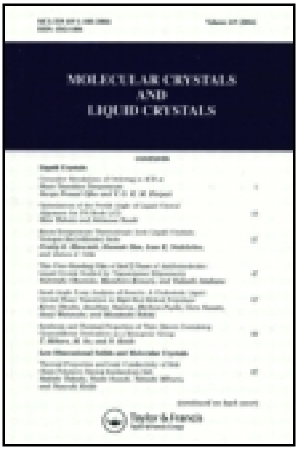

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Optical Studies of the Monolayer Films of Diazole-Containing Porphyrins at the Air-Water Interface

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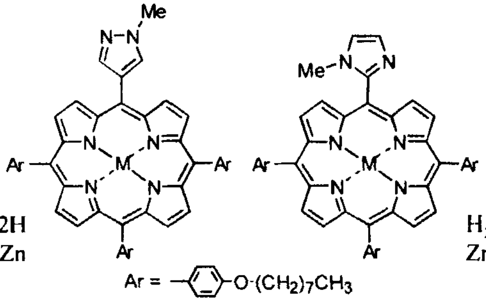
Optical properties of the monolayers of 5-(1-methylimidazol-2-yl)- 10,15,20-tris(*p*-octyloxyphenyl)porphyrin, 5-(1-methylpyrazol-4-yl)-10,15,20-tris(*p*-octyloxyphenyl)porphyrin and their zinc(II) complexes have been studied. The π-A isotherms and UV-vis spectra have revealed that the zinc(II) complexes form coordination assemblies between peripheral nitrogen atom and central zinc(II) ion at the air-water interface with very tight molecular packing.

Keywords: porphyrin; pyrazole; imidazole; monolayer; coordination; supramolecular chemistry

INTRODUCTION

Porphyrin derivatives have been extensively studied because of their potential capability for photoelectronic applications such as artificial light-harvesting system, photoinduced molecular switches and photonic wires[1]. To realize such photoelectronic applications, it has been of great importance to control the mutual orientation among the porphyrin molecules. Over the past two decades, the Langmuir-Blodgett (LB) method has been widely used to construct the ordered films of porphyrins and many attempts have been devoted to handle the molecular orientation. Recently, five-membered rings such as pyrazole and imidazole have been shown to be useful functional groups to construct porphyrin assembly by intermolecular hydrogen bonding and coordination[2-4]. In the present study, we extended this approach and studied the formation of monolayers of the porphyrins having one pyrazole (H_2PzP) and imidazole (H_2ImP) ring and its zinc(II) complexes (ZnPzP and ZnImP) with an aim of constructing stable and ordered monolayers using intermolecular coordination.



H_2PzP : M=2H
ZnPzP : M=Zn

H_2ImP : M=2H
ZnImP : M=Zn

EXPERIMENTAL

The diazolylporphyrins, H_2PzP and H_2ImP were synthesized by the Adler-Longo method using pyrrole, *p*-octyloxybenzaldehyde, and corresponding diazolecarboxaldehyde (i.e. 1-methylpyrazole-4-carboxaldehyde or 1-methylimidazole-2-carboxaldehyde), followed by zinc(II) insertion using a conventional method.

The surface-area (π-A) isotherms of these porphyrins were measured using an NL-LB-MWC trough (Japan Laser Electronics Lab. Co. Japan). The monolayers were formed by spreading the chloroform solution of porphyrins (1mg/mL) onto the Millipore purified water subphase (17.8 MΩ•cm) with a microsyringe at 10±1°C. After spreading, the monolayer was allowed to equilibrate for at least 5 min, then compressed at a rate of 10cm^2/min. The electronic absorption spectra were recorded in chloroform solution with a V-570 spectrophotometer (Jasco, Japan) and for the monolayers with an IMUC 7000 spectrophotometer(Otsuka Electronics Co. Japan).

RESULTS AND DISCUSSION

Monolayers of Metal-free Porphyrins

The π-A isotherms of H_2PzP and H_2ImP on pure water are shown in Figure 1a. Reproducible curves were obtained, and stable monolayers were formed. The mean molecular areas of H_2PzP and H_2ImP were estimated to be 95 and 124 $Å^2$, respectively. It is known that the molecular area of the porphyrin core is ca. 225 $Å^2$ based on the space filling CPK model. In this study, all of the porphryins showed smaller molecular areas than 225 $Å^2$, indicating that the porphyrin cores are tilted with respect to the water surface and/or partially overlapped. The mean molecular areas of these metal-free porphyrins are similar to that of reported mono-pyridylporphyrin (115 $Å^2$) having three similar hydrophobic octadecyloxyphenyl groups but one pyridine ring as a hydrophilic group instead of the diazole ring[5]. H_2ImP showed slightly larger molecular area (124 $Å^2$) than H_2PzP, suggesting that the difference in the position of nitrogen atoms in the diazole ring is reflected in the molecular orientation. From these comparisons, it follows that the methylpyrazole or methylimidazole has much the same degree of hydrophilicity as the conventional pyridyl group.

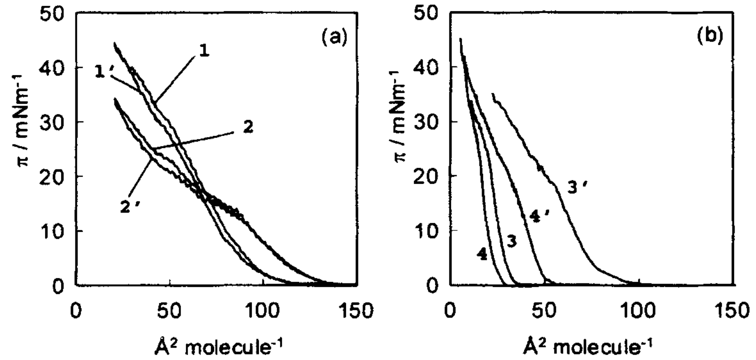


FIGURE 1 π-A isotherms of diazolylporphyrins. **1** : H_2PzP, **2** : H_2ImP, **3** : ZnPzP, **4** : ZnImP. Curves with a prime letter denote the isotherms spreaded in the presence of excess 1-methylimidazole.

The absorption spectra of H_2PzP and H_2ImP are very similar to each other in solution and at the air-water interface(Figure 2a and 2b). In chloroform solution, these porphyrins showed a sharp Soret band around 420nm typical of metal-free porphyrins. At the air-water interface, red shifts by 15nm were observed in the Soret band compared with those in solution, but the dependence of the peak position on the surface pressure was not observed. These shifts are larger than those caused by a change of a non-polar to a polar environment and may be interpreted in terms of the exciton model developed by Kasha[6]. One plausible model for the observed red shifts is the head-to-tail type aggregate which has been observed for several metal-free porphyrin monolayers[7].

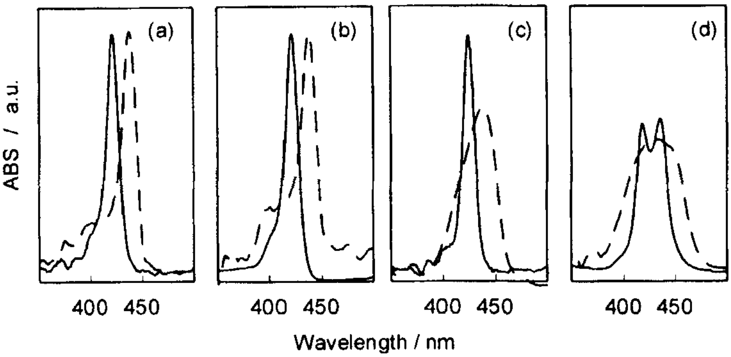


FIGURE 2. Absorption spectra of diazolylporphyrins in chloroform solution (solid lines) and at the air-water interface(broken lines). (a): H_2PzP, (b): H_2ImP, (c): ZnPzP, (d): ZnImP.

Monolayers of Zinc(II) Porphyrins

Zinc(II) porphyrins are known to adopt 5-coordinated structure and their coordination assemblies using various types of ligands have been reported[8] though many of them dissociate in polar environment such as methanol or water. However, zinc(II) porphyrins studied here, especially ZnImP, showed an unusual trend at the air-water interface. The mean molecular areas for these zinc(II) porphyrins are 22 and 31 $Å^2$ for ZnImP and ZnPzP, respectively(Figure 1b). These values are surprisingly small for this class of compounds because the molecular area of the porphyrin would be *ca.* $90Å^2$ if the porphyrin ring lies vertical to the aqueous surface[9]. What makes the molecular areas so small? One possible explanation for the unusually reduced molecular area may be the intermolecuar coordination between central zinc(II) ion and nitrogen atom in the peripheral diazole ring, which may cause very tight molecular packing. To examine the existence of coordination at the air-water interface, an excess (500 eq.) of methylimidazole was added to the spreading porphyrin solutions. In the presence of these ligands, the molecular areas of ZnImP or ZnPzP were drastically increased, though the molecular area and the π-A isotherm profile of H_2ImP and H_2PzP were unchanged (Figure 1). These results strongly indicate the intermolecular coordination between central zinc(II) ion and nitrogen atom in the peripheral imidazole or pyrazole groups at the air-water interface.

Before considering the possible molecular orientation at the air-water interface, it may be important to note the self-assembly of these zinc(II) porphyrins in chloroform solution (spreading solutions). In chloroform, ZnImP showed the split Soret band, which is the same spectral pattern as that reported for zinc(II) bisimidazolylporphyrin that forms a mutually coordinated dimer in solution[2]. Though the existence of intermolecular coordination of ZnPzP was uncertain from the absorption spectra, formation of a coordinated trimer at the higher concentration (above ca. 10^{-4}M) is indicated from the our rescent study on the self-assembly of zinc(II) monopyrazolylporphyrin using ^{1}H NMR spectra[11]. Consequently, formation of specific coordination assembly (ZnImP dimer and ZnPzP trimer) was suggested in the spreading solution because the concentration is relatively high (*ca.* 0.9mM). On the other hand, though the coordination in the monolayer was indicated, these zinc(II) porphyrins showed an extremely broad spectral pattern at the air-water interface that is quite different from those in solution (Figure 2c and 2d). These spectral changes suggested that the self-assembly in spreading solution is not maintained at the air-water interface. As expected from the π-A isotherms, the broad spectral profile was ascribed to the intermolecular interaction caused by coordination at the air-water interface because the spectra became sharp when spread with the excess of methylimidazole or methylpyrazole. From these results, formation of coordination assemblies with different structures compared with those in solution is indicated for the monolayers of ZnPzP and ZnImP, which is expected as a coordination polymer structure. The possibility for another film structure, such as that composed by ZnImP dimer, can not excluded though it seems unlikely favored considering the hydrophilic-hydrophobic balance of those assemblies.

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