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Aggregation and self-organization of hydrophilic azobenzene dye Langmuir–Blodgett films

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Abstract

Langmuir–Blodgett (LB) films of azobenzene dye of 2-hydroxyl-3-(4-methoxyl)-naphthanilide-azodiphenyl (AS-RL) and its hybrid films with behenic acid (BA) and octadecylamine (ODA) were investigated by tapping mode atomic force microscopy and ultraviolet visible light absorption spectroscopy. Wavy line-shaped or fingerprint-like dye aggregates were observed in the pure dye LB films. BA and ODA were used to modulate *and control* the structure of the dye aggregates and different patterns resulted in changing the molar ratio of dye molecules in the composites films, such as long lines (AS-RL/BA = 1:2), sheets (AS-RL/ODA = 1:2), wide lines (AS-RL/ODA = 1:1), and ordered lines (AS-RL/ODA = 2:1).

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1. Introduction

Azobenzene dyes are a kind of important photosensitive materials, which can be used in many fields such as electrophotography, static copy, laser printing, hologram, and production of organic p–n heterojunction solar energy cells [1–8]. An important consideration in such applications is assembling the azobenzene dyes into thin films by procedures such as spin coating, casting, vapor deposition, or Langmuir–Blodgett (LB) technique. Among these methods, the LB technique enables fabrication of ordered monolayers and organized molecular assemblies with well-defined molecular orientation on desired substrates. The LB films of carboxyazobenzene compound on solid substrates have also been studied [3,5,8–12]. Usually pure azobenzene dyes do not form a stable monolayer and the dye molecules tend to aggregate at the air–water interface. So long-chain amphiphilic fatty acid and amine were often used as additive to disperse these dye molecules. Among the available additive, fatty acid and fatty amine with long chains are often chosen as the prototypical materials for LB films [13].

Zhao et al. have shown that the structure of dye molecules has a strong influence on the superstructures of the aggregates as well as the environmental conditions, such as surface pressure, different additives, which means the assistant materials for stabilization of Langmuir film at air–water interface [14–17]. In the latter case, hydrogen bond, hydrophobic interaction, and π–π interaction may play roles in the formation of aggregates [14]. Several other studies have also shown that the number and the length of hydrophilic headgroups on the azobenzene or additives can influence the orientation and packing of azobenzene molecules [9,18]. In this paper, we report a study on the control of the configuration of 2-hydroxyl-3-(4-methoxyl)-naphthanilide-azodiphenyl (AS-RL) aggregates at air–water interface by the addition of behenic acid (BA) and octadecylamine (ODA), for they have different hydrophilic headgroups. Atomic force microscopy (AFM) was used to investigate the surface morphology of the membranes of AS-RL and its mixed films with BA or ODA.

2. Experimental details

2.1. Materials

The additives of BA and ODA were purchased from Sigma (99%); The azobenzene dye of AS-RL was from Zhejiang University, which was synthesized and purified according to literature [18]. The molecular structure of AS-RL dye is shown

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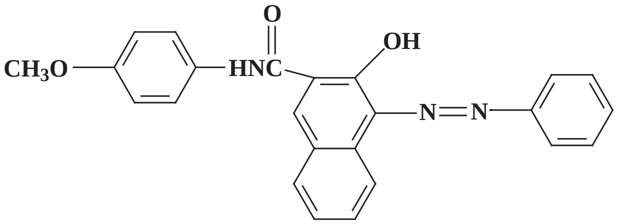

Scheme 1. The molecular structure of AS-RL dye.

in Scheme 1. The deionized water was from the ionic exchange colophony ($T = 20$ °C, $\rho = 15$ MΩ).

2.2. Substrates preparation

Cleaving a fresh mica surface was first pressed some adhesive tape against the top mica surface, then peeled off the tape. The hydrophilic quartzes were first put into the solution with volume ratio of $H_2SO_4/H_2O = 1{:}5$ at 80 °C for 30 min, then rinsed by pure water, finally dried in air at room temperature naturally. They were both used as the support for preparing LB films.

2.3. Sample preparation

The deposition of LB films was performed on a France LB 105 trough (96×38 cm^2) with subphase of pure water (pH = 6.2, 23 ± 1 °C). The chloroform solutions of AS-RL, AS-RL/BA = 1:1 and AS-RL/ODA = 1:1 mixture were spread on the subphase by drops. After 30 min evaporation of the solvent, the floating film was compressed by a mobile teflon barrier at the max speed of 20 mm/min, and at the same time, π–A isotherm was recorded. Mica and quartz substrates were immersed in the subphase, then pulled out with a dipping speed of 4 mm/min at a constant surface pressure of 1, 25 and 30 mN/m.

2.4. Instruments

Tapping mode AFM (Seiko Instruments Inc., SPI 3800/SPA400) was employed to image the LB films. A pyramid-like silicon nitride cantilever with a nominal spring constant of 0.09 N/m was used. The cantilever was 100 μm long and 4 μm wide. The tip integrated on the cantilever had an apex radius of ~20 nm and the typical imaging force was repulsive. Each image consisted of 256 lines with 256 pixel points per line. Ultraviolet visible light (UV–vis) absorption spectra of the AS-RL solution and its LB films were obtained by Heλios α (UNICAM, Britain).

3. Results and discussions

3.1. π–A isotherms of AS-RL, AS-RL/BA and AS-RL/ODA film at air–water interface

The pressure-area isotherms of AS-RL and AS-RL/BA, AS-RL/ODA films on pure water subphase are shown in Fig. 1. The isotherm of pure AS-RL (curve *a*) shows that the dye molecules is in the gel phase at ambient temperature. Its average molecular area is 0.21 nm^2 at the surface pressure of 30 mN/m. For the mixed films, the flats occurred for both curve *b* and *c*, which began at the surface pressure of 11.1 mN/m for AS-RL/ODA (curve *c*) and 2.7 mN/m for AS-RL/BA (curve *b*), respectively. Moreover, the collapse pressure was higher for curve *b* (above 32 mN/m) than that for curve *c* (about 25 mN/m).

From the structure of AS-RL molecules, it can be inferred that the intermolecular and intra-molecular hydrogen bonds can be formed between hydroxyl groups on azobenzene and its adjacent N atoms. As a result, the dye molecules will interact with each other with the increasing lateral pressure at air–water interface, then forming aggregates. In addition, it is likely to be that there are interactions between BA(ODA) molecules and AS-RL molecules by forming intermolecular hydrogen bonds. Generally, there will appear flats at certain surface pressure in pressure-area isotherms due to the molecules aggregation at air–water interface. The absence of flat for pure AS-RL film suggests that the configuration of AS-RL aggregates changes little by little under lateral pressure at air–water interface. Whereas for the mixed films, both π–A isotherms of BA/AS-RL and ODA/AS-RL show that flats occurred. Apparently, the change of the AS-RL configuration resulted from the adding of BA(ODA). We also observed that the initiative pressure for flat is 2.7 mN/m for AS-RL/BA composite film, which is far below than 11.1 mN/m for AS-RL/ODA mixed film. This indicates that the interactions between AS-RL/ODA are stronger than that between AS-RL/BA and the change of the AS-RL configuration needs higher lateral pressure in AS-RL/ODA mixed film. At the same time, the lower collapse pressure for curve *c* also demonstrates this point.

3.2. Absorption spectra of the AS-RL aggregates

Fig. 2 shows the absorption spectra of the AS-RL in chloroform solution and its 13-layered LB films, which were deposited on hydrophilic quartz substrates at the surface pressures of 25 mN/m. Curve *a* is the absorption spectrum of AS-RL molecules in chloroform solution. From this figure, two

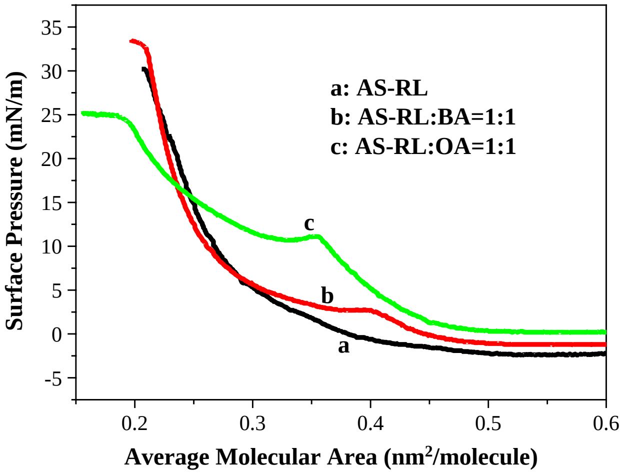

Fig. 1. π–A isotherms of AS-RL (a), AS-RL/BA = 1:1 (b) and AS-RL/ODA = 1:1 (c) film at air–water interface.