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Porphyrins in Reverse Micelles: the Side-chain Length and the Triplet-state Lifetime

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Abstract: Using bis(2-ethylhexyl) sodium sulfosuccinate (AOT) as surfactant, two amphiphilic porphyrin terminated with imidazole were studied in AOT/*iso*-octane/water reverse micelles, intending to mimic the relationship between microenvironments in organism and the amphiphilic properties of porphyrins for photodynamic therapy drugs.

Keywords: Porphyrin, triplet-state, lifetime, reverse micelle.

There are two major mechanisms for the photodynamic therapy (PDT): type I and type II mechanisms[1]. In either type, the photoreaction proceeds *via* the lowest excited triplet state of the sensitizer[2], which consequently influences the efficiency of the photosensitizing action. Porphyrin derivatives are potentially PDT drugs for the high triplet quantum yields and their long lifetimes of the excited triplet state[3], and amphiphilic porphyrins are especially regarded as the most important type among these porphyrinic compounds. The lifetime of the excited triplet state of the sensitizer is very sensitive to the environments where the sensitizer localizes and the status of the sensitizer presents per se[4,5]. In this study we use two amphiphilic porphyrins terminated with imidazoles as the model compounds to investigate the influences of the microenvironments on the properties of amphiphilic porphyrin. Considering the ability to control the size and properties of the water pool, the reverse micelle is an interesting model candidate to mimic the water pockets that are often found in various bioaggregates such as proteins, membranes, and mitochondria. Here, we use bis (2-ethylhexyl) sodium sulfosuccinate (AOT) as surfactant to probe properties of the porphyrins in AOT /*iso*-octane/water reverse micelles.

Results and Discussion

The amphiphilic porphyrins herein used are 5-[4-(12-imidazol-*N*-yldodecyloxy)phenyl]-10, 15, 20-tris(4-methylphenyl)porphyrin (**1**) and 5-[4-(8-imidazol-*N*-yloctyloxy)phenyl]

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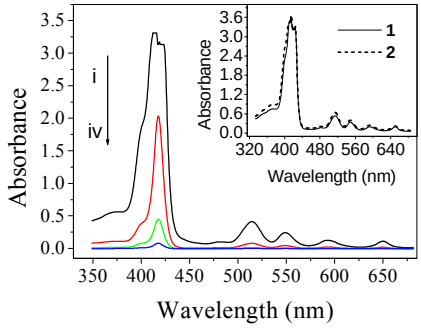
-10, 15, 20-tris(4-methylphenyl)porphyrin (**2**). The concentration of AOT in *iso*-octane (IOA) was kept at 0.1 mol·L^{-1} and the molar ratio of water to AOT, w_o (w_o = [water] /[AOT]), was maintained at 4 throughout this paper. The photolysis was performed as previously reported except that the excitation wavelength was 532 nm and an Ar-saturated reverse micelle solution was used[6]. Monolayers were prepared on a model 622 NIMA Langmuir-Blodgett trough and the procedure was reported elsewhere[7]. Triplet lifetimes were treated from kinetic analysis of the transient decays by using Levenberg-Marquardt nonlinear fitting programs.

Considering that tumor necrosis can only occur when the number of absorbed photons exceeds a so-called damage threshold[8], we chose a relatively high concentration of 2.3 × 10^{-5} mol L^{-1} for porphyrin in reverse micelle solution. Compounds **1** and **2** would tend to form aggregates at such a concentration even in good solvent.

Figure 1 Absorption spectra of compound **1** in reverse micelle solutions[a]. The inset shows the absorption spectra of **1** and **2** in reverse micelle solution[b]



[a]The concentrations of **1** are (i) 2.3 × 10^{-5}, (ii) 4.6 × 10^{-6}, (iii) 9.2 × 10^{-7}, and (iv) 1.8× 10^{-7} mol·L^{-1}. [b]The concentrations of **1** and **2** are 2.3 × 10^{-5} mol·L^{-1}, respectively

Table 1 Triplet state lifetimes recorded at 445 nm for compounds **1** and **2** in reverse micelle solutions with w_o = 4

Compound	Lifetime (τ)[a] and		pre-exponential factors (*a*)[a]	
	τ_1 (μs)	a_1	τ_2 (μs)	a_2
1	75.5	0.92	1390	0.08
2	171	0.48	1550	0.52

[a]Derived from the fittings of lifetime decays by the equation: $I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$

The absorption spectra of compounds **1** and **2** in 0.1 mol·L^{-1} AOT/ *iso*-octane/water reverse micelles at w_o = 4 were measured. Both compounds show H-aggregate absorptions, strong absorptions abutting against the short wavelength wing of the original B bands (**Figure 1**).

The surface pressure-area isotherms of the compounds **1** and **2** are presented in **Figure 2**. Compound **2** gives a higher collapse pressure than **1**. The limiting areas per molecule of compounds **1** and **2** are about 82 Å^2 and 77 Å^2, respectively, suggesting that the films collocate more tightly as the length of side chains increases, which, in turn,

might be the result of the better balance between the hydrophilic and hydrophobic groups in **2**. As there is so far no theory correlating the amphiphilicity and the collapse pressures, we can only consider that the one containing smaller area per molecule but longer side-chain length is more likely to act as a surfactant, *i.e.*, it has the self-assembling ability which usually results from the amphiphilicity of compound.

Figure 2 Surface pressure-area isotherms of **1** and **2** at the air/water interface (20 ± 1°C)

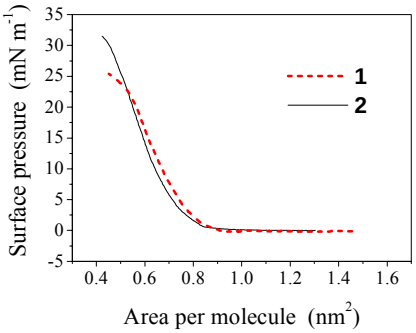
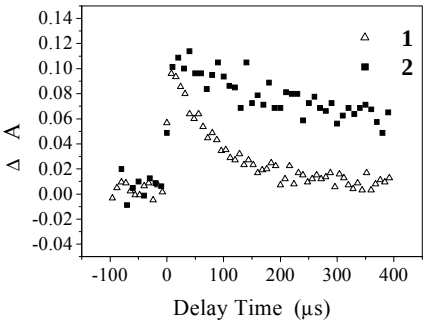


Figure 3 A typical comparison of excited state decays at 445 nm for **1** and **2** in reverse micelles[a]



[a] w_o = 4 after excitation at 532 nm

The dynamic decays of the triplet states of **1** and **2** in reverse micelles at 445 nm were measured by laser flash photolysis at 532 nm. The lifetimes of excited triplet state of compounds in reverse micelles vary with the side-chain length.

Poor fitting parameters are obtained when fitting the decays at 445 nm to a monoexponential law, but the quality of the fitting was improved when a biexponential law was used (see **Table 1**). For compound **1**, there exist two components, one having a lifetime of 75 μs, and the other 1390 μs. For compound **2**, the lifetime can be divided to 171 μs and 1550 μs, respectively.

The biexponential decay may be explained in terms of the coexistence of different status for porphyrins in reverse micelle solutions. If we assume there exists an equilibrium between monomers and aggregates, it can be reasonably concluded that the slow decay represents the monomer-dominating part and the fast one may result from the aggregate-dominating part[9]. The higher the fraction of monomer in all porphyrin, the longer the excited lifetime will be. Thus the biexponential decay may indicate that there are at least two states of the porphyrin molecules in reverse micelles.

As can be seen in **Table 1**, the fraction of long-lifetime component of compound **2** is remarkably larger than that of compound **1**. **Figure 3** shows a comparison of excited decays at 445 nm between the porphyrins at w_o = 4, indicating the overall lifetime of **2** is also longer than **1**. These imply that porphyrins with different side chain have distinct status in the reverse micelles. The status of porphyrin in reverse micelle solution can be partially determined by two factors: the driving force for aggregation of porphyrins, and the dispersion of porphyrins in detergent resulting from the amphiphilic property. The amphiphilic interaction becomes weak between detergent molecules, and for porphyrins

with amphiphilic property, the aggregating would become predominated. As the amphiphilic property improved, porphyrin would be easier to set its hydrophilic part in the polar phase and correspondingly the hydrophobic part in the apolar phase, in another word, detergent molecules would intervene the porphyrins more easily and prevent porphyrins from aggregation efficiently. Thus compound **2** is more amphiphilic than **1** based on the behavior in monolayer. It would have the stronger tendency to disperse among the detergent molecules in monomer mode and the longer excited triplet state lifetime.

In summary, two amphiphilic porphyrins were studied in AOT/*iso*-octane/water reverse micelles, intending to mimic the relationship between microenvironments in organism and the amphiphilic properties of porphyrins for PDT drugs. The high amphiphilic quality would promote the firm embedding of porphyrin molecules in the interfacial region of reverse micelles. Such an embedding may shift porphyrins from aggregated to monomeric form in reverse micelles and, accordingly, the slower excited-state decay may increase the efficiency of the photosensitizer in PDT. The effect of amphiphilic properties on the states of porphyrins in microenvironments provides a light on the synthesis of other amphiphilic porphyrins for PDT drugs.

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