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Structural study on the alternating Langmuir–Blodgett films deposited with two complementary barbituric acid and melamine derivatives

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Abstract

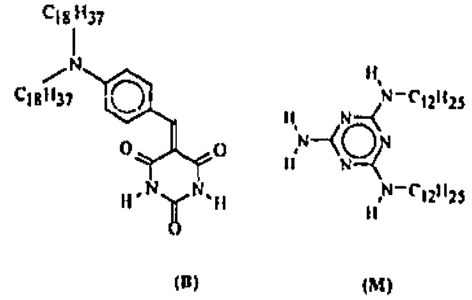
Alternating Langmuir–Blodgett films were deposited with two complementary molecules: 5-(4-*N*,*N*-dioctadecyl aminobenzylidene)-2,4,6-(1H,3H)-pyrimidinetrione (B) and 4-amino-2,6-didodecylamino-1,3,5-triazine (M). Pressure–area isotherms were recorded. The transfer behavior of the alternating films was compared with that of the separate films of B. X-ray diffraction measurements confirm that the alternating films have a genuinely alternating structure: MBMB...MB. Transmission FTIR measurements reveal that in the separate films B is exclusively self-aggregated through the hydrogen bonding between the $C=O$ and N–H on the barbituric ring of B, and in the alternating films new hydrogen bonds are formed between B and M at the expense of those of the initial self-aggregation. Polarized attenuated total reflectance Fourier transform infrared spectroscopy measurements show that in the alternating films the hydrocarbon chains stand almost vertically, in comparison with the separate films of B as well as of M. It is found that in the alternating films the 2-position carbonyl on the barbituric ring of B is perpendicular to the film plane. It is concluded that the interlayer hydrogen bonding between B and M gives rise to a better film structure.

Keywords: Langmuir–Blodgett films; Deposition process; Structural properties

1. Introduction

Ultrathin ordered organic films have recently aroused considerable interest due to their technological potential as a novel class of materials with tailor-made electrical and optical properties. In developing ordered molecular films, the Langmuir–Blodgett (LB) [1–5] method and various procedures for the "self-assembly" of organic molecules at surfaces [5–10] are examples of techniques that produce functional assemblies through manipulating the architecture, orientation and density of molecules. Relatively recently, Allara gave a summary of critical issues for application of organized molecular assemblies at surfaces, and compares film characteristics of LB assemblies and self-assemblies [11]. LB assemblies are known to lack thermodynamic stability, since the LB film preparation is far from thermodynamic equilibrium. The metastable LB films transferred onto solid substrates may reorient, resulting in structural defects. In contrast, molecular self-assembly is the self-association of organic molecules into a defined architecture in thermodynamic equilibrium via noncovalent bonds. In particular, molecular recognition-directed self-assembly is the spontaneous binding of complementary subunits to form a supermolecule of thermodynamic and kinetic stability.

We have tried to design an experiment that combines the features of both the self-assembly and LB method. The following molecules are synthesized: 5-(4-*N*,*N*-dioctadecyl aminobenzylidene)-2,4,6-(1H,3H)-pyrimidinetrione (B) and 4-amino-2,6-didodecylamino-1,3,5-triazine (M) [12] (Scheme 1).



(B) (M)

Scheme 1.

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The two molecules have the following features. First, B and M are typical LB materials, possessing long hydrophobic chains and hydrophilic heads. Second, the barbituric acid head that B contains and the melamine head that M contains are typical molecular components. The molecular recognition directed self-assembly of 2,4,6-triaminopyrimidine and barbituric acid derivatives has been studied [13]. It is expected that hydrogen bonding induced self-assembly of M and B occur during and/or after their alternating depositions in a head-to-head, tail-to-tail fashion. Third, B has the right molecular geometry for non-linear optical applications. The non-linear optical properties of the alternating films of M and B have been reported [14]. This paper gives a detailed study on the structure of the alternating films of M and B.

2. Experimental

The LB films were deposited with a KSV 5000 LB double trough. B and M were dissolved in chloroform of concentration 2×10^{-4} M and 1.0×10^{-3} M respectively. The subphase was deionized and double distilled water and its pH was 5.5. According to the previous study on the recognition of M and B at the air–water interface by injecting the chloroform solution of M under water, this pH of 5.5 is the optimal one [15]. Various substrates were used, such as CaF_2, quartz, mica and silicon. Deposition of the first layer of B onto these substrates is always successful and deposition of successive layers of B are never successful. Silicon attenuated total reflectance (ATR) crystals were also used as substrates. The ATR crystals were parallelograms, with a 30° angle of incidence with respect to the parallel faces. The temperature was kept at 20.0°. For both M and B, the transfer pressures were 25 mN m^{-1} and the deposition speeds were 5 mm min^{-1}.

Infrared spectra were recorded with a Bruker IFS-66V (Germany) Fourier transform infrared (FTIR) spectrometer. Polarized FTIR-ATR spectra were taken with s- and p-polarized light. The spectra consist of 200 scans at 4.0 cm^{-1} resolution.

3. Results and discussions

3.1. Pressure–area isotherms and transfer behavior

As shown in Fig. 1, the pressure–area isotherms of both B and M on pure water at 20.0 °C give collapse pressures at about 45 mN m^{-1} and collapse areas at approximately 0.4 nm^2 per molecule. This collapse area should reflect that the molecules stand almost vertically on water at the collapse pressure. Both B and M contain two long hydrocarbon chains and one octadecyl chain is known to have an area about 0.2 nm^2 when standing vertically on water. The transfer behavior of M and B differs considerably. Separate Y-type deposition of M onto CaF_2 is successful, with apparent transfer ratios around 0.8. However, separate depositions of B onto CaF_2 fail, whether Z-type or Y-type. Table 1 lists the transfer ratios of B during the separate Y-type depositions and its transfer ratios during its alternating deposition with M. It is seen that separate Y-type depositions of B onto CaF_2 slides fail, while the alternating ones are successful.

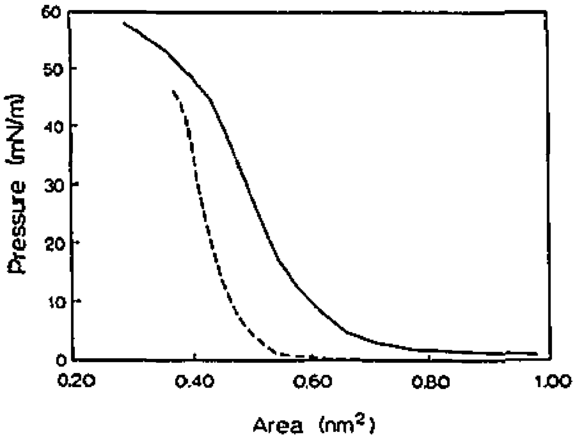


Fig. 1. Pressure–area isotherms of the monolayers of M and B on pure water at 20.0 °C. (1) Dashed line, M. (2) Solid line, B.

Table 1
Apparent transfer ratios (TR) of B during its separate Y-type and alternating depositions with M

Separate Y-type		Alternating with M	
Layer	TR	Layer (up)	TR
1	1.2	1	1.1
2	0.3	3	1.1
3	0.8	5	0.9
4	0.6	7	0.9
5	0.9	9	0.9
6	0.4	11	0.8
7	0.7	13	0.9
8	0.4	15	1.1
9	0.6	17	1.0
10	0.4	19	1.0
11	0.5	21	0.9

This transfer behavior of B may be explained by the self-aggregation of B. B contains a barbituric acid head. Barbituric acids tend to aggregate through intermolecular hydrogen bonding between the N–H and C=O [16]. This self-aggregation of barbituric acids should account for the failure in the separate Y-type deposition of B. During the alternating transfer M serves 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-aggregation of B. This is confirmed through infrared measurement of the alternating films.

X-ray diffraction measurements confirm the layer structure of the alternating films of M and B. Three samples were prepared for X-ray measurements: 19-layer Y-type films of B (BY), 19-layer Y-type films of M (MY), and 22-layer alternating films of M and B. As shown in Fig. 2 and Table 2, BY has a period of 5.19 nm, which indicates that BY has a genuinely Y-type structure, i.e. head-to-head and tail-to-tail. Since a straight octadecyl chain is known to be about 2.5 nm

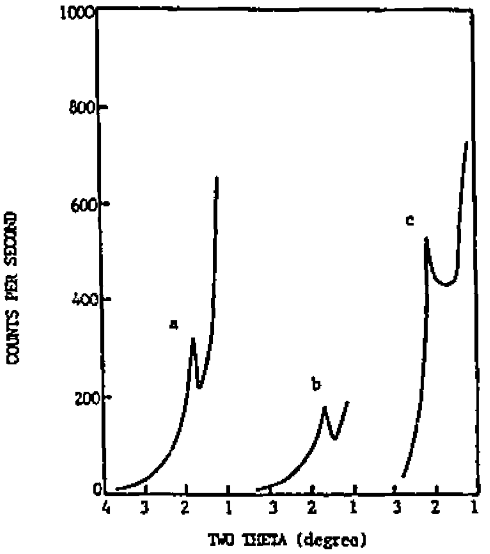


Fig. 2. X-ray diffraction patterns of the various LB films of M and B using Cu Kα(0.154 nm). (a) 22-layer alternating films of M and B. (b) 19-layer Y-type films of B; (c) 19-layer Y-type films of M.

Table 2
First Bragg peak position of the various films of M and B (Cu Kα, $\lambda = 0.154$ nm) on calcium fluoride

LB films	2θ	Period
Alternating films of M and B	1.82°	4.85 nm
Separate Y-type films of M	2.15°	4.11 nm
Separate Y-type films of B	1.63°	5.19 nm

long, the period 5.19 nm means that the octadecyl chains of B are almost perpendicular to the film plane. The film MY has a period of 4.11 nm, which also indicates that MY has a genuinely Y-type structure and that the dodecyl chains of M are almost perpendicular to the film plane. The alternating films of M and B have a period of 4.85 nm, which is approximately half the period of MY (4.11 nm) and that of BY (5.19 nm). This means that the alternating films of B and M have a genuinely alternating structure: BMBM...BM, and that the alkyl chains of both B and M stand nearly vertically in the films.

3.2. Transmission FTIR spectra

Transmission FTIR measurements of the films deposited on calcium fluoride slides reveal that in the separate Y-type films B is exclusively self-aggregated, with all N–H on the barbituric ring hydrogen bonded to the C=O. The hydrogen bonding effect is revealed in the N–H stretching region. Curve (a) in Fig. 3 is the IR spectrum of the Y-type films of B and two broad bands are observed at 3049 and 3187 cm^{-1}. The stretching vibration of free N–H on barbituric ring is known to be a sharp band near 3400 cm^{-1} [17]. The two broad bands at 3049 and 3187 cm^{-1} should be hydrogen-bonded modes of N–H stretching: N–H...O=C. Curve (b) is the IR spectrum of the Y-type films of M. The following detailed analysis shows that in the Y-type films there are both free and hydrogen-bonded N–H of the melamine ring of M. The sharp

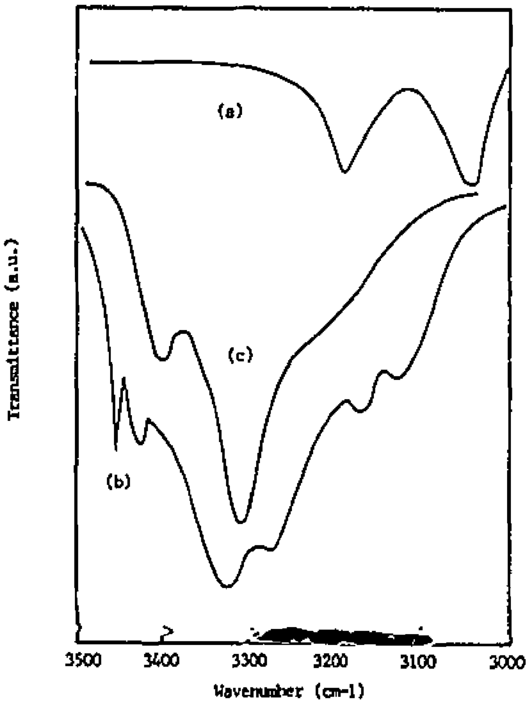


Fig. 3. Transmission FTIR spectra of the LB films deposited on CaF$_2$ at 25 mN m^{-1}. (a) 19-layer Y-type films of B; (b) 19-layer Y-type films of M; (c) 22-layer alternating films of M and B.

band at 3454 cm^{-1} is known to be free N–H stretching vibration of the secondary amine that joins the hydrocarbon chain and the melamine head of M [18]. The band at 3420 cm^{-1} is due to the free symmetric N–H stretching vibration of the primary amine of the melamine head, according to our recent temperature-dependent measurement of M in the solid state. The many bands within 3350–3000 cm^{-1} are assigned to hydrogen-bonded N–H stretching vibrations of the melamine head.

In spectrum (c) of Fig. 3 there is neither a band corresponding to the N–H stretching vibration of self-aggregated barbituric acids (3049 and 3187 cm^{-1}), nor a band corresponding to that of monomeric barbituric acids (3400 cm^{-1}). Thus the N–H of B should be hydrogen bonded to the melamine ring of M.

3.3. Polarized ATR-FTIR spectra

Polarized ATR-FTIR was used to determine the orientation of groups in the LB films relative to the film normal. Three samples were prepared at 25 mN m^{-1}:

|⊗—— ; |——⊕ ; |——⊕...⊗——

where | stands for the substrate, ⊗—— for B, ——⊕ for M, and ... for hydrogen bonds between the heads of M and B. The orientation of the hydrocarbon chain is defined by the angle Θ between the hydrocarbon chain axis and the film normal.

The absorbances of the antisymmetric and symmetric methylene stretching at 2916 cm^{-1} and 2850 cm^{-1} were recorded with s-polarized and p-polarized light. From the absorbance data, a dichroic ratio D defined as $D=A_y/$

(A_x+A_z) was calculated, where (A_x+A_z) is the absorbance with p-polarized light and A_y is the absorbance with s-polarized light. The angle θ is determined from the dichroic ratios of both the 2916 cm^{-1} and 2850 cm^{-1} band. [19] The tilt angle Θ of the chains in the alternating films is 26°, while the Θ of the alkyl chains in one layer M film is 35°, and the Θ for one layer B film is 30°. It seems that the interlayer hydrogen bonding between M and B in the alternating films has the effect of improving the packing behavior of the hydrocarbon chains of both M and B.

Polarized ATR-FTIR spectra in the carbonyl stretching region give the orientation angles of the barbituric acid head of B in the LB films. The orientation of the barbituric ring is characterized by the direction of the 2-position carbonyl, that is, the axis through the 2-position and 5-position carbons in the ring. The transition moments of the 4,6-CO symmetric stretching vibration and the 2-CO stretching vibration are known to be polarized along this axis [16]. Fig. 4 is the ATR spectra of a one-layer B film. The two bands at 1725 and 1700 cm^{-1} are due to the 4,6-CO symmetric stretching and 2-CO stretching vibration, respectively. The 1658 cm^{-1} band is due to 4,6-CO antisymmetric stretching. The transition moments of the former two bands are both polarized along the 2-position carbonyl, while the latter is away from it by 60°.

The two spectra in Fig. 4 are respectively s- and p-polarized spectra. The electric vector of the s-polarized light is parallel to the film plane. The electric vector of the p-polarized light has an angle of 30° with the film plane, and thus has a component along the film normal. As shown in Fig. 4, the s- and p-polarized spectra of one layer B film are similar, indicating that there is no anisotropy for the 1725 and 1700 cm^{-1} bands of this film. Consequently, the 2-CO in this film has an angle near 54.7°(the magic angle) with respect to the film normal. The similarity of s- and p-polarized spectra reflects the random orientation of the barbituric ring.

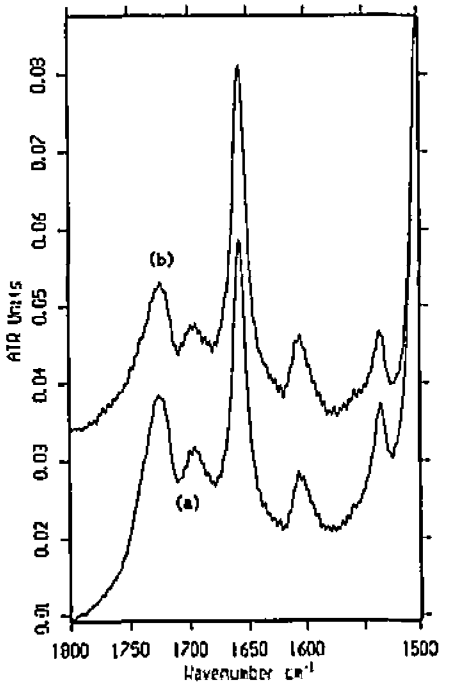


Fig. 4. Polarized ATR-FTIR spectra of a one-layer B film at 25 mN m^{-1} on silicon ATR crystals: (a) s-polarized; (b) p-polarized.

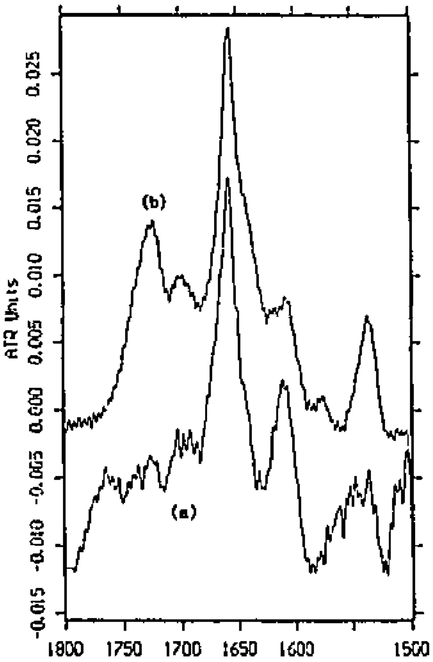
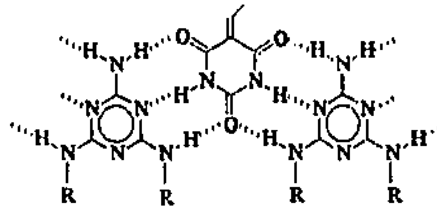


Fig. 5. Polarized ATR-FTIR spectra of double layer film of B and M at 25 mN m^{-1} on silicon ATR crystals: (a) s-polarized; (b) p-polarized.



Scheme 2.

However, the 2-CO in the alternating films is along the film normal. As shown in Fig. 5, the 1725 and 1700 cm^{-1} bands are very weak and nearly not discernible in the spectrum obtained with s-polarized light, but appear as strong bands in the p-polarized spectrum. Because the absorption intensity of a band is proportional to the square of the cosine of the angle between the transition moment and the electric vector of the incident light, the 2-CO in the alternating films is almost perpendicular to the film plane.

With this vertical alignment of the 2-CO in the alternating films, it is predicted that the number and direction of the intermolecular hydrogen bonds connected to the barbituric ring be symmetrical with respect to the film normal. The hydrogen bonding pattern in the alternating films is proposed in Scheme 2. This hydrogen bonding pattern has already been proposed by Lehn et al. [13], and meets our recent study on the molecular recognition between M and 5-[4-dodecyloxybenzylidene]-2,4,6-(1H, 3H)-pyrimidinetrione in chloroform [20].

4. Conclusion

Alternating Langmuir–Blodgett films of two complementary molecules M and B were successfully deposited. X-ray diffraction measurements prove the alternating structure: MBMB...MB. In order to reveal the joining mechanism of M and B at the interface of two adjacent layers, FTIR measurements were conducted. From unpolarized FTIR measurements we concluded that new hydrogen bonds C=O...H–N between B and M are formed. From polarized ATR-FTIR measurements we concluded that the interlayer hydrogen bonding between B and M has the effect of orienting the 2-position carbonyl of B perpendicular to the film plane. A hydrogen-bonding pattern between B and M in the alternating films were proposed, based on the above FTIR results.

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