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A novel pH-controlled transfer process of 5,10,15-tri(4-hydroxyphenyl)-20-(4-hexadecyloxyphenyl) porphyrin in CTAB micelles

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Abstract

By analysis of the UV–visible and fluorescence spectra of 5,10,15-tri(4-hydroxyphenyl)-20-(4-hexadecyloxyphenyl)porphyrin (**P**) in different microenvironments of micelle and solvent solutions, a novel pH-controlled transfer process of **P** in CTAB micelle was reported. In neutral CTAB micelles, porphyrins may locate at the inner layers of micelles. With pH increases to 11.19, the porphyrin can be completely deprotonated and transfers to the outer surface of CTAB micelle. The investigation of kinetics of porphyrin complexing with Cu(II) indicates that the metallation rate of porphyrins in CTAB micelles could also be controlled by changing pH.

Keywords: Porphyrin; CTAB; Micelle; Location; Metallation

1. Introduction

Binding of porphyrin and metalloporphyrin guests to models for membrane hosts has attracted much interest due to the possibility of understanding many biological and photochemical processes, such as photosynthesis, oxygen transport, oxidation–reduction, and electron transport. It has been shown that porphyrins anchored to lipid bilayers and micelles could be applied successfully for reversible binding of dioxygen or nitric oxide in aqueous solutions [1,2]. Incorporation of porphyrins into micelles dramatically influences the aggregation mode and location of these molecules and alters their metallation rate and nitric oxide transfer rate [2–4]. Generally, it is suggested that hydrophobic porphyrins could penetrate the lipid regions of the membranes and distribute into protein-rich membrane domains [5], while highly polar species were assumed to partition mainly into the aqueous compartments [6]. Recently, the interaction of water-soluble synthetic porphyrins with ionic micelles and reversed micelles has been studied intensively [4,7–9]. In the present of ionic surfactants below their critical micelle concentration (CMC), both water-soluble ionic porphyrins [10–13] and some meso-tetraaryl-substituted picket fence porphyrins [14] have been shown to form aggregates. Above the CMC, micelles are usually considered only as a means to solubilize the aggregates of porphyrin derivatives into monomers [7–10,15,16].

So far, however, a structural understanding is still unclear, especially for the solubilization site of porphyrinic molecules, because of their versatile substituents. Although some efforts have been made to study porphyrin aggregation and location in micelle surfactant solutions as well as aqueous solutions, most of them have concentrated on water-soluble porphyrinic molecules, and there are still few reports about controlling amphiphilic porphyrin transfer processes in CTAB micelles. On the other hand, metallation in microheterogeneous media has been less investigated despite its biological occurrence [17,18]. We have reported previously the results of studies of the location, metallation, and aggregation of series of amphiphilic porphyrins in nonionic and anionic micelles [19–22]. In this work, cationic cetyltrimethylammonium bro-

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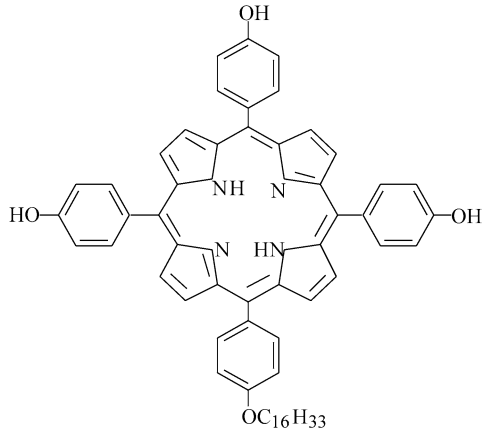

Fig. 1. Structure of the amphiphilic porphyrins **P**.

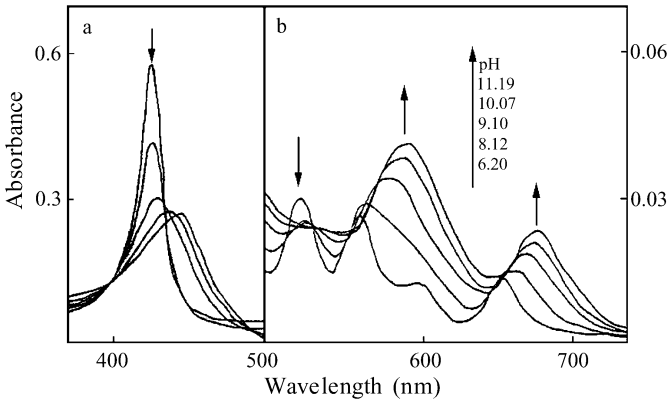

Fig. 2. UV–visible spectra of **P** in different pH CTAB micelle aqueous solutions. $[\mathbf{P}] = 2.2 \times 10^{-6}$ mol dm^{-3}; $[\text{CTAB}] = 2.5 \times 10^{-3}$ mol dm^{-3}.

mide (CTAB) micelles were used as the simplest model for membranes and potential reaction centers to gain more insight into the nature of amphiphilic porphyrin guest interaction with biological structure hosts. 5,10,15-Tri(4-hydroxyphenyl)-20-(4-hexadecyloxyphenyl) porphyrin (**P**) was solubilized in CTAB micelle solutions (see Fig. 1). The coexistence of the big porphyrin moiety and the long hydrophobic chains in the same molecule suggests that such molecules can be solubilized in organic solvents as well as in the nonpolar regions of micelles; their conjugated π electronic structures relate to the Soret band, and Q bands would not be affected by the substituted chains. Based on this property, we report a novel pH-controlled transfer process of **P** in CTAB micelles.

2. Experimental

The amphiphilic porphyrins **P**, 5,10,15-tri(4-hydroxyphenyl)-20-(4-hexadecyloxyphenyl) porphyrin, were synthesized as reported in the literature [23–25]. CTAB was an analytical reagent and was recrystallized twice from 90% ethanol. Water was doubly distilled after passing through an ion-exchange resin column. All the organic solvents were analytical grade pure and used without further purification.

CTAB micelle, aqueous, and organic–water mixture solutions of porphyrins were prepared by injection of a certain amount of 2.5×10^{-3} mol dm^{-3} dioxane solution of porphyrins into different solvents to obtain 25-ml solutions. The ratio of dioxane and water or other mixture solvents was greater than 1000, so the effects of trace of dioxane on the solution polarity could be neglected. After 20 min of sonication, the fluorescence spectra of solutions were recorded on a Shimudu UV-3100 spectrophotometer and a Perkin Elmer LS50B fluorescence spectrophotometer using a 1-cm quartz cell. The pH value of the solution was measured by a pH-250 pH meter and the pH value of solutions was controlled by 1.5 mol dm^{-3} NaOH and 1:4 HCl aqueous solutions. The kinetic processes of porphyrins incorporated with Cu(II) were studied at room temperature by adding a certain amount of 0.1 mol dm^{-3} $CuSO_4$ aqueous solution into different pH porphyrin CTAB micelle solutions and then the UV–visible spectra of the mixture solutions at different reaction times were recorded.

3. Results and discussion

3.1. Deprotonization of P in CTAB micelles

Fig. 2 shows the titration UV–vis spectra of **P** in CTAB micelle solutions. It can be seen from this figure that at pH 6.20, **P** shows a strong Soret band at 423 nm and four Q bands at 520, 560, 595, and 655 nm. With pH increasing to 11.19, the Soret band of porphyrin at 423 nm experiences obvious broading and decrease, while the four Q bands of **P** gradually disappear and two new Q bands appear at 585 and 675 nm. The number of Q bands observed changes from 4 to 2, indicating that **P** has a higher molecular symmetry (D_{4h}) similar to that of metal porphyrins [26]. However, the present system contains only one kind of metal ion, Na^+, that is difficult to complex. Hence, this phenomenon indicates that hydrogen atoms bonded to the pyrrole nitrogen atoms of the **P** moiety may also be deprotonized to form $\mathbf{P}^{5-}$ ions (Fig. 3) similar to **P** in strong basic aqueous solutions when the bulk pH approaches 11.19 (see Table 1).

It should be pointed out that the complete deprotonization of **P** could take place only in strong basic aqueous solutions (such as 1.5 mol dm^{-3} NaOH aqueous solution); it could not be observed in pH 11.19 aqueous solutions (see Table 1). However, it was found that the **P** moiety could be deprotonized to form $\mathbf{P}^{5-}$ ions in pH 11.19 CTAB micelle solutions. This function is based on the surface potential properties of CTAB micelles. The relationship between surface potential and surface effective concentration of H^+ (α_H) of micelle is shown by the equation [27]

$$\alpha_H^i = \alpha_H^w e^{-F\Psi/RT}, \tag{1}$$

where α_H^i and α_H^w are the effective concentrations of H^+ ions in micelle surface and bulk aqueous phase respectively, F is Faraday constant, Ψ is the surface potential of micelle, T is temperature in Kelvin, and R is the Boltzmann constant. As we know, that cation surfactant CTAB micelle exhibits a positive surface potential ($\Psi > 0$), $\alpha_H^i \ll \alpha_H^w$ according to Eq. (1). This means that the pH value of the CTAB micelle surface is greater than that of the bulk aqueous phase. In fact, Fromherz and Masters [28] have found that the surface potential of CTAB micelles is about 148 mV, which corresponds to an increase