−water interface, which is most possibly responsible for obtaining 35 Å^2/molecule of the limiting molecular area since the limiting molecular area of one alkyl tail should be 21 Å^2/molecule as reported previously.[6]

Additional important experimental evidence is that the NAEDTDU monolayer can be easily deposited onto an OTS-modified hydrophobic substrate with a deposition ratio near 1.0 by adopting conventional vertical upward dipping technique, whereas the deposition ratio of the NAEDTDU monolayer on the hydrophilic substrate such as a mica slide is exceedingly lower than 0.1 with the same method. The thickness of a NAEDTDU LB monolayer is about 5.5 ± 0.1 nm as determined using AFM (image Figure 2) and ellipsometric measurements, suggesting that the molecules

---

* To whom correspondence should be addressed. Zhanchen Cui, College of Chemistry, Jilin University, 119# Jie Fang Road, Changchun 130023, P. R. China. E-mail: cuizc@jlu.edu.cn. Tel: +86-431-8924107. Fax: +86-431-8923907.
† Jilin University.
‡ Fudan University.
§ Jilin University Region.

(1) (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley & Sons: New York, 1991. (b) Ashwell, G. J. *J. Mater. Chem.* **1999**, *9*, 1991−2003. (c) Delaire, J. A.; Nakatan, K. *Chem. Rev.* **2000**, *100*, 1817−1845.

(2) (a) Gao, L. H.; Wang, K. Z.; Huang, C. H.; Zhao, X. S.; Xia, X. H.; Li, T. K.; Xu, J. M. *Chem. Mater.* **1995**, *7*, 1047−1049. (b) Dunne, D.; Hodge, P.; Ali-Adib, Z.; McKeown, N. B.; West, D. *J. Mater. Chem.* **1998**, *8*, 1391−1397. (c) Clays, K.; Armstrong, N. J.; Ezenyilimba, M. C.; Penner, T. L. *Chem. Mater.* **1993**, *5*, 1032−1036. (d) Ashwell, G. J.; Dyer, A. N.; Green, A.; Sato, N.; Sakuma, T. *J. Mater. Chem.* **2000**, *10*, 2473−2476. (e) Ashwell, G. J.; Maxwell, A. A.; Green, A. *J. Mater. Chem.* **2002**, *12*, 2192−2196.

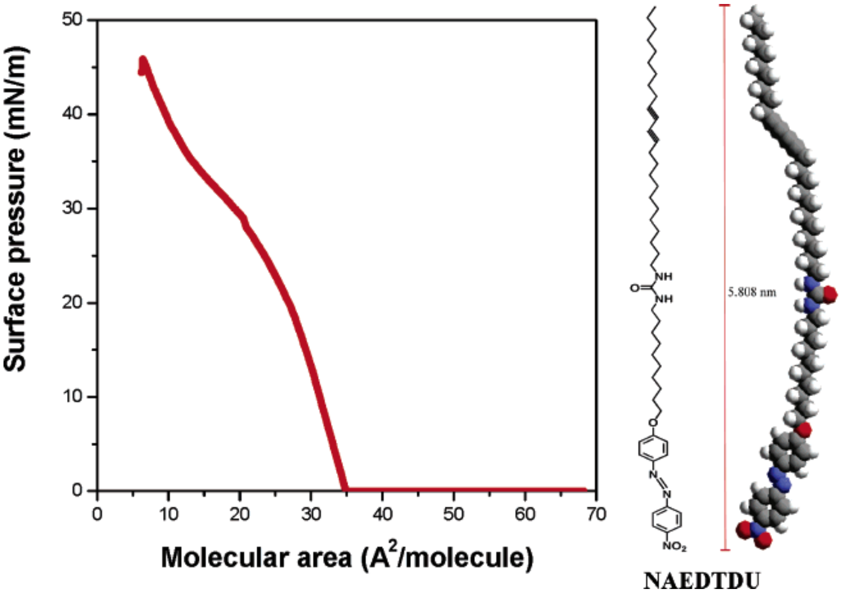
(3) (a) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383−2420. (b) Koyano, H.; Bissel, P.; Yoshihara, K.; Ariga, K.; Kunitake, T. *Chem. Eur. J.* **1997**, *3*, 1077−1082. (c) Weck, M.; Fink, R.; Ringsdorf, H. *Langmuir* **1997**, *13*, 3515−3522. (d) Huo, Q.; Russell, K. C.; Leblanc, R. M. *Langmuir* **1998**, *14*, 2174−2186. (e) Seki, T.; Fukuchi, T.; Kobayashi, T.; Ichimura, K. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2217−2223.

(4) Huo, Q.; Russev, S.; Hasegawa, T.; Nishijo, J.; Umemura, J.; Puccetti, G.; Russell, K. C.; Leblanc, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 7890−7897.

(5) Seki, T.; Fukuchi, T.; Ichimura, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2807−2816.

(6) (a) Mino, N.; Tamura, H.; Ogawa, K. *Langmuir* **1991**, *7*, 2336−2341. (b) Seki, T.; Fukuchi, T.; Ichimura, K. *Langmuir* **2002**, *18*, 5462−5467.

10.1021/cm048482r CCC: $30.25



NAEDTDU

Figure 1. The surface pressure–area (π–A) isotherm of compound NAEDTDU monolayer on the pure water subphase.

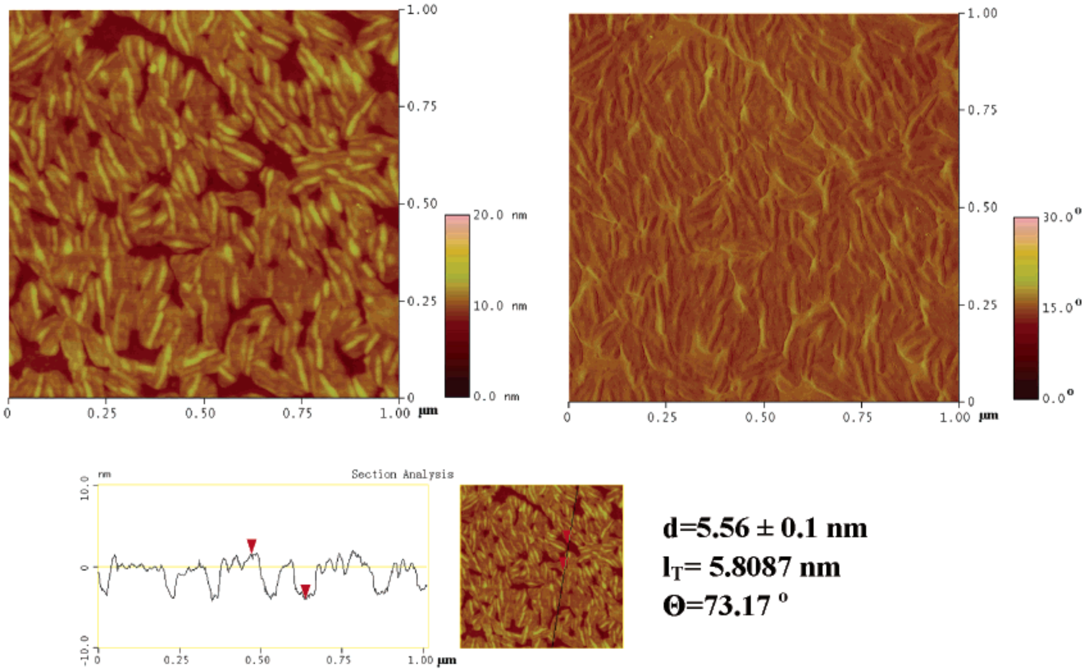


Figure 2. The height mode (left) and phase mode (right) AFM images of the NAEDTDU LB monolayer on a silicon substrate that was covered with an OTS monolayer. The surface roughness of the OTS-modified substrate is less than 0.15 nm. d, the thickness of the LB monolayer; l_T, the theoretical length of the molecule NAEDTDU; Θ, the estimated molecular tilt to the plane of the substrate.

in the monolayer stand up on the substrate with approximately 17° tilt to the normal of the substrate. *(The largest value of the monolayer film thickness should be not more than 3.2 nm according to the traditional Langmuir monolayer model of NAEDTDU. See Supporting Information.)* Like the presumed nontraditional LB monolayer model (Figure 3), it is highly possible for our molecules to form a stable and linear hydrogen-bonding network between the urea groups, leading to the formation of peculiar aggregation in the monolayer which differs from the structures in known reports.[7]

As supposed above, it is the nitro instead of the alkyl tail group of NAEDTDU that should downwardly exist on a substrate like their behavior on the air–water interface in terms of the analysis of the π–A isotherm. To confirm this, a comparison of the contact angles for water on the resulting LB monolayer and a monolayer of 4-nitrobenzenethiol assembled on a gold substrate[8] was made. As a result, the contact angle of water on our LB monolayer (94 ± 2°) is larger than that on the monolayer of 4-nitrobenzenethiol (63 ± 2°). Therefore, it is believed that the alkyl tail moiety of NAEDTDU is upward to the air.

Due to photopolymerizable diacetylene, all the LB monolayers and multilayers can be photopolymerized by UV

---

[7] (a) Pasquier, C.; Tieke, B.; Zahir, S.; Bosshard, C.; Günter, P. *Chem. Mater.* **1991**, *3*, 211–213. (b) Kajikawa, K.; Yamada, T.; Yokoyama, S.; Okada, S.; Matsuda, H.; Nakanishi, H.; Kakimoto, M.; Imai, Y.; Takezoe, H.; Fukuda, A. *Langmuir* **1996**, *12*, 580–583.

[8] Ulman, A. *Chem. Rev.* **1996**, *96*, 1533–1554.

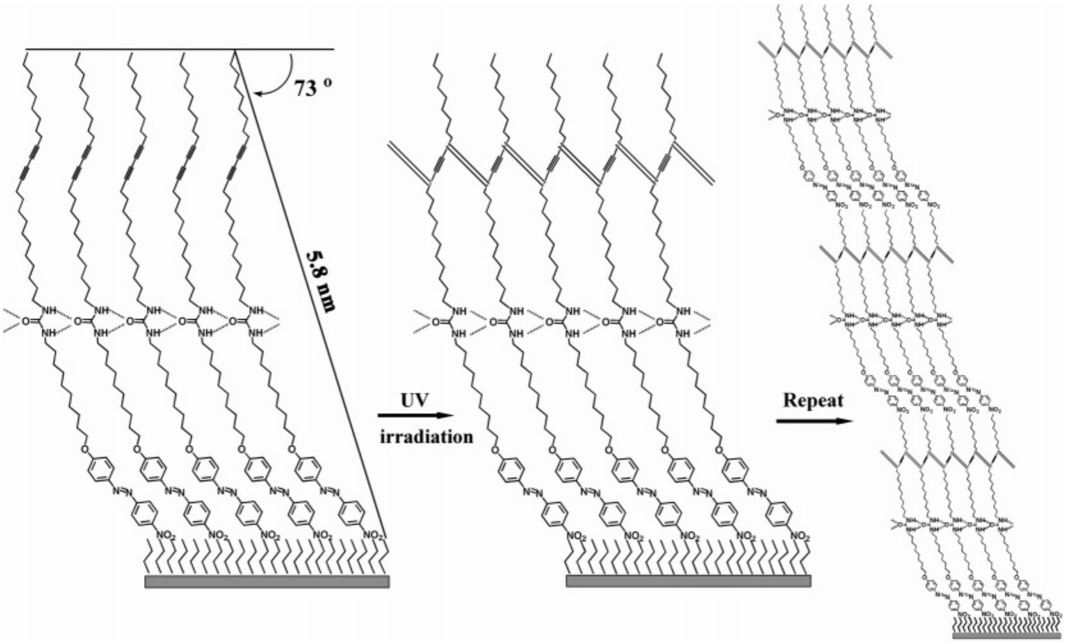


Figure 3. The proposed models of the nontraditional Langmuir−Blodgett monolayer and multilayer of NAEDTDU on the OTS-modified substrates.

irradiation and the irradiated films presented obvious blue form. The details of the photopolymerization are consistent with previous reports.[9] The polymerization of a LB monolayer provides indirectly additional influential support for our nontraditional LB model again since the topochemical photopolymerization of diacetylenes requires a repeating distance of less than 5 Å between diacetylene groups.[10]

As expected, relatively large SHG intensities were observed from the LB monolayer and multilayer since the polar molecule NAEDTDU arranged to form the non-centrosymmetric structure. In particular, we studied the thermal stability of SHG activity of LB multilayer films, an important characteristic for material application, before and after UV irradiation by in situ heating incident SHG technique. Figure 4 indicates that a 17-layer LB multilayer film of NAEDTDU on one side of a quartz glass after irradiation retained >55% of the original polar order up to 120 °C. In contrast, only 50% of the original SHG value remained for a nonirradiation 17-layer LB multilayer when it was heated to just 93 °C. It is obvious that the thermal stability of SHG activity of the LB films was improved substantially after photopolymerization, which is probably explained as below: Via the polymerization of diacetylene, the movement of the polar chromophores was effectively restricted and the ordered orientation of the chromophores in the irradiated films was stabilized to a certain extent. *(But owing to the suppleness of the molecular chain of OTS which served as the bottom, the materials will not possess higher thermal stability of SHG activity)*. This inferrer has also been substantiated in spectroscopy and in topography (see Supporting Information). First, it is noticed that accompanied with the appearance of polydiacetylene characteristic absorbance in 640 nm, the maximum UV−vis absorption of the photopolymerized film is red-shifted from 342 to 352 nm as result of disordering of oriented arrangement of molecular aggregates.[11] Meanwhile, a very large red-shift (342 to 366 nm) can be observed in the maximum UV−vis absorbance spectrum of the nonphotopolymerized film, suggesting the higher disordering. On the other hand, the improvement of thermal stability of the LB films after photopolymerization could also be observed in their AFM images which were obtained when the heated films were cooling. Compared with the surface

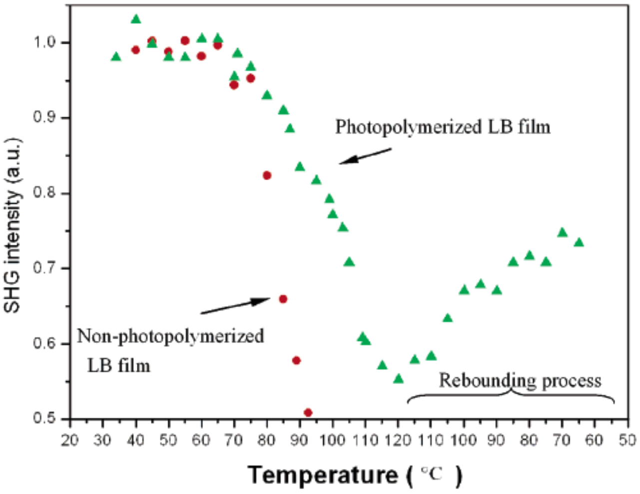


Figure 4. The thermal stability of SHG intensity of a photopolymerized 17-layer NAEDTDU LB film and a non-photopolymerized similar LB film.

---

[9] (a) Kodali, N. B.; Kim, W.; Kumar, J.; Tripathy, S. K.; Talwar, S. S. *Macromolecules* **1994**, *27*, 6612−6619. (b) Sarkar, A.; Okada, S.; Nakanishi, H.; Matsuda, H. *Macromolecules* **1998**, *31*, 9174−9180. (c) Sarkar, A.; Okada, S.; Matsuzawa, H.; Matsuda, H.; Nakanishi, H. *J. Mater. Chem.* **2000**, *10*, 819−828. (d) Mino, N.; Tamura, H.; Ogawa, K. *Langmuir* **1991**, *7*, 2336−2341.

[10] (a) Coe, S.; Kane, J. J.; Nguyen, T. L.; Toledo, L. M.; Wininger, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 86−93. (b) Kuriyama, K.; Kikuchi, H.; Kajiyama, T. *Langmuir* **1998**, *14*, 1130−1138. (c) Cai, M.; Mowery, M. D.; Menzel, H.; Evans, C. E. *Langmuir* **1999**, *15*, 1215−1222.

[11] (a) Schwartz, H.; Mazor, R.; Khodorkovsky, V.; Shapiro, L.; Klug, J. T.; Kovalev, E.; Meshulam, G.; Berkovic, G.; Kotler, Z.; Efrima, S. *J. Phys. Chem. B* **2001**, *105*, 5914−5921. (b) Wang, Y.; Wang, X. J.; Chuai, X. H.; Fu, N.; Cui, Z. C.; Yi, M. B.; Zhang, D. M.; Yang, B. *Polym. Int.* **2004**, *53*, 1106−1112. (c) Lee, J. Y.; Park, E. J. *J. Polym. Sci., Part A: Polym Chem.* **2002**, *40*, 1742−1748.

topographies before heating, the photopolymerized 17-layer LB film can still retain the topography of the layer-by-layer structure despite the appearance of clear defects in film surface after being heated to 120 °C. Conversely, the layer-by-layer structure in the similar but non-photopolymerized film was completely destroyed even if the temperature was only up to 90 °C.

In addition, most interesting, we discovered that, after the photopolymerized films were heated until their SHG intensity decreased to about 55% of the original value, the SHG intensity of these photopolymerized LB monolayer and multilayer films exhibited the unique phenomenon of rebounding to approximately 75% of the original value upon the falling back of the environmental temperature (rebounding process in Figure 4). However, in the case of the non-photopolymerized LB films, this rebound or recovery phenomenon has not been observed. Although the details of mechanism of this rebound are not very clear at present, it is considered that the photopolymerization of diacetylene brought thermodynamically stable coalition of molecular aggregates in regionality that would be predominantly responsible for the unique rebounding of SHG activity.[12] We believe that the improvement of the thermal stability and the SHG rebounding or self-recovery phenomenon both attributed to the photopolymerization of diacetylene will provide promising motivation for the development of second-order nonlinear optical materials.

Acknowledgment. The authors are grateful to Dr. Liyan Wang and Dr. Guang Lu for providing us significative help. This work was supported by Major State Basic Research Project (G2000036604), Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT), National High Technology Development Project (2001.AA.312160) and NSFC (NO. 200340062).

Supporting Information Available: Synthesis of NAEDTDU and its monolayer models according to traditional and nontraditional concepts; details of film characterization of UV−vis absorption and atomic force microscopy (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM048482R

---

(12) (a) Heflin, J. R.; Figura, C.; Marciu, D.; Liu, Y.; Claus, R. O. *Appl. Phys. Lett.* **1999**, *74*, 495−497. (b) Lee, S. H.; Balasubramanian, S.; Kim, D. Y.; Viswanathan, N. K.; Bian, J. K.; Tripathy, S. K. *Macromolecules* **2000**, *33*, 6534−6540.