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Aggregation and supramolecular chirality of achiral amphiphilic metalloporphyrins

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ABSTRACT

Metalloporphyrin derivatives with three hydrophobic dodecyl chains and a hydrophilic ester or carboxylic acid substituent were designed in order to clarify the effect of the central metal ions on the aggregation as well as the supramolecular chirality in the Langmuir–Schaefer films. All the metalloporphyrins showed good spreading behavior on water surface and can be transferred onto solid substrates. The transferred films were characterized by a variety of methods including UV–visible spectroscopy, circular dichroism (CD) spectroscopy, FTIR spectroscopy, atomic force microscopy (AFM) and scanning electron microscope (SEM) measurements. It has been found that the copper derivative forms J-aggregates as well as H-aggregates in the film. Moreover, the film showed strong CD signals. Change from the ester substitution to carboxylic acid caused the decrease of the supramolecular chirality. On the contrary, the zinc derivative showed only a negligible CD signal although the corresponding free base could assemble into a chiral assembly. A possible mechanism for the subtle relationship between supramolecular chirality and molecular structures has been proposed.

1. Introduction

Porphyrin, which has four conjugated pyrrole rings, plays very important roles not only in the field of life science, but also in the development of novel functional materials [1]. In many cases, the properties of the porphyrins functional systems are related to the self-assembly of their metallic derivatives [2–5]. For example, the well known photosynthetic centers for light-induced charge separation in frond can just be regarded as the most ingenious metalloporphyrin supramolecular assemblies which were fabricated by nature [6].

Moreover, the self-assembly of metalloporphyrins are usually involved with chirality, which is one of the most essential driving forces for the metalloporphyrin self-assemblies and endues the corresponding supramolecular systems with various important functions [7]. In principle, the chirality could either be exhibited within molecular level or be shown in the level of supramolecular assemblies [8]. However, the constructions of chiral porphyrin assemblies from achiral porphyrins are always extremely challenging, and were only carried out in a few particular cases [9–12].

Recently, we have found that some achiral molecules could form chiral assemblies through air/water interfacial organization [13–15]. Previously, we have shown that a series of achiral porphyrin derivatives with different alkyl chain substitutions could also form chiral molecular assemblies at the air/water interface. We have further investigated the effect of the alkyl chain substitutions on the supramolecular chirality of the formed molecular films and revealed that the porphyrin derivative with three hydrophobic dodecyl chains and one hydrophilic substituent (TPPA3) could form nice chiral assemblies on pure water surface [16]. Moreover, we have demonstrated that molecules with relatively bulky headgroup and long hydrophobic chain tend to give supramolecular chirality at air/water interface. In the case of supramolecular chiral assemblies from free base TPPA3, both hydrophobic interaction between the alkyl chains and the π–π stacking between the headgroups serve as very important driving force, and π–π stacking is believed to play a predominant role [10,16].

In this paper, we extend our work to the effect of the central metal ions. As is known porphyrins are easily react with the metal ions from their central nitrogen group and the introduction of the metal ions can greatly affect the properties of the porphyrin as well as their assemblies. We synthesized the zinc and copper derivatives of TPPA3 and investigated their assemblies at the air/water interface. A totally different aggregation behavior and supramolecular chirality were found from these two analogs at air/water interface. Furthermore, transformation of one ester group of CuTPPA3 to carboxylic acid again varies the supramolecular chirality of corresponding assemblies.

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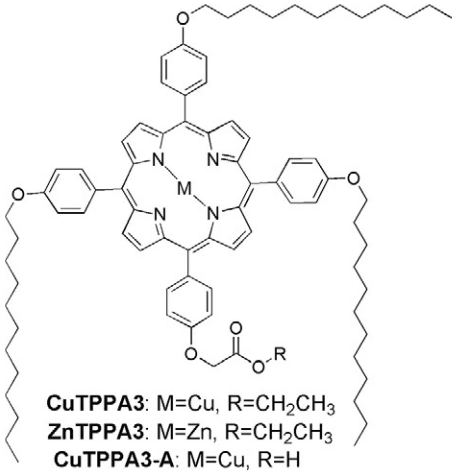

Scheme 1. Chemical structures of the CuTPPA3, ZnTPPA3 and CuTPPA3-A.

2. Materials and methods

2.1. Materials

5-[4-((Ethoxycarbonyl)methoxy)phenyl]-10,15,20-tri(4-(dodecyloxyphenyl) porphyrin (TPPA3) was synthesized as previously reported. All other starting materials and solvents were purchased from Aldrich, Acros Organics or Beijing Chemicals and used as received unless otherwise stated. Chloroform was purchased from Beijing Chemicals and distilled before use. Milli-Q water (18.2 MΩ cm) was used in all the cases. Zinc and copper derivatives (ZnTPPA3 and CuTPPA3) of TPPA3 were synthesized according to standard procedure, by reacting with zinc acetate and copper acetate, respectively [17]. The hydrolyzed derivates of CuTPPA3 (CuTPPA3-A) were prepared by refluxing CuTPPA3 with KOH in THF/methanol/water (10:5:1) mixture and subsequently acidification with diluted HCl (Scheme 1). The final product was confirmed by high resolution mass spectroscopy. HRMS (FAB): CuTPPA3: 1330.7423 (m/z calcd. for [$C_{84}H_{106}CuN_4O_6 + H$] 1330.7487); ZnTPPA3: 1331.7423 (m/z calcd. for [$C_{84}H_{106}ZnN_4O_6 + H$] 1331.7482); CuTPPA3-A: 1300.7023 (m/z calcd. for [$C_{82}H_{102}CuN_4O_6 - H$] 1300.7017).

2.2. Methods

Chloroform solutions (ca 4.5×10^{-5} mol L^{-1}) of the amphiphilic metalloporphyrins were carefully spread onto the Milli-Q water subphases in order to form Langmuir films. After allowing 30 min for the evaporation of solvents, the π–A isotherms of the spreading films were recorded at $20 \pm 0.2\,^{\circ}\mathrm{C}$ by compressing the Langmuir films at a speed of 5 cm^2/min. Quartz substrates were cleaned by the mixed chromic acid and washed with water thoroughly, which were again managed to be hydrophobic by rubbing the substrates with ferric stearate. The monolayers were transferred onto solid supports (Quartz substrates) at different surface pressures by a horizontal lifting technique to get the LS multilayer films, which were subjected to UV–vis and CD spectra measurements. For the SEM measurements, 20-layer of CuTPPA3 LS films were transferred onto clean hydrophobic silicon plate at 30 mN/m. In the process of measuring CD spectra, the multilayer film on the quartz plate was placed perpendicular to the light path and continuously rotated within the film plane, using a home made attachment to avoid the possible linear dichroism (LD) in the films [18–20]. In the progress of measuring AFM, one layer of porphyrin LB film was deposited onto freshly cleaved mica by using the vertical lifting method, with the upstroke lifting speed of 3 mm/min.

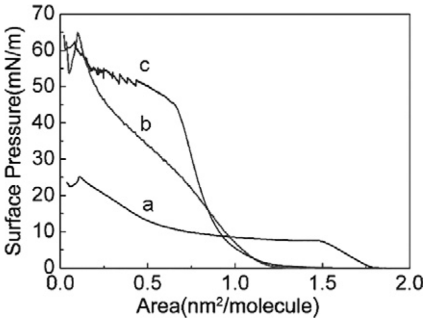

Fig. 1. Surface pressure–area (π–A) isotherms of the spreading films from three amphiphilic metalloporphyrins on aqueous subphase at $20 \pm 0.2\,^{\circ}\mathrm{C}$: (a) ZnTPPA3; (b) CuTPPA3; (c) CuTPPA3-A.

High resolution mass spectral data were obtained by using an Apex II FT-ICR mass spectrometer. Measurements of surface pressure–area (π–A) isotherms and film depositions were carried out on a KSV minitrough (Helsinki, Finland). UV–vis spectra were measured with a JASCO UV-630 spectrometer. CD spectra were recorded with a JASCO J-810 spectropolarimeter. AFM measurements were performed by using a tapping-mode atomic force microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA), with a silicon cantilever probes. All AFM images are shown in the height mode without any image processing except flatting. Scanning Electron Microscope (SEM) images were taken on a filed emission SEM (Hitachi S-4300, 15 kV).

3. Results and discussions

3.1. Surface pressure–area (π–A) isotherms of the spreading films on water surface

Fig. 1 shows the surface pressure–area (π–A) isotherms of the monolayers of three amphiphilic metalloporphyrins at $20 \pm 0.2\,^{\circ}\mathrm{C}$ on water surface. A clearly different interfacial behavior such as the limiting molecular areas and transition points was observed depending on both the center metals and little hydrophilic substituted groups. For porphyrin ZnTPPA3 (Fig. 1a), the onset of the surface pressure appeared at a 1.75 nm^2/molecule. A transition point started from 10 mN/m and followed with a long plateau region, the monolayer collapsed at a lower surface pressure of 25 mN/m. These results indicated that ZnTPPA3 flatly aligned on water surface at the beginning and then vertically orientated upon compression. However, CuTPPA3 exhibits the similar properties like its free base analogue TPPA3 [16] (Fig. 1b), the extrapolated molecular areas from the linear part of the π–A curves are about 1.2 nm^2/molecule. CuTPPA3-A gives a typical π–A curve obtained from typical amphiphilic molecules [21] and showed the same onset of the surface pressures (Fig. 1c). The limiting molecular area of the isotherm is 0.9 nm^2/molecule. The molecular areas of both CuTPPA3 and CuTPPA3-A are very close to the area occupied by a perpendicularly orientated tetraarylporphyrin molecule [22,23], indicating that the macrocyclic ring arranged in a vertical way in the monolayer.

3.2. UV–vis spectra of the LS films

Fig. 2 shows the UV–vis spectra of the three amphiphilic metalloporphyrins in chloroform solutions as well as those of the 20 layers LS films deposited on quartz plates from water subphase at $20 \pm 0.2\,^{\circ}\mathrm{C}$. In chloroform solution, the three compounds showed almost the same UV–vis spectra with Soret band at 421 nm and the Q-band at 545 nm, which is typical of the metalloporphyrin absorption. When these compounds were fabricated into LS films,