

## Effect of Interlayer Molecular Recognition on the Structural and Non-linear Optical Properties of Alternating Langmuir-Blodgett Films of Two Complementary Molecular Components

Y.-Z. Ren<sup>a</sup>, S.-G. Chen<sup>a</sup>, X.-D. Chai<sup>ad\*</sup>, Y.-W. Cao<sup>a</sup>, W.-S. Yang<sup>a</sup>, R. Lu<sup>a</sup>,  
G.-Li<sup>b</sup>, A.-D. Lu<sup>b</sup>, M.-X. Gong<sup>c</sup>, Y.-B. Bai<sup>a</sup>, T.-J. Li<sup>a</sup> and J.-M. Lehn<sup>d\*</sup>

<sup>a</sup>Department of Chemistry, Jilin University, Changchun, 130023, P.R. China

<sup>b</sup>Changchun Institute of Physics, The Chinese Academy of Sciences

<sup>c</sup>Department of Fundamental Sciences, Jiamusi Institute of Technology, 154007

<sup>d</sup>Chimie des Interactions Moléculaires, Collège de France, 11 Place Marcelin Berthelot, 75005 Paris, France

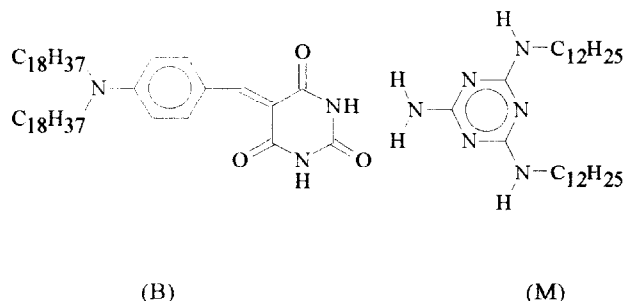
### Abstract

Alternating Langmuir-Blodgett films were successfully deposited with two complementary molecular components: 5-(4-N, N-dioctadecylaminobenzylidene)-2, 4, 6-(1H, 3H)-pyrimidinetrione (B) and 4-amino-2, 6-didodecylamino-1, 3, 5-triazine (M). It was found that the interlayer molecular recognition improved the deposition of B. Preliminary studies were made about the effect of interlayer molecular recognition on the second harmonic generation and UV-visible absorbance of the charge transfer band of B.

### 1. INTRODUCTION

Langmuir-Blodgett (LB) technique has been well known to fabricate ultrathin ordered organic assemblies [1]. In recent years a fascinating field is developed in an attempt to build supermolecular assemblies through the LB method [2]. Pallacin [2] has summarized the different ways of supermolecular engineering in LB films, one among which is the alternating deposition method. This method can provide a supermolecular structure in which distinct molecules can join closely through non-covalent bonds at the interface between adjacent layers.

In this paper two complementary molecular components are used to construct alternating multilayers: 5-(4-N, N-dioctadecylaminobenzylidene)-2, 4, 6-(1H, 3H)-pyrimidinetrione (B) and 4-amino-2, 6-didodecylamino-1, 3, 5-triazine (M) [3].



The two molecules have the following features. First, B and M are typical "LB" materials, possessing long hydrophobic

chains and hydrophilic heads. Second, B is a typical nonlinear optical material. Its barbituric head is an electron acceptor, the tertiary amine is a donor, and the dipole moment directs from the former to the later. Alternating depositions of B and M can give a non-centrosymmetric structure in which constructive summation of the dipole moments should result in second harmonic generation (SHG). Third, in the alternating films the heads of M and B are expected to join through hydrogen bonds, presumably via triple hydrogen bonds proposed by Lehn [4]. The interlayer recognition is expected to influence the structural and non-linear optical properties of the multilayer.

### 2. EXPERIMENTAL

The LB films were fabricated with a KSV5000 LB trough. B and M, dissolved in Chloroform of concentration  $2 \times 10^{-4}$  M and  $1.0 \times 10^{-3}$  M respectively, were spread to the subphase of deionized and double distilled water. The substrates were hydrophilic  $\text{CaF}_2$ , on which one layer of B was precoated, and successive layers were then deposited. The transfer pressures for both M and B were 25mN/m. For the SHG experiment we used the linearly polarized fundamental beam (1064 nm) of a Q-switched Nd:YAG laser, which is incident on the sample at  $45^\circ$ ; the frequency doubled light (532 nm) was detected in reflection [5]. The calculation of molecular hyperpolarizability followed the method in reference [6]. For measurement of  $\epsilon$  unpolarized light of normal incidence on the films was used.

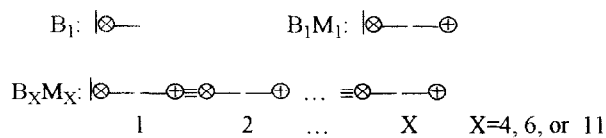
### 3. RESULTS AND DISCUSSIONS

#### 3.1. Molecular recognition improved transfer of B

The pressure-area isotherms of both B and M on pure water at 20.0 °C give collapse pressures at about 45mN/m and collapse areas at approximately 0.4nm<sup>2</sup> per molecule. Separate Y-type deposition of B onto CaF<sub>2</sub> was not successful. Although the transfer ratio of the first layer was almost unity, that of the second layer was only 0.25. On the other hand, alternating depositions of B and M were successful, with stable transfer ratios of both M and B around unity.

The well-known self-aggregation of barbiturates through intermolecular hydrogen bonding [7] may help to interpret the failure in the separate Y-type deposition of B. On the other hand, during the alternating transfer M acts as an "assembler" and assembles B through the complementary binding sites. New hydrogen bonds between B and M are thus formed at the expense of those of the initial self-association of B.

Five samples were prepared: B<sub>1</sub>, B<sub>1</sub>M<sub>1</sub>, B<sub>4</sub>M<sub>4</sub>, B<sub>6</sub>M<sub>6</sub>, B<sub>11</sub>M<sub>11</sub>, whose structures run as follows:



where | stands for the substrate,  $\otimes$ — for B, — $\oplus$  for M, and  $\equiv$  for possible triple hydrogen bonds between the heads of M and B. It is noteworthy that B in the first layer of the above alternating films is free of any interlayer bonding, as compared to that in the successive layers. In the following discussions we shall distinguish two cases: B free in the first layer and B bonded in successive layers.

#### 3.2. The absorption coefficient of B in interlayer bonding

The charge-transfer transition of B occurs at 480 nm. The transition dipole moment of this band is along the donor-acceptor linkage. Its tilt angle relative to the film normal is determined by polarized UV-visible spectroscopy [8] to be about 57° for all the films, without discernible differences.

However, the molar extinction coefficients  $\epsilon$  of the 480nm band differ considerably. The  $\epsilon$  obtained from the films B<sub>1</sub> and B<sub>1</sub>M<sub>1</sub> are both around  $4.3 \times 10^4$ ; while the  $\epsilon$  of B which is interlayer bonded in the multilayer B<sub>X</sub>M<sub>X</sub> is about  $1.3 \times 10^4$  for X=4, 6, 11 (by subtracting the absorbance of the first free layer). Here  $\epsilon$  has been calculated from the absorbance of the LB films, hence it is related to both the direction and the magnitude of the transition dipole moment. Since there is no difference in the tilt angles of the charge transfer transition moment of the free and bonded B, the remarkable decrease in  $\epsilon$  must indicate that the transition dipole moment of the 480nm band has been reduced

after interlayer bonding. This implies that the melamine head of M, bonded with the barbituric head of B, acts as an electron pusher against the charge transfer transition of B: D→A≡ $\oplus$ , where D and A stand for the donor and acceptor of B respectively, and  $\oplus$  for the melamine head.

#### 3.3. The non-linear polarizability of B in interlayer bonding

The second order non-linear molecular polarizabilities  $\beta$  of B in the films B<sub>1</sub> and B<sub>1</sub>M<sub>1</sub> are nearly the same, both around  $8.9 \times 10^{-29}$  e.s.u. (Table 1). They are calculated according to the method proposed by Berkovic and Shen et al [6]. For obtaining the  $\beta$  of the hydrogen bonded molecules in B<sub>X</sub>M<sub>X</sub>, the influence of free B in the first layer is carefully subtracted; then normalization for one layer of B is done. The  $\beta$  of B in interlayer bonding is in the range  $2.0$ – $2.4 \times 10^{-29}$  e.s.u. (Table 1), significantly less than that of free B. Since there is no difference in the tilt angles of the charge transfer transition moment of the free and interlayer bonded B, the decrease in  $\beta$  indicates that the dipole moment of B is reduced after hydrogen bonded with M. This again, implies that M serves as an electron pusher, as described in the above section.

Table 1

The hyperpolarizability  $\beta$  of B free and bonded in various films

	interlayer bonded B			
	B <sub>1</sub> (free)	B <sub>4</sub> M <sub>4</sub>	B <sub>6</sub> M <sub>6</sub>	B <sub>11</sub> M <sub>11</sub>
$\beta \times 10^{-29}$ e.s.u.	8.9	2.0	2.3	2.4

Spectral results on the recognition pattern will be published. Supplementary materials are available upon request.

#### REFERENCES

1. H. Fuchs, H. Ohst and W. Prass, *Adv. Mater.*, 3 (1991) 10.
2. S. Palacin, *Thin Solid Films*, 178 (1989) 327.
3. (a) Y. W. Cao, X. D. Chai, S. G. Chen, T. J. Li, *Chemical Journal of Chinese Universities*, 11 (1994), in the press.  
(b) S. G. Chen, X. D. Chai, Y. W. Cao, T. J. Li, *The Chinese Journal of Chemistry*, 1994, in the press.
4. J.-M. Lehn, M. Mascal, A. DeCian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, (1990) 479.
5. G. Li, X. R. Xu, *Chin. Journ. of Luminescence*, in the press.
6. Th. Rasing, G. Berkovic, Y. R. Shen, S. G. Grubb and M. W. Kim, *Chemical Physics Letters*, 130 (1986) 1.
7. For example, B. M. Craven and E. A. Vizzini, *Acta Crystallogr., Sect. B*, B27 (1971) 1917.
8. Y. Z. Ren, W. Liu, M. Y. Han, M. L. Gao, Y. Y. Zhao, T. J. Li and J. Yang, *Thin Solid Films*, 229 (1993) 249.