

## Novel Mixed LB Films of Porphyrin and Phthalocyanine Based on Molecular Recognition

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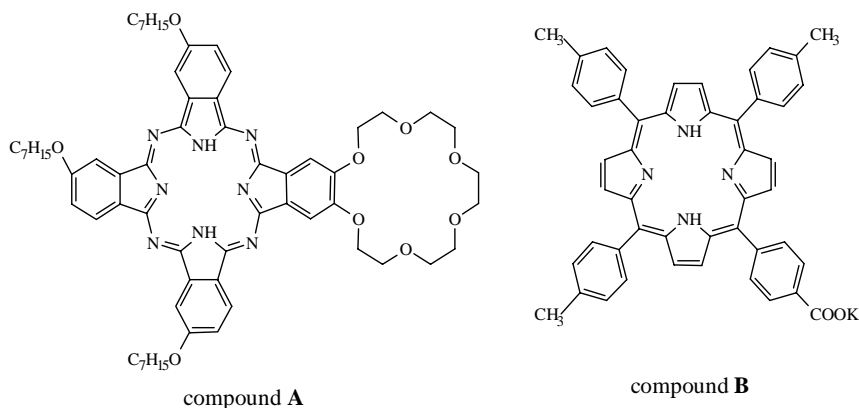
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**Abstract:** The potassium salt of monocarboxylic substituted porphyrin and mono crown ether substituted phthalocyanine can form heterodimer in solution and this kind of heterodimer can be fabricated into highly ordered LB films. The structures of the film were identified by absorption spectra, polarized absorption spectra and low angle X-ray diffraction methods.

**Keywords:** Phthalocyanine, porphyrin, LB film.

Phthalocyanines are synthetic substances related to the naturally occurring porphyrins. Its thermal and chemical stability makes it very useful in molecular electronics<sup>1</sup>. The LB films of phthalocyanine have been widely studied in the past decade. But few reports on the mixed LB films of phthalocyanine and porphyrin have been published<sup>2,3</sup>. Here we report a novel mixed LB film fabricated by depositing porphyrin and phthalocyanine in one layer based on molecular recognition.

**Figure 1.** The structure of compound A and B

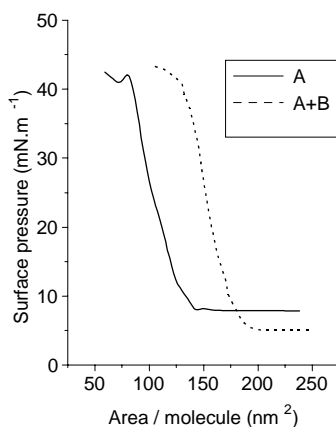


Asymmetrically substituted phthalocyanine **A** and porphyrin **B** are shown in **Figure 1**. **A** was prepared in our laboratory<sup>4</sup>. **B** was prepared following the method of Lind-sey<sup>5</sup>, and identified by <sup>1</sup>HNMR and FD-MS.

On excitation of the solution of equal molar mixture of **A** and **B** in CHCl<sub>3</sub> at 515 nm (phthalocyanine has no absorption at this wavelength, and only porphyrin can be excited), the fluorescence of porphyrin was quenched significantly by phthalocyanine while fluorescence quenching was not observed when **A** was replaced by symmetrically tetra-substituted phthalocyanine without the crown ether substituent. This may be ascribed to the complexation of crown ether rings with potassium ions of porphyrin and to the formation of the heterodimer of porphyrin and phthalocyanine.

The mono-layers were prepared by spreading the solution of **A** and equal molar mixture of **A** and **B** in chloroform on water subphase. From the  $\pi$ -A isotherms the area per molecule of **A** in pure **A** film and the area in the mixed film were calculated to be 1.2 nm<sup>2</sup> and 1.8 nm<sup>2</sup> by estimation respectively. The increase of the mono-molecular area is significant. This indicates that the molecules of **B** in the mixed film are inserted among the molecules of **A**.

**Figure 2.**  $\pi$ -A isotherms of A(—) and A+B(-----) on water surface



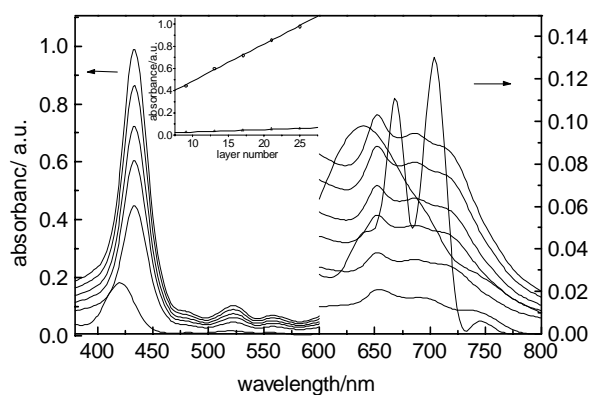
The monolayers can be transferred to the substrates by vertical dipping method. **Figure 3** shows the absorption spectra of the films with different layer numbers. The linear relationship between the absorption of the film at 428 nm and 653 nm and the layer number (inset figure) indicates that the transfer of the monolayer is complete and stable. From the spectra we can also see that the shape of the absorption spectra of **A** in the mixed LB films is different from both that of the LB films containing only **A** and that of **A** in solution. This indicates that **A** in the mixed LB films did not form self-aggregate which was always found in LB films of pure **A** and did not exist in mono-molecule state like that in solution.

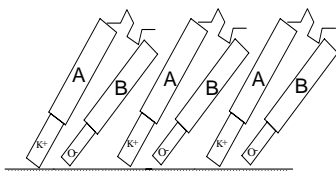
**Table 1.** The orientation angles of the porphyrin and phthalocyanine ring determined from polarized UV-vis absorption spectra\*

	0°			45°			$\theta(^{\circ})$	$\varphi(^{\circ})$
	$A_{//}$	$A_{\perp}$	$D_0(A_{//}/A_{\perp})$	$A_{//}$	$A_{\perp}$	$D_{45}(A_{//}/A_{\perp})$		
A (650nm)	0.172	0.142	1.211	0.205	0.191	1.073	65.8	41.2
B (434nm)	0.916	0.826	1.109	0.998	0.886	1.126	51.8	41.5

\*The refraction index of porphyrin and phthalocyanine film are  $n_{pr}=1.43$  and  $n_{pc}=1.5$  respectively<sup>7</sup>

Following the method of Yoneyama<sup>6</sup>, we can calculate the orientation angles of porphyrin and phthalocyanine rings in the mixed film from the polarized UV-Vis absorption spectra. The results (**Table 1**) indicated that porphyrin rings and phthalocyanine rings possessed slightly different orientation angles. The molecules of porphyrin and phthalocyanine stand in a face to face way. The interaction between porphyrin and phthalocyanine makes the shape of the absorption spectra of the mixed film different from that of the pure phthalocyanine film. Low angle X-ray diffraction experiments indicated that the thickness of the mixed LB films was 1.7 nm, which was smaller than that of the LB films containing pure compound A (2.2 nm). This might be ascribed to the increase of the space among phthalocyanine molecules in which the alkyl chains can be bent freely when the porphyrin molecules are inserted into the layer of phthalocyanine molecules. The structure of the mixed films may be depicted as shown in **Figure 4**.

**Figure 3.** Absorption spectra of the mixed LB films with different layer number (3,5,9,13,17,21) (—), the LB film of pure compound A (-----) and compound A in dilute solution (-----). The inset show the liner relationship between the absorbance of the mixed film at 434nm or 650nm and the layer number

**Figure 4.** Proposed structure of the mixed film of A and B

The fluorescence of porphyrin was quenched completely by phthalocyanine in the mixed film. The studies of the photophysical process between porphyrin and phthalocyanine in the film are now in progress.

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