

Side-Chain-Controlled Aggregation of Amphiphilic Porphyrins in Thin Langmuir-Blodgett Films

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This paper is dedicated to Professor Tohru Takenaka on the occasion of his retirement.

Aggregation behaviors of amphiphilic porphyrins with one (THPPH1), two (*cis*-THPPH2 and *trans*-THPPH2), three (THPPH3) and four (THPPH4) hexadecyloxyphenyl chains have been investigated in Langmuir-Blodgett (LB) films by means of UV-vis absorption spectroscopy and Cu (II) metallation. For the LB films of THPPH1, *cis*- and *trans*-THPPH2, the Soret absorptions are red-shifted (434nm) relative to the solution value (420nm), where as the Q-state absorptions are essentially unaltered. For the films of THPPH3 and THPPH4, the Soret bands are split into two components; one is red-shifted (440nm) and the other blue-shifted (398nm) with respect to the dilute solution value. The spectral data are interpreted in terms of exciton interactions between the porphyrin Soret excited states and are used to deduce the molecular arrangement of the porphyrin macrocycles in the films. When transferred from the monolayers on aqueous Cu (II) subphase, the LB films of THPPH1, *cis*-THPPH2, *trans*-THPPH2 and THPPH3 give the Q-state bands at 552 and 518 nm, being characteristic of copper-porphyrin complex, and the film of THPPH4 gives the Q-state absorption bands identical with those of its free base form. Time dependence of Cu (II) metallation of the LB films of these amphiphilic porphyrins demonstrate the metallation rate on the order of THPPH1 > *cis*-THPPH2 > *trans*-THPPH2 > THPPH3 > THPPH4.

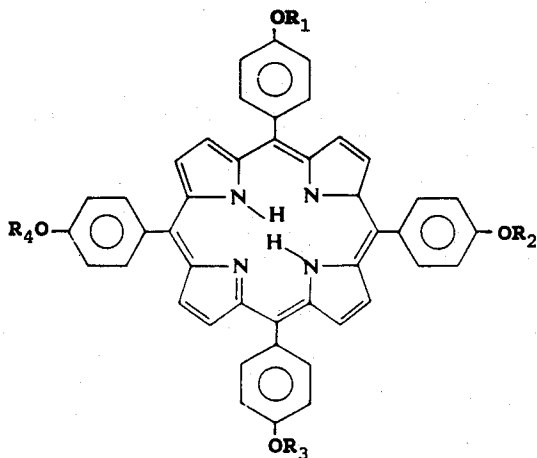
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INTRODUCTION

In recent years, the Langmuir-Blodgett (LB) films composed of porphyrins attract considerable interest since the ordered assemblies of porphyrinic molecules provide a promising way to facilitate extremely fast and vectorial electron transfer as occurred during biological photosynthesis [1,2]. The electronic structure of the assemblies, which directly determines the primary charge separation, is greatly dependent upon molecular aggregation and interaction in the LB films [3,4]. Most significant aspect of the electronic structure of porphyrin aggregates is excitonic state which is dependent on the stacking fashion and the extent of molecular order in the aggregates. Various exciton interactions and related molecular arrangement in porphyrin aggregates in LB film [5-10] have been investigated but few attention has been paid to the relationship between the aggregation behavior and side-chain substitution on porphyrin macrocycle. On the other hand, the molecular aggregation and interaction in LB films are closely related to those in spread monolayers on the water surface. Therefore, studies of molecular states in spread monolayers are essential to understand the molecular

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THPP: $R_1=R_2=R_3=R_4=H$

THPPH1: $R_1=CH_3(CH_2)_{15}^-$, $R_2=R_3=R_4=H$

cis-THPPH2: $R_1=R_2=CH_3(CH_2)_{15}^-$, $R_3=R_4=H$

trans-THPPH2: $R_1=R_3=CH_3(CH_2)_{15}^-$, $R_2=R_4=H$

THPPH3: $R_1=R_2=R_3=CH_3(CH_2)_{15}^-$, $R_4=H$

THPPH4: $R_1=R_2=R_3=R_4=CH_3(CH_2)_{15}^-$

aggregation and interaction in LB films. In this paper we systematically prepare hydroxyphenyl porphyrins with one (THPPH1), two (*cis*-THPPH2 and *trans*-THPPH2), three (THPPH3) and four (THPPH4) hexadecyl chains, and examine the aggregation behaviors of these long-chain substituted porphyrins in spread monolayers and LB films by means of UV-vis absorption spectroscopy and Cu(II) metallation.

EXPERIMENTAL

The sample of *meso*-tetra (*p*-hydroxyphenyl) porphyrin (THPP) was prepared by condensation of *p*-hydroxybenzaldehyde with pyrrole according to a literature procedure [11,12]. The absorbance of Soret band of the sample at 420 nm assured a purity higher than 98%. To prepare the long-chain substituted porphyrins, the THPP was hexadecylated by 1-bromohexadecane in ethanol solution of potassium hydroxide (reflux for 48 h). The products, *meso*-(hexadecyloxyphenyl) porphyrins, were separated and then purified by means of thin layer chromatography over silica gel G using a mixture solvent of chloroform and ethanol as eluent for four times. The structures of the amphiphilic porphyrins, THPPH1, *cis*-THPPH2, *trans*-THPPH2, THPPH3 and THPPH4 were characterized by chemical analysis, mass spectroscopy, infrared and H-NMR spectroscopy [13].

The π -A isotherms were measured on a KSV-5000 computer-controlled film balance system at 18°C. Water (pH 5.2, resistivity 18M Ω /cm) was doubly distilled after passing through an ion-exchange resin column. Each π -A curve was reproducible. Cu (II) ion incorporation into the spread monolayers on water surface was performed by injecting aqueous CuSO₄ solution under monolayer a surface pressure maintained at set values. The concentration of Cu (II) ion in subphase was estimated to be 10⁻³M.

LB films were deposited on both sides of quartz plates (35×9×1mm) which had been cleaned by successive sonication in ethanol, acetone, chloroform and distilled water for 10 min each, and soaked in reflux isopropanol for four hours. To study the incorporation of Cu (II) ion into the LB films, the plate with LB film was first immersed in 10⁻³M aqueous solution of CuSO₄ for a given period, and then was subject to the UV-vis spectroscopic measurement.

The UV-vis spectra were recorded on a Beckman DU-7 spectrophotometer.

RESULTS AND DISCUSSION

Surface Pressure-Area Isotherms

Let us first examine the π -A isotherms of the amphiphilic porphyrins on pure water surface since they offer a basic clue to explore the physical states of the porphyrin molecules in the surface spread monolayers. Figure 1 show the π -A isotherms of monolayers of the five amphiphilic porphyrins on pure water. The π -A isotherm of THPPH4 is indicative of a condensed film at higher surface pressure. The extrapolated molecular area is 48Å², being consistent with that observed for the monolayer of 5, 10, 15, 20-tetrakis [4-(1-octyloxy) phenyl] porphyrin [4]. This area value is close to the long-side cross sectional area (44 Å²) perpendicular to the porphyrin macrocycle plane [4], suggesting that the porphyrin plane of THPPH4 tends to stand, rather than lie, on the water surface.

Monolayer of THPPH3 exhibits a liquid-like expanded phase with no obvious collapse for surface pressure up to 60 mN/m. Similarly, the π -A isotherm measured for *cis*-THPPH2 shows a liquid-like expanded phase, shifting a little toward lower surface area region relative to that of THPPH3. These facts predict that THPPH3 and *cis*-THPPH2 molecules do not form tightly condensed aggregates in the spread monolayers.

The π -A isotherms for *trans*-THPPH2 and THPPH1 monolayers display a big slope at higher surface pressure region with collapse pressure at ca. 48 and ca. 36 mN/m, respectively. These two π -A isotherms shift appreciably to the larger surface area side with respect to that of THPPH4. This implies that *trans*-THPPH2 and THPPH1 monolayers are in a more expanded state as compared with that of THPPH4. The extrapolated areas are $A=82 \text{ \AA}^2$ for *trans*-THPPH2, and 87 \AA^2 for THPPH1, respectively, suggesting that macrocycle plane tends to lie on the surface of water. This contrasts distinctly with the case of THPPH4 monolayer mentioned above.

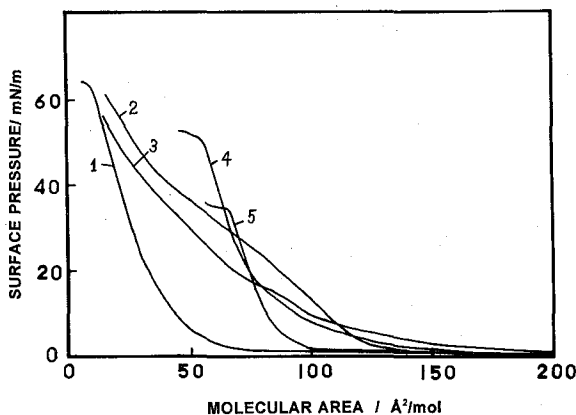


Fig. 1. π -A isotherms of the amphiphilic porphyrin monolayers on pure water: 1, THPPH1; 2, THPPH3; 3, *cis*-THPPH2; 4, *trans*-THPPH2; 5, THPPH1

Absorption Spectra of LB films

Figure 2 shows UV-vis absorption spectra of 1-monolayer LB films of the five amphiphilic porphyrins transferred from the corresponding monolayers on pure water. The spectrum of chloroform solution (10^{-6}M) of THPPH4 is also displayed in this figure for comparison. The spectra are divided into two wavelength regions: Soret band region from 350 to 450 nm and Q-band region from 450 to 700 nm. It is seen that the spectral feature of the Soret band varies considerably with the substituted site and number of the side chain on the porphyrins, and that the Q-band presents a four-peak pattern irrespective of the porphyrin species which is characteristic of free base-porphyrin [11-13].

Soret band maximum for THPPH4 in the chloroform solution is observed at 420 nm which is identical with that for the other four porphyrins (not shown), being typical of the molecularly dispersed state. In the LB films, the Soret band shifts to 434 nm with half band width of 31.3 nm for THPPH1, to 432 nm with half band width of 25.6 nm for *cis*-THPPH2 and to 432 nm with half band width of 27 nm for *trans*-THPPH2, respectively. These spectral data can be used to analyze the molecular arrangement in the porphyrinic aggregates in the

LB films. According to the molecular exciton theory established by McRae and Kasha [14], the blue shift relative to the monomer band corresponds to linear aggregate with transition dipoles parallel to each other and ordered perpendicular to the stacking direction (so-called H-aggregates). On the other hand, the red shift results from the chromophore arrangement with dipoles parallel to each other but greatly inclined from the normal to the stacking direction (so-called J-aggregates). The wavelength shift due to the exciton formation depends on the center-center distances between the interacting dipoles, their relative orientations and the number of monomers in the aggregates. Therefore, the red shifts observed for the LB films of THPPH1, *cis*-THPPH2 and *trans*-THPPH2 indicate that the porphyrin macrocycles aggregate in J-like fashion. Furthermore, the Soret bandwidth at half-height can be employed as a measure of the molecular order in the aggregate. In principle, the higher molecular order

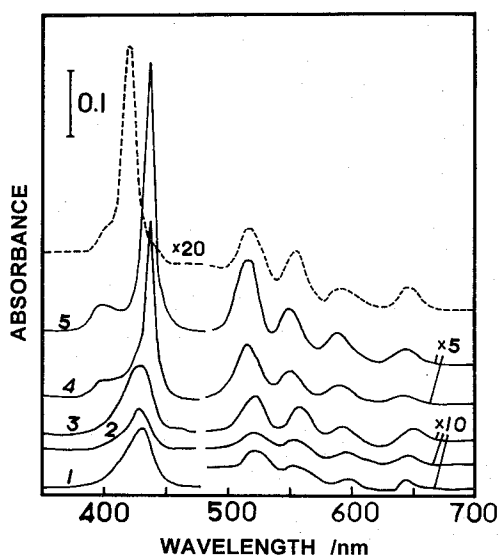


Fig. 2. UV-vis absorption spectra of 1-layer LB films of the amphiphilic porphyrins deposited on quartz plates: 1, THPPH1; 2, *cis*-THPPH2; 3, *trans*-THPPH2; 4, THPPH3; 5, THPPH4. Spectrum of THPPH4 in chloroform solution (10^{-6} M) is also displayed for comparison (dashed line).

corresponds to sharper Soret band and vice versa [3]. In contrast, for the THPPH3 and THPPH4 LB films, the Soret absorption is split into two bands: a strong and sharp band at 440 nm, and a weak band at 398 nm, whereas the Q-state absorption feature remains unaltered with respect to that of the monomeric porphyrin (see Fig. 2). These results are simi-

lar with that observed for LB films of several four-chain substitute porphyrins and has been interpreted by formation of exciton states in which two degenerated Soret-state transition dipoles perpendicular each other in a porphyrin macrocycle result in two absorptions, one is red shifted while the other blue shifted relative to the monomeric absorption [3,4]. The aggregate with such a kind of exciton manifold was depicted as so-called stack-of-card model in which porphyrin macrocycles are stacked in such a way that one dipoles arranged in mutually parallel fashion, which corresponds to the red shifted band, while the other in head-to-tail, which corresponds to the blue-shifted band. These arguments allow a conclusion that a well ordered porphyrin aggregate is obtained for THPPH3 and THPPH4 by LB technique, which is consistent with the consideration resulted from the water surface monolayer experiment stated above.

Incorporation of Cu(II) Ion into Monolayers and LB Films.

For the purpose to further examine the aggregation of the porphyrin in the spread monolayers and LB films, the incorporation of Cu(II) ion into these porphyrinic assemblies are investigated. Subsequent to the injection of aqueous CuSO₄ solution under the spread monolayer on water surface maintained at a set surface pressure, the monolayer was transferred onto a quartz plate. Since the metallation of porphyrins causes a spectral change in the Q-band region, whether Cu(II) ions incorporate into the porphyrins in the monolayer can be inspected by the UV-vis absorption spectrum of the respective film transferred from the surface monolayer.

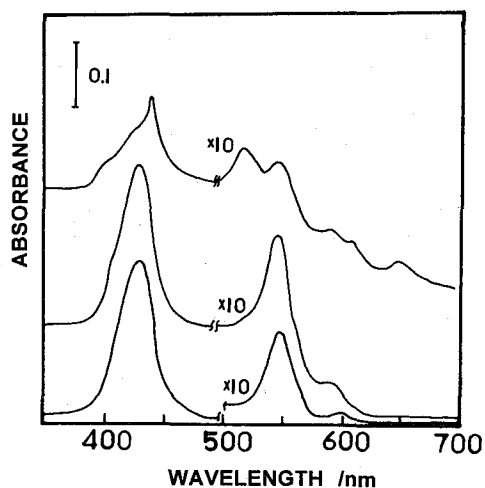


Fig. 3. UV-vis absorption spectra of LB films of THPPH1 (bottom), *trans*-THPPH2 (middle) and THPPH3 (top) transferred from monolayers on aqueous Cu(II) subphase.

Figure 3 represents absorption spectra of the LB film transferred from THPPH1 and *trans*-THPPH2 monolayer at 20 and 25 mN/m, respectively, after incubation for 20 minutes on the aqueous Cu (II) subphase. The spectral feature of the Soret band is similar to that of the respective LB film shown in Fig. 2 expect for slight broadening. However, the feature of the Q-band reegion is entirely different from that of the LB films transferred from the monolayer on pure water. Tow bands are observed in the Q-band region: the stronger one appears at 530 nm and the weaker one 585 nm, which is characteristic of Cu (II) complex of porphyrins [4] . These facts are indicative of complete metallation of the porphyrins in the monolayers. Similar result was also obtained for *cis*-THPPH2. In contrast, THPPH3 metallated even after incubation for 2 hours on aqueous Cu (II) subphase, as evidenced by the spectrum in Fig. 3. For the THPPH4 in monolayer maintained at 50 mN/m (condensed region) , no trace of metallation was found under the same conditions.

Further, the dynamic process of the metallation of the porphyrins in the LB films was investigated by monitoring the time-dependent absorbance of the band at 530 nm. Figure 4 shows the time dependence of the absorbance. As is seen, the THPPH1, *cis*-THPPH2 and *trans*-THPPH2 films can be completely metallated by Cu (II) within a short period, which reflects an exposure of the porpryrin macrocycles to the film surface to a great extent. In contrast, the metallation in the THPPH3 film is limited with a lower rate and no trace of the metallation is found for the THPPH4 film. These facts are considered as follows. It is reasonably supposed that the reactivity of the porphyrins with Cu (II) is not affected by the substituents on the phenyl groups linked with the porphyrin macrocycles. Therefore, it is most likely that the metallation rate is controlled by the orientation of the porphyrin ring and by the rate of penetration of Cu (II) into the LB films which is directly governed by the packing state of the porphyrins in the films. Interestingly, it is noted that the metallation rate of the LB films increases with the increase of the molecular area extrapolated from the respective π -A isotherm shown in Fig. 1.

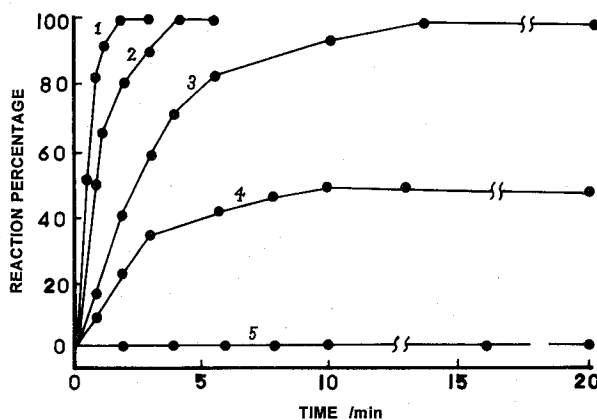


Fig. 4. Time dependences of the Cu (II) metallation percentage of the 1-layer LB films of the amphiphilic porphyrins: 1, THPPH1; 2, *cis*-THPPH2; 3, *trans*-THPPH2; 4, THPPH3; 5, THPPH4.

CONCLUSION

The present work reveals that the formation of porphyrin aggregates in LB films can be controlled through substituting varied number of long hydrocarbon chains on porphyrin macrocycle at different substitutive sites. J-like aggregates are formed with somewhat poor order in the LB films of one- and two-chain substituted porphyrin (THPPH1, *cis*-THPPH2 and *trans*-THPPH2). In the case of three- and four-chain porphyrins (THPPH3 and THPPH4), Soret-state split aggregates are obtained in the LB films in which the porphyrin macrocycles are arranged in a stack-of-card fashion, one kind of dipoles being in parallel packing while the other head-to-tail packing.

Monolayers and LB films of the one- and two-chain porphyrins (THPPH1, *cis*-THPPH2 and *trans*-THPPH2) allow Cu (II) ion penetration with relatively rapid rate. In contrast, Cu (II) ion penetrated slowly in the three-chain porphyrin (THPPH3) film and does not penetrate in four-chain porphyrin (THPPH4) film. These findings provide additional demonstration of porphyrin macrocycle aggregations in the LB films.

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