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## **Absorption Spectral Study of Mixed Chiral Amino Acid Porphyrin Langmuir-Blodgett Films**

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## ABSORPTION SPECTRAL STUDY OF MIXED CHIRAL AMINO ACID PORPHYRIN LANGMUIR-BLODGETT FILMS

Key words: Chiral amino acid porphyrin; mixed monolayer; Langmuir-Blodgett films

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### ABSTRACT

Absorption spectra were performed on Langmuir-Blodgett films of a new chiral amino acid porphyrin (Py) and its mixture with stearic acid (SA). Vertical uniformity of the LB films has been demonstrated by the linear relationship between the absorbance and the layer number of films. J-Aggregates were present when the film was transferred at various surface pressures and at different molar ratios of Py and SA. However, no aggregation was present for the molecules in the adjacent monolayers. The observed optical absorption spectra of mixed films were markedly dependent on the combination of Py. When the molar ratio of Py was increased from 0.05 to 0.75, the absorption peaks of Soret and Q bands bathochromically shifted ca. 5.5 and 2.2 nm. When the deposited pressure was increased from 5 to 35 mN/m, the absorption peaks of Soret and Q bands bathochromically shifted ca. 3.7, 3.2 nm and 3.5, 2.2 nm for pure Py and 1:3 Py-SA mixed LB films, respectively. On a hydrophobic substrate, the LB films showed a red shift of ca. 4.5 nm for Soret band compared with that on the hydrophilic substrate owing to their different environments.

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## **INTRODUCTION**

The design and synthesis of artificial molecular systems aimed at mimicking the structure and/or function of photosynthetic centers have attracted much interest recently.<sup>1-3</sup> Mixed lipid-porphyrin Langmuir-Blodgett (LB) films provide models for studying important photophysical processes in natural systems that contain porphyrin chromophores in ordered hydrophobic environments of proteins and membranes.<sup>4,5</sup> For example, photoinitiated electron-transfer processes in the self-assembled mixed porphyrin-lipid LB films provide useful information in understanding the importance of organization in these complex biological systems. Also, LB film consisting of porphyrin and its analogues are of interest in molecular devices such as: storage,<sup>6</sup> memory,<sup>7</sup> solar energy devices,<sup>8</sup> sensors,<sup>9</sup> and low-dimensional conductors.<sup>10</sup> It is considered that tailed chiral amino acid porphyrins and their complexes are good models of natural porphyrin-protein supramolecular assemblies.<sup>11-13</sup> So far, little is known about the preparation and property of this kind of porphyrin LB films. In this paper, we wish to report the structure and assembling property of a new tailed porphyrin with covalent-linked substituted L-phenylalanine for mixed monolayer assemblies with stearic acid prepared in various molar ratios and at different deposition pressure.

## **EXPERIMENTAL**

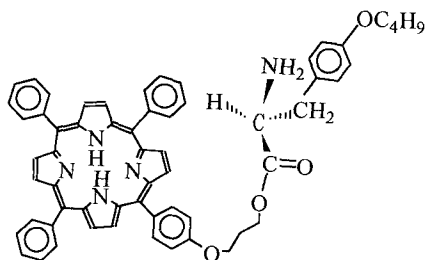
### **Reagents**

Stearic acid (SA) was obtained from Sigma Chemical Co. All the other chemicals were of A.R. grade, purchased from Shanghai Chemical Reagents Co. Doubly distilled water from a quartz distiller was used as the subphase. The tailed chiral amino acid porphyrin (Py, its structure is illustrated in Scheme 1) was synthesized in our laboratory and the details will be reported elsewhere.

### **Formation of Mixed Stearic Acid-Porphyrin LB Films.**

The formation of air-water monolayers and deposition of the LB films were carried out according to a previous paper.<sup>14</sup> The monolayers were transferred onto a hydrophilic, or a hydrophobic, quartz substrate at a certain surface pressure by the vertical dipping method. All work was carried out in a dust-free box at a temperature of 25°C.

The quartz glass slides were washed in detergent and sonicated in a bath sonicator (ultrasonic cleaner). After the glass slides were washed in deionized water, they were cleaned by heating (70°C) in a mixture of 30% H<sub>2</sub>O<sub>2</sub> and



**Scheme 1** The molecular structure of tailed chiral amino acid porphyrin (Py)

concentrated  $\text{H}_2\text{SO}_4$  (30:70 v/v) for 30 min. After they were thoroughly rinsed with deionized water, the glass slides were stored under water.<sup>14</sup> The hydrophobic substrates were prepared from the clean hydrophilic plates by silanation using dichlorodimethylsilane.

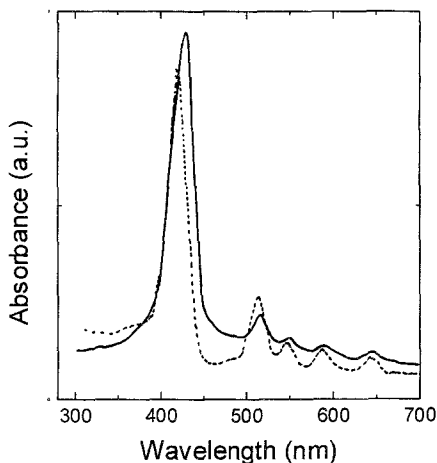
### **Measurements**

Electronic spectra were measured with a Shimadzu Model 3100 UV-VIS-NIR recording spectrophotometer. Measurement of surface pressure-area ( $\pi$ -A) isotherms and the deposition of LB films were carried out with a WM-2 Langmuir Trough System, which is a fully computerized and programmable apparatus fitted with two moveable Teflon barriers.

### **RESULTS AND DISCUSSION**

The absorption spectra of Py in a chloroform solution ( $2.5 \times 10^{-5}$  mol/L) and in 12-layer LB films (9-layers in each side) deposited on hydrophilic quartz glass were shown in Fig. 1. The absorption peaks of the LB films occurred at 432 nm (Soret band), 518, 552, 593 and 649 nm (four Q bands), but the absorption maxima are located at 415, 516, 549, 591 and 647 nm, respectively, for the solution spectra. The absorption spectra of LB films show considerable line broadening and larger red shift (17 nm) for the Soret band and a small red-shift (2~3 nm) for the Q bands compared with the solution spectra.

The red shift of the absorption maximum has been correlated to the anti-parallel type aggregation (J-aggregation) of chromophores<sup>15</sup> according to the



**FIG.1** UV-visible spectra of Py in 12-layer LB films deposited from pure water subphase (solid line) and in  $2.5 \times 10^{-5} \text{ mol dm}^{-3}$   $\text{CHCl}_3$  solution (dashed line).

molecular excitation model.<sup>16,17</sup> That is, the red shift indicates that the molecules of Py in the LB films exist as J-aggregates form.<sup>18</sup> Such J-aggregation has also been observed with the mixed LB film of Py and SA, possibly indicating that the presence of SA does not prevent the aggregation of Py.

The intensity of absorption peaks of the Py LB films is proportional to the number of the LB films (Fig. 2), indicating that the monolayer deposition is reproducible and the deposited LB films have an ordered multilayer structure.

However, the band positions do not shift with the increase in number of monolayers. It illustrates that there is significant aggregation for the molecules in the adjacent monolayers. Similar phenomena were also observed for the mixed LB films of 1:2 and 1:3.

In the mixed LB films of Py and SA, the nature of the interactions between Py and SA was influenced by the molar ratios of Py to SA. The absorbance of LB films increased with the increase of the molar fraction of Py. A linear relationship of the absorbance to the molar fraction of Py can be obtained (Fig. 3). It can be interpreted as the increase of the concentration of chromophore (porphyrin) with the increase of  $x_{\text{Py}}$ . Since the absorbance of SA in the LB films can hardly be

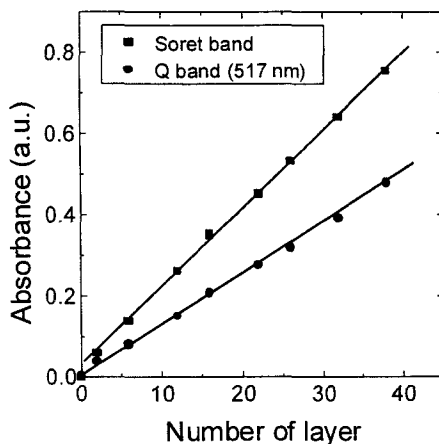
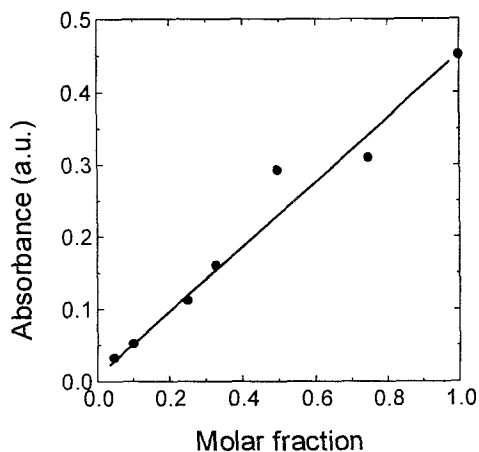


FIG.2 Plot of the absorbance against the number of Py LB films.

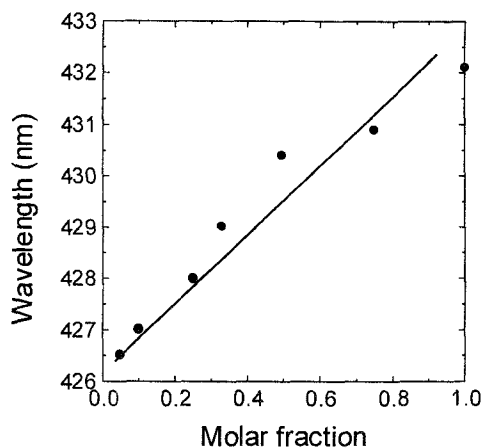
measured in the absorption region compared with Py, so SA can be regarded as an “inert” molecule to regulate the two-dimensional number density of Py. Fig. 3 further suggested the good in-plane uniformity of the Py molecules in the mixed LB films.

The position of the absorption peaks of Py-SA mixed LB films changed with the molar ratio of Py. For example, the Soret bands in 1:1 and 1:19 LB films deposited at 20 mN/m on hydrophilic quartz substrate bathochromically shift to 431 and 427 nm, respectively. Fig. 4 showed the plot of the absorption wavelength of 12-layer mixed LB films of Py and SA deposited in different molar ratios. With the increase of the molar fraction of Py from 0.05 (1:19) to 0.75 (3:1), the absorption wavelength of the Soret band bathochromically shifted ca. 5.5 nm. However, the Q band only bathochromically shifted ca. 2.2 nm (for example, from 516.4 to 518.6 nm). These different shifts indicated a different structure for the aggregate and/or possibly a different degree of aggregation for Py in the mixed LB films with different molar ratios.

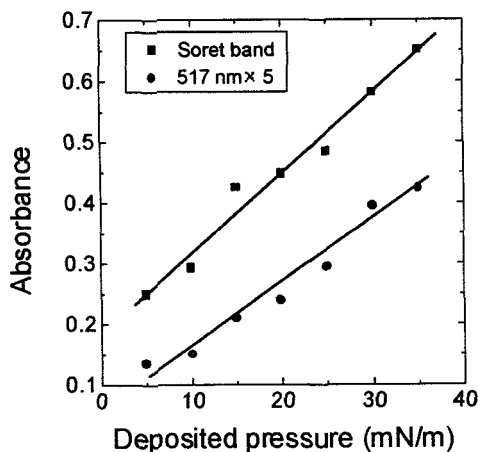
The effects of the deposited pressure on the UV-visible spectra of both pure Py and Py-SA mixed LB films were investigated. There are apparent differences in the spectra of LB films deposited at different pressures both in the change in magnitude of the absorbance and the wavelength.



**FIG.3** Plot of the absorbance of 12-layer mixed LB films of Py and SA deposited in different molar ratios.



**FIG.4** Plot of the absorption wavelength of 12-layer Py-SA mixed LB films deposited in different molar ratios.

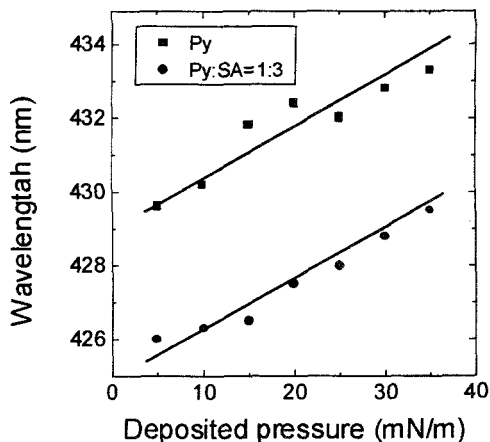


**FIG.5** Plot of the absorption wavelength of 12-layer Py LB films deposited in different surface pressure.

Fig. 5 shows the dependence of the absorbance of the Soret band and one of the Q bands (517 nm) in the UV-visible spectra of Py-SA LB films deposited at different surface pressures. Fig. 6 shows the dependence of the absorption wavelength of the Soret band in the UV-visible spectra of LB films of Py and 1:3 Py-SA mixture on deposited pressure. It can be seen that with the increase of deposited pressure, the absorbance of LB films increases, and the absorption peaks shift to longer wavelength. When the deposited pressure increases from 5 to 35 mN/m, the Soret band bathochromically shifted ca. 3.7 and 3.5 nm for pure Py and 1:3 Py-SA mixed LB films. However, the Q bands only shifted ca. 3.2 and 2.2 nm. This can be interpreted as the increase of the ordering of Py in the LB films with the increase of the deposited pressure.

It must be noted that the absorbance of the LB films is greatly increased with the increase of deposition pressure. Although the increase of absorbance may have resulted from the increase of the Py concentration in LB films at higher surface pressure, most of the increase resulted from the ordered arrangement of Py molecules. For example, with the increase of deposited pressure from 5 to 35 mN m<sup>-1</sup>, the absorbance of the Soret band of 1:3 Py-SA LB film increased from





**FIG.6** Plot of the absorbance of 12-layer LB films against the deposition pressure.

0.08 to 0.22, but the area of the mixed monolayer on the Langmuir trough only decrease 16% (from 281 to 236 cm<sup>2</sup>).

The UV-visible spectra of the mixed LB films of Py and SA (1:3 molar mixture) were comparatively investigated on both hydrophobic and hydrophilic substrates. On a hydrophobic substrate, the mixed Py-SA system shows a red shift of ca. 4.5 nm for the Soret band (436.5 nm) compared with that on the hydrophilic substrate. This observation of differing shift for two different types of substrates may reflect the differing environments experienced by Py molecules. The structural differences between a film on the water surface and that on a solid substrate can influence the aggregation behavior. It has been shown<sup>19</sup> that aggregation of an adsorbed dye on the water surface is to some degree destroyed upon transfer to a substrate, and it was suggested that this was due to the higher roughness of the substrate surface or the modified ion environment. A similar explanation can account for the observation in the present study that the hydrophobic substrate is more favorable for J-aggregation. When transferred to a hydrophilic substrate, the Py aggregates are in contact with the substrate surface. The different ion environment of the quartz surface, as well as any surface roughness have direct influences upon the aggregates.<sup>20</sup> In the case of transfer to a

hydrophobic substrate, the alkyl chains of the Py-SA complex interact with the hydrophobic surface of the substrate. It results in less intrusion of the substrate on the dye aggregates.

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