

## The Macrocycle Plane Orientation of Phthalocyanine and Porphyrin Derivatives on an Air-water Interface

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**Abstract.** Systematic research on monomolecular layer of phthalocyanine (Pc) and porphyrin (Por) derivatives has been finished. In this paper an attention is focused upon the orientation and characterization of molecular macrocycle planes of some Pc and Por derivatives in monomolecular layer by means of the the surface pressure-area ( $\pi$ -A) isotherm method.

### Introduction

Phthalocyanine (Pc) and porphyrin (Por) derivatives, as highly conjugated and symmetric disk-shaped molecules, exhibit a wide variety of physical, chemical and electrical properties. The monolayer and nanometer assembly films of these macrocycle derivatives by means of Langmuir-Blodgett (LB) technique allow functional molecules to be arranged in a highly ordered structure and offer the possibility of application in many aspects[1-3]. Since structural studies of Pc and Por films have fallen far behind to the studies of their physical properties, of particular interests are is focused upon determination of the orientation of molecular macrocycle plane in the film based on the traditional methods and improve technique.

### Experiments and Preparation of the Film

For improving the film forming properties the copper phthalocyanine (CuPc) and Por derivatives synthesized were as following. (1) Symmetrically substituted macrocycles. (2) Asymmetrically substituted macrocycles, as shown in Table 1. CuPc were prepared according to the procedures reported by Snow et al [4-5]. Details of the preparation and characterization were described elsewhere[5-6]. Porphyrins were prepared according to the method reported in our previous paper [7]. KSV-5000 Langmuir trough (Finland) with a Wilhelmy balance and domestic LB trough were employed for the surface pressure-area ( $\pi$ -A) isotherm measurements and the LB films fabrication.

### Studies of the Orientation of Macrocycle Planes

The molecular orientation of various Pc and Por macrocycle plane in ordered films has systemically been studied by the information of area per molecule from  $\pi$ -A isotherm. Among these  $\pi$ -A isotherms representative isotherm of CuPc[dtpp]<sub>4</sub> and TPIATPP are shown in Fig. 1. The collapse pressure of molecules and the area per molecule obtained by extrapolating the  $\pi$ -A curve (or the limiting area at zero pressure) and other properties of CuPc and Por derivatives listed in Table 2. It is seen that the area occupied by per molecule in the films of asymmetrically substituted CuPc is larger than that of symmetrically substituted CuPc, where the former differs from the latter in possessing long and asymmetrically hydrophilic substituents. These polar groups would render the greater adhesion of macrocycle plane face to the water and lesser cohesion between ring planes. As the minimum plane area occupied by macrocycle of CuPc molecule would be 1.6 nm<sup>2</sup> and the surface area of the ring edge is 0.4-0.8 nm<sup>2</sup> [8]. According to the area per molecule found in our study, the monomolecular area for CuPc in film are less than that of real CuPc macrocycle plane area, and the measured CuPc area of 0.45-1.2 nm<sup>2</sup> is incompatible with an arrangement of the macrocycle plane

parallel to the water surface for which values near 1.6 nm<sup>2</sup> are measured. In the same reason the rings are not perpendicular to the surface either. These indicate a tilted of the planes of macrocycle with respect to one another as sketched in Fig. 2. For porphyrins, the area occupied by per molecule in the films of natural source porphyrin-asymmetrically PP and near symmetrically substituted Porphyrin C is similar. In addition for case of four symmetrically substituted groups, the area occupied by per molecule in the films of TPIATPP is larger than that of CdOCITPP with substituted central metal ion-Cd, where the former differs from the latter in possessing long substituent chains.

**Table 1. Schematic structure of the copper phthalocyanine and Porphyrin derivatives**

$\text{CuPc} (-\text{COOCH}_2\text{CH}_2\text{OCH}_3)_4$	$\longrightarrow$	$\text{CuPc}[\text{mec}]_4$
$\text{CuPc} (-\text{COOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$	$\longrightarrow$	$\text{CuPc}[\text{bec}]_4$
$\text{CuPc} (-\text{O}-\text{C}_6\text{H}_4-\text{C}_5\text{H}_{11})_4$	$\longrightarrow$	$\text{CuPc}[\text{dtp}]_4$
$\text{CuPc} (-\text{O}-\text{C}_6\text{H}_4-\text{C}_5\text{H}_{11})_3 (-\text{O}-\text{C}_6\text{H}_4-\text{COOH})$	$\longrightarrow$	$\text{CuPc-cp}[\text{dtp}]_3$
$\text{Por} (-\text{CH}(\text{CH}_3)-\text{S}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH})$	$\longrightarrow$	<b>Porphyrin C</b>
<b>5,10,15,20-tetra-(p-iso-pentyloxy-carbonyl-benzene) porphine</b>	$\longrightarrow$	<b>TPIATPP</b>
$\text{Por} (-\text{CH}=\text{CH}_2)$	$\longrightarrow$	<b>PP</b>
<b>5,10,15,20-tetrakis(4-Cl-phenyl)-21H, 23H-porphine Cd</b>	$\longrightarrow$	<b>CdOCITPP</b>

Some explanations of above is as follows: 1. While Pc and Por molecules are laid on the water surface at zero pressure, the macrocycle prefer to ‘lie flat’. Because in initial spreading process on the air-water ‘lie flat’ tendency of the ring plane is produced by the intermolecular and varied external force function, especially the hydrophilic carboxyl group have tend to water surface. This can be deduce through the analysis of construction of the molecular model and mechanics. It is that the equilibrium position of the macrocycle plane model should indeed lie flat, and later as surface pressure increases, the hydrophilic carboxyl group stays in the water while the rest of the molecule is pushed up by external force. Final the plane becomes ‘tilted’. 2. The maintenance of such a vertical orientation of the ring planes in the presence of the water surface implies that there are strong attractive interactions between the rings that tend to make them assume a card-pack orientation. Hence, when the surface pressure increases further, the ring plane model only becomes tightly under the mechanics rules.

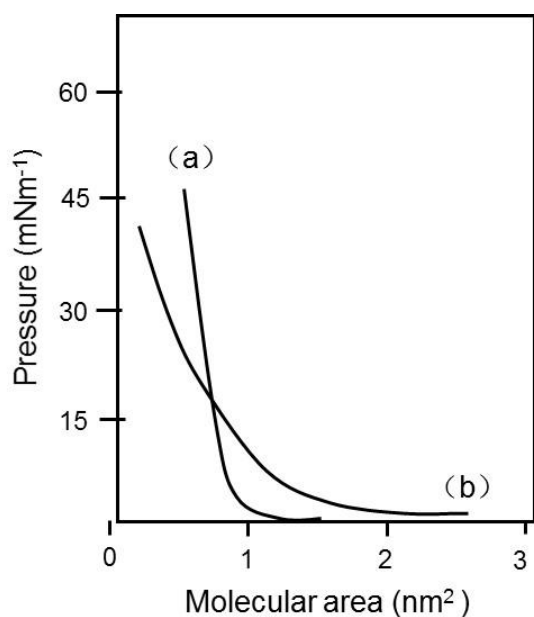


Fig. 1 A normal surface pressure-area (p-A) isotherm of Pc and Por ; (a) CuPc[dtpp]<sub>4</sub> ; (b) TPIATPP.

Table 2. Parameters of the  $\pi$ -A isotherm about CuPc and Porphyrin layer on air-water interface

Samples	Collapse Pressure	Select Transfer	The occupied area per molecule (nm <sup>2</sup> )		
			Under Zero Pressure	Under Collapse Pressure	Under Transfer Pressure
	mNm <sup>-1</sup>	mNm <sup>-1</sup>	Pressure	Pressure	Pressure
CuPc[mec] <sub>4</sub>	36	25	1.01	0.45	0.70
CuPc[bec] <sub>4</sub>	36	25	1.02	0.51	0.72
CuPc[dtpp] <sub>4</sub>	43	30	1.01	0.48	0.64
CuPc-cp[dtpp] <sub>3</sub>	44	30	1.20	0.45	0.75
Porphyrin C	43	30	1.15	0.41	0.51
TPIATPP	42	30	1.60	0.22	0.78
PP	44	25	1.20	0.40	0.76
CdOCITPP	51	25	0.64	0.20	0.45

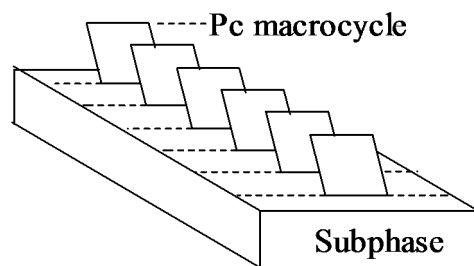


Fig. 2 Sketch of the arrangement of CuPc macrocycle

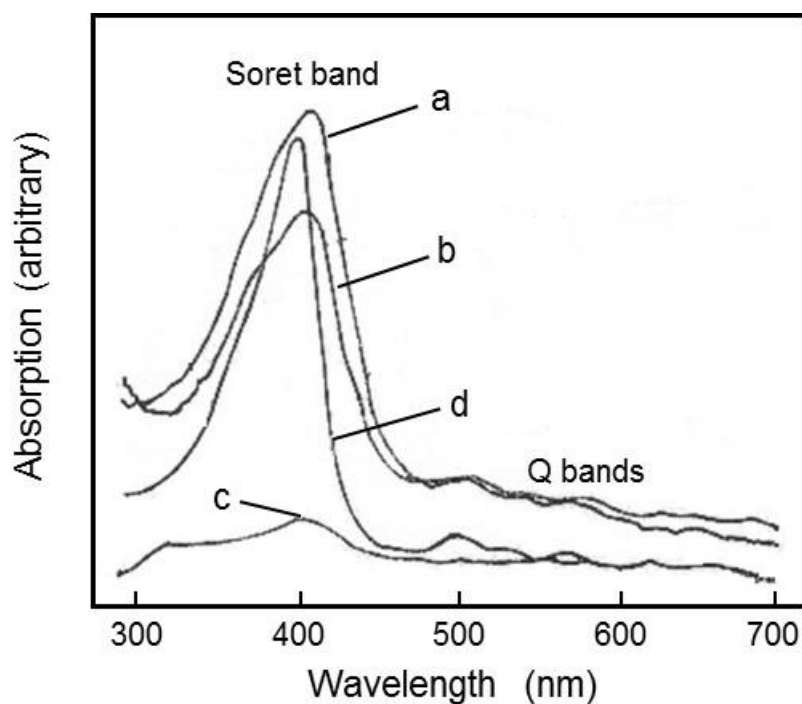


Fig. 3 UV-vis absorption spectra of Porphyrin C in multilayers and solution. a. 17 layers; b. 11 layers; c. 5 layers; d. solution.

### Spectroscopic Study

One of the striking characteristics of ordered organic molecular films is the orientation of the layer molecule, which determines the functional feature of the films and continues to attract research interests. The plane dichroism of Pc and Por derivative films have further been characterized by us using UV-Vis, IR and fluorescence spectra [5, 9]. In the case of UV-vis absorption of Phthalocyanine (Pc) and Porphyrin (Por) derivative films, while the number of the layers is below three, the absorption is very weak comparing with that of solution. Representative absorption spectra of

Porphyrin C are shown in Fig. 3. The absorption spectra of monolayers and multilayers of porphyrins exhibit a distinct red shift of the Soret band relative to its value in solution samples. There is also a red shift of a smaller magnitude in the Q bands. The Soret bands exhibit significant broadening compared with those in solution. These shifts and broadenings are typical of aggregates of organic molecules for both porphyrins and phthalocyanines .

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