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Structural Multiplicity of Monomers of an Amphiphilic Porphyrin at the Outer Surface of CTAB Micelle

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Abstract: A synthesized amphiphilic porphyrin, 5,10,15-tri(*p*-hydroxyphenyl)-20-(*p*-hexadecyl-oxyphenyl) porphyrin, can take a transfer process for the porphyrin moiety from the inner core to the outer surface layer of cetyltrimethylammonium bromide (CTAB) micelle. The increasing of FWHH of the Soret band was attributed to the multiplicity of porphyrin monomers related with deprotonation degree, arrangement, orientation, and position of porphyrin moiety at the surface area rather than the aggregates associated with irregular orientation of neighboring porphyrins.

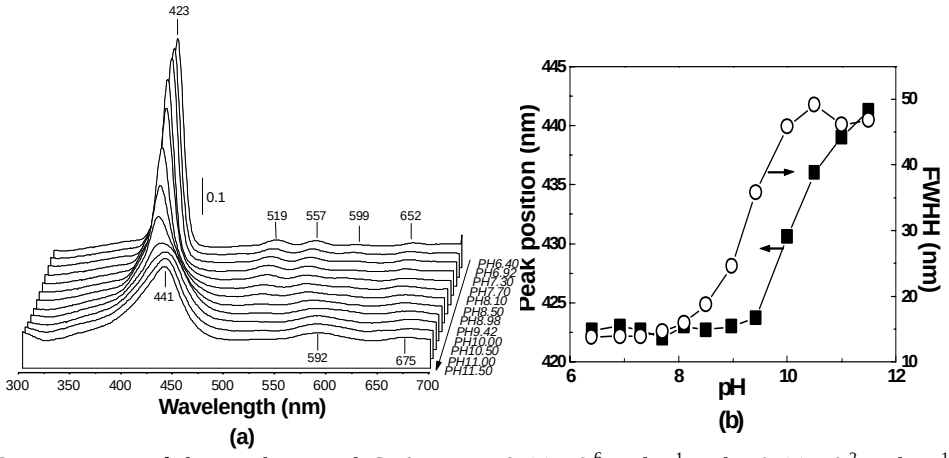
Keywords: Amphiphilic porphyrin, solubilization site, aggregation.

Aggregation of porphyrins in different media, such as in solvents with various polarity[1,2], in surfactant solutions of different concentrations[3-6], in membrane media[7], *etc*., has attracted an increased interest in the past years. It is well accepted that the Soret bands are sensitive to solvent microenvironment and aggregation forms of porphyrins. Thus spectral characteristics, such as full width at half height (FWHH), peak position, are common parameters to understand the solubilization site and aggregation behaviors of porphyrinic molecules in membrane media[3-7]. Broadening of Soret bands is generally thought to be mainly caused by aggregation of porphyrins in most cases[1-4]. However, a kind of highly ordered J-aggregate of a porphyrin in dilute surfactant solution was found to show a sharp Soret band similar to that of monomeric porphyrins[5]. In this case, it is necessary to exam what kinds of another factors decide Soret bandwidth except the order state of porphyrin aggregates. With taking advantage of an amphiphilic tretrahydoxyphenylporphyrin, *ie*., there is great increase for the hydrophilic ability of this porphyrin when the four hydoxyphenyl groups are deprotonated, we have found that the porphyrin can be transferred from the inner core to the outer surface of the CTAB micelle with increasing bulk pH. In this communication, an amphiphilic porphyrin has been controlled to be transferred monomerically from the inner core to the outer surface of CTAB micelle. It is pointed out that the multiplicity of monomeric porphyrins at the surface area is also a factor broadening the Soret band.

Results and Discussion

CTAB solutions containing 5,10,15-tri(*p*-hydroxyphenyl)-20-(*p*-hexadecyloxyphenyl)-porphyrin, the amphiphilic porphyrin with one hexadecyl chain as hydrophobic part and three hydroxyphenyl groups as hydrophilic parts, was achieved by adding 10 μL of its 2.72×10^{-3} mol.L^{-1} tetrahydrofuran (THF) solution into 10mL of 2.0×10^{-2} mol.L^{-1} CTAB surfactant solution. The mixed solution was sonicated for 20min. UV-visible absorption spectra were obtained by using a UVIKON S-10 spectrophotometer.

Figure 1 (a) Bulk pH-dependent UV-vis spectra of the amphiphilic porphyrin in CTAB Solutions. (b) The FWHH value and peak position of Soret band at various bulk pH.



Concentrations of the porphyrin and CTAB are 2.8×10^{-6} mol.L^{-1} and 2.0×10^{-2} mol. L^{-1} respectively.

Figure 1 (a) shows the pH-dependent UV-spectra. The Soret band has a red-shift from 423 to 441 nm and its FWHH value is increased from 14 to 47 nm when increasing the bulk pH value from neutral pH to basic pH (see **Figure 1** (b)). Especially, two new Q bands appear at 592 nm, 675 nm instead of the four Q bands at 519, 557, 599, 652 nm with the increase of bulk pH value from pH 6.40 to 11.50.

Similar spectral changes of Soret band induced by addition of KNO_3 or peptide have been reported and have been attributed to the aggregation of the cationic or anionic porphyrins[3,8]. However, the porphyrin in this paper is amphiphilic rather than cationic or anionic. It has a very low solubility in aqueous solution in neutral pH since its hydrophilic ability is very weak. It should trend to be solubilized in micelle microenvironment because of the existence of the hexadecyl chain and the hydrophobic porphyrin moiety. The narrow bandwidth (14 nm) of the Soret band at neutral pH indicates that the high concentration ratio (about 7000:1) between CTAB and the porphyrin makes it sure that the solubilized porphyrin is monomeric in the inner core of

the CTAB micelle[5]. However, the hydroxyphenyl groups can be deprotonated in basic solutions and the hydrophilic ability of the porphyrin will be increased accompanying the deprotonation process. Therefore, the spectral changes shown in **Figure 1** (a) undoubtedly correspond to the change of solublization site of the porphyrin moiety related to the deprotonation process because only bulk pH was experimentally changed from pH 6.40 to pH 11.50 in this experiment. Especially, the spectral parameters are very similar between the porphyrin in pH 11.50 CTAB solution and in 1.5 $mol.L^{-1}$ NaOH aqueous solution according to **Table 1**. Only two Q bands appear for both cases, indicating that the four nitrogen atoms of the porphyrin have a same environment similar to that of metal porphyrins. Because the system contains only one kind of metal cation, *ie*., Na^+. Thus, the two hydrogen atoms bonded to the nitrogen atoms of the pyrrole rings can be thought to be also left intact during the deprotonation of the hydroxyphenyl groups. Such fact indicates that the porphyrin moiety should be in a strong basic environment when the bulk pH of the CTAB solution arrives to pH 11.50. Only the outer surface of the CTAB micelle can provide strong basic environment when considering the effect of surface potential of micelles (148 mv for the CTAB micelle corresponding to a 2.5 pH unit increase relative to the bulk pH[9,10]).

Table 1 Spectral parameters of the amphiphilic porphyrin in pH11.50 CTAB solution and in strong basic aqueous solution

solvent	Soret band		Q bands (nm)	
	λ max (nm)	ε (Lmol-1cm-1)		
pH11.50 CTAB solution	441	7.5×10^4	592	675
1.5mol.L^{-1}NaOH aqueous solution	436	7.9×10^4	583	673

As discussed above, the porphyrin moiety should exist in monomeric form in the inner core of CTAB micelle at neutral pH according to its very narrow FWHH (14 nm). While the porphyrin moiety will be located at the outer surface of the CTAB micelle when the bulk pH arrives to pH11.50. Therefore, the change of FWHH values in **Figure 1** (b) is a representation of the transfer process of porphyrin moiety from the inner core to the outer surface of the CTAB micelle. Cationic porphyrins have been found to be dispersed monomericly on the surface anionic micelles[11] while anionic porphyrins tend to be located on the cationic micellar surface in monomeric form[12]. There is a similar occasion between this experiment and the reference 12 when porphyrin is located on the outer surface of CTAB micelle. Furthermore, the molar ratio between CTAB and the porphyrin is very high (about 7000), and the porphyrin exists in monomeric state in the CTAB micelle at neutral pH. It can be suggested that there is no more than one porphyrin per micelle. On the other hand, there would be no contact between any two micelles because of the electric double layer repulsion between the micelles. Therefore, the increase of FWHH value after the porphyrin moiety moving into the surface area of CTAB micelle is not a characteristic of its aggregates but from complex forms of the monomers, which may be concerned with deprotonation degree, orientation, arrangement and position of the porphyrin moiety in the surface area.

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