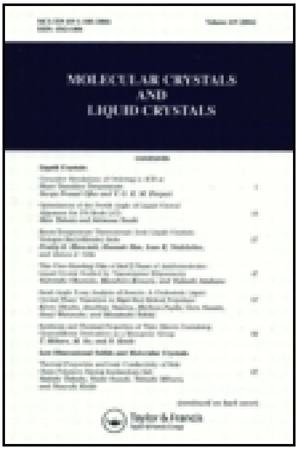

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Orientation Control of Porphyrin in the Mixed Monolayer at the Air-Water Interface by Adding Long-Chain n-Alkanes

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ORIENTATION CONTROL OF PORPHYRIN IN THE MIXED MONOLAYER AT THE AIR-WATER INTERFACE BY ADDING LONG-CHAIN *N*-ALKANES

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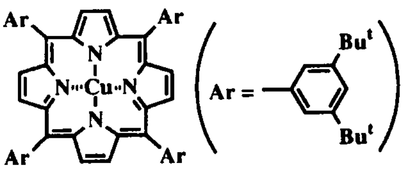
Abstract We have reported that a small amount of long chain *n*-alkane can drastically change the orientation of copper porphyrin in the mixed LB films. In this study the orientation of porphyrin in the mixed monolayer with and without *n*-hexatriacontane at the air-water interface was examined. The p-polarized reflection spectrum of the monolayer containing *n*-hexatriacontane at 45° incidence showed two peaks in the Soret region as in the spectra of the corresponding LB film, suggesting that the orientation of porphyrin in the monolayer is similar to that in the LB film. Further, the λ_{max} and the intensity ratio of these peaks did not change during the compression, indicating that the orientation of the porphyrin is determined before the film compression and preserved during the compression and the film transfer.

INTRODUCTION

Orientation control of functional molecules in LB films is one of the most attracting subjects in this field.[1-3] We have reported that the orientation of the porphyrin without long alkyl chains in the mixed LB film with cadmium icosanoate can be controlled by adding a small amount of *n*-alkane such as *n*-hexatriacontane ($CH_3(CH_2)_{34}CH_3$, abbreviated as HA hereafter) or *n*-octadecane.[4,5] Electron spin resonance and polarized UV/vis absorption spectroscopies have revealed that the macrocycle plane of the copper porphyrin is almost perpendicular to the film surface in the LB film containing HA whereas the macrocycle plane tilts in the LB film without *n*-alkane.

In this paper we study the orientation of porphyrin in the mixed monolayer at the air-water interface, *i.e.*, the orientation before the film transfer, to investigate at which stage the interaction between porphyrin and HA becomes significant and the orientation of porphyrin is controlled.



PM

EXPERIMENTAL

Meso-tetrakis(3,5-di-*t*-butylphenyl)porphinatocopper(II)[6] (abbreviated as PM hereafter) was used in this study. A chloroform solution of molar mixing ratio PM/icosanoic acid/HA = 1.5/10/x (x = 0 or 0.5) was spread onto an aqueous subphase of pH 6.0, containing 4.0×10^{-4} M of $CdCl_2$ and 5.0×10^{-5} M of $KHCO_3$ at 17°C. All the monolayer experiments were performed on a Lauda Filmwaage. The reflection spectra were obtained with an Otsuka Electronics IMUC7000 multi channel photodetector. P- or s-polarized light was introduced to the water surface with an optical fiber at 45° incidence. The spectra were recorded as the ratios of the reflection intensities in the presence and absence of the mixed monolayer for p- and s-polarized light independently.

RESULTS AND DISCUSSION

Orientation of PM in the Mixed Monolayer with and without HA at the Air-Water Interface

Figure 1 shows the polarized reflection spectra of the monolayer with the mixing ratio 1.5/10/0.5 at 25 mN m^{-1}. A positive and an negative band were observed at around 425 and 400 nm, respectively, in the p-polarized spectrum. In the s-polarized spectrum only a positive band at around 425 nm was observed in this region.

The orientation and the aggregate structure of PM and HA in the monolayer are similar to those in the LB film. Negative and positive Δ(reflectance) with p-polarized light shows that the transition moments of the bands are rather perpendicular and parallel to the water surface, respectively.[7] The transition moments of the 400-nm and 425-nm bands are thus considered to be rather perpendicular and parallel, respectively, with respect to the water surface. These two bands originating from the splitting of the Soret band have been observed in the p-polarized UV/vis absorption spectrum of a four-layer LB film with the mixing ratio 1.5/10/0.5 (Figure 1, inset), showing that the aggregate

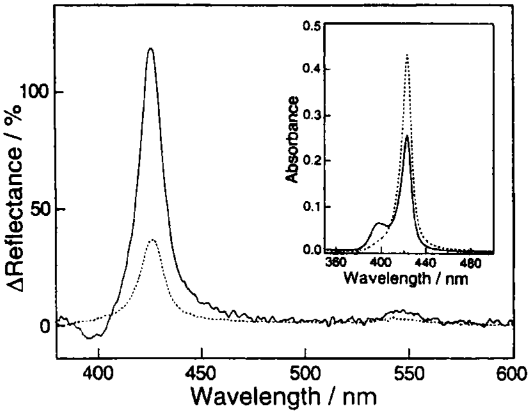


FIGURE 1 UV/vis reflection spectra of the monolayer with the mixing ratio PM/C20/HA = 1.5/10/0.5 at 45° incidence: p-polarized (solid line) and s-polarized (dashed line) spectra. The inset shows the absorption spectra of the corresponding four-layer LB film at 45° incidence: p-polarized (solid line) and s-polarized (dashed line) spectra.

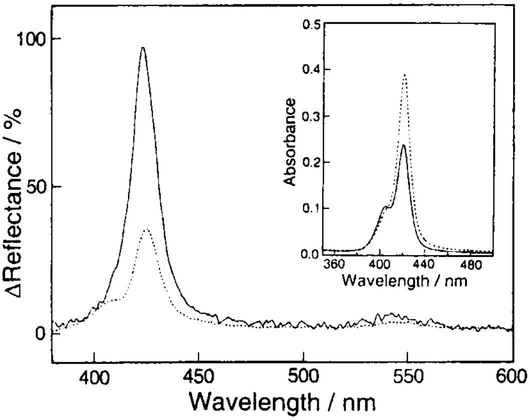


FIGURE 2 UV/vis reflection spectra of the monolayer with the mixing ratio PM/C20 = 1.5/10 at 45° incidence: p-polarized (solid line) and s-polarized (dashed line) spectra. The inset shows the absorption spectra of the corresponding four-layer LB film at 45° incidence: p-polarized (solid line) and s-polarized (dashed line) spectra.

structure of PM is substantially the same in the monolayer and the LB film. Qualitatively the same orientation of the transition moments of these bands has been concluded in the LB film using ESR and polarized absorption spectroscopies.[4] Thus the orientation of PM is unchanged during the film transfer.

The orientation and the aggregate structure of PM in the monolayer without HA are similar to those in the LB film. Intense reflection was observed at around 420 nm in both of the p-polarized and s-polarized spectra. No negative band is, however, seen in the p-polarized spectrum whereas a shoulder is recognized at around 405 nm in the s-polarized one (Figure 2). The transition moment of the 405-nm band is considered to be rather inclined from the normal of the water surface and the disappearance of the 405-nm band in the p-polarized spectrum is probably due to the overlapping with the intense 420-nm band. The results agree well with those of the corresponding LB film since in the p-polarized absorption spectrum, an out-of-plane and an in-plane band were also observed at around 405 nm and 420 nm, respectively (Figure 2, inset). The out-of-plane transition moment is inclined in the LB film without HA,[4] which is similar to the monolayer case.

The results show that the orientation of PM in the mixed monolayers with and without HA at the air-water interface is similar to that in the corresponding LB films: the orientation of PM is qualitatively preserved during the film transfer.

Orientation Change of PM during the Film Compression

The orientation of PM was found to be preserved during the film compression. Figure 3 shows the p-polarized reflection spectra of the mixed monolayer of the mixing ratio 1.5/10/0.5 with various surface area. The λ_{max} and the intensity ratio of the two bands remain unchanged during the compression. Further, intense reflection due to an island structure was occasionally observed even when the area is much larger: the shape of the reflection spectrum is similar to those in Figure 2. These results indicate that the

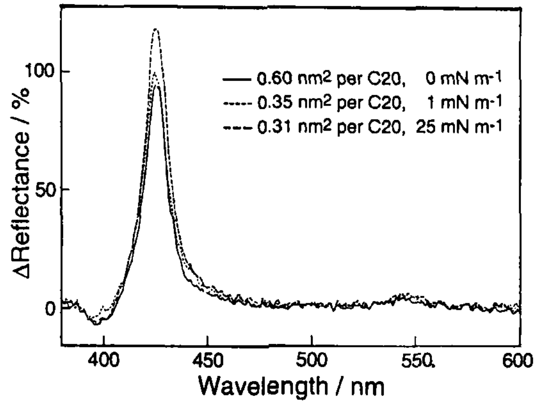


FIGURE 3 P-polarized UV/vis reflection spectra of the monolayer with the mixing ratio PM/C20/HA = 1.5/10/0.5 at 45° incidence with various surface area. The intensity of the reflection spectrum at 0 mN m^{-1} changes continually due to the movement of the floating islands on the water surface.

orientation of PM in the mixed monolayer does not change throughout the film compression: even in the floating islands seen before the film compression, the orientation of PM is similar to that in the LB film. The specific intermolecular interaction between PM and HA is significant and the orientation of PM is controlled before the compression of the film, probably during the evaporation of the solvent. The above results rule out the possibility that the tilt angle of PM changes due to the rearrangement of the molecules during the compression.

CONCLUSIONS

This study shows that the specific intermolecular interaction between PM and HA seems to be significant before the film compression and that the orientation of PM is determined at this stage, probably during the evaporation of the solvent. This orientation is preserved during the film compression and the film transfer onto solid substrates. The interaction between PM and HA seems to be strong in the sense that the orientation and the aggregate structure of PM do not depend much on the substrate to which the monolayer or the LB film is attached.

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