Monomerization of Cationic Phthalocyanine in AOT Reversed Micelles[†]

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Introduction

Owing to their intense absorption in the red visible region (ca. 700 nm) and desirable photophysical properties,[1] phthalocyanines behave as efficient photosensitizers which can be used in photodynamic therapy for various diseases,[2] virus sterilization of red blood cells,[3] and photooxidation of mercaptans in petroleum distillates.[4] One of the problems affecting the sensitizing ability of these pigments stems from their intrinsic aggregation tendency due to the large π conjugated systems.[5] The resulting aggregates provide an efficient nonradiative energy relaxation pathway, reducing the triple-state population and singlet oxygen quantum yield.[6] The aggregation is particularly strong in aqueous media as a result of hydrophobic interactions.[7] Hydrophilic and nonaggregated phthalocyanines are therefore extremely rare despite their great potential in various applications.[8]

One of the strategies to enhance the formation of monomeric phthalocyanines involves the use of surfactants or other substances which can create a micro-heterogeneous environment.[9] While most of the studies focused on

Chart 1
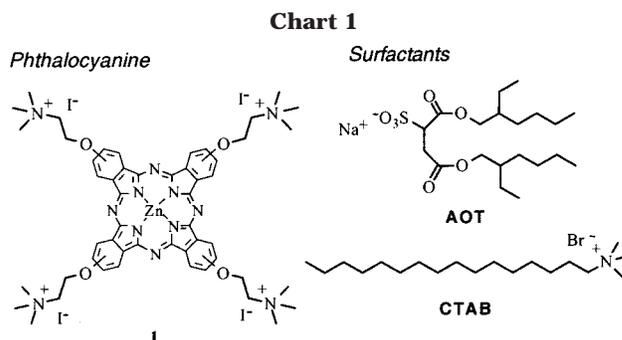
the anionic sulfonated or carboxylated phthalocyanines in micellar systems,[10] related investigation on cationic phthalocyanines is virtually unknown.[11] It is worth noting that certain bacterial cell walls have a high degree of negative charge. Cationic phthalocyanines may penetrate the cell wall barrier readily making them of particular value in the treatment of infectious diseases.[2a,12] Studies of the photophysical properties of polycationic phthalocyanines in various media are therefore of special importance. In this paper, we describe the monomerization of the water-soluble cationic tetrakis[2-(trimethylammonium)ethoxy]phthalocyaninatozinc(II) tetraiodide (**1**) in anionic sodium bis(2-ethylhexyl)sulfosuccinate (AOT) reversed micelles (Chart 1). The behavior of **1** in cationic *n*-hexadecyltrimethylammonium bromide (CTAB) reversed micelles has also been examined and compared with that in AOT reversed micelles. Despite the fact that reversed micellar systems are excellent models to mimic membrane functions and the water pockets which are often found in various bioaggregates, little has been known about the behavior of water-soluble phthalocyanines in these biologically related media.[10f,g]

Experimental Section

Materials. Phthalocyanine **1** was prepared according to the literature method.[13] The surfactants AOT (Fluka, ≥99.0%) and CTAB (Acros, 99+%) were used without prior purification. Water purified by a Millipore system was employed. All other solvents were of spectrophotometric grade and were used as received.

Instrumentation. UV−vis spectra were taken on a CARY 5G UV−Vis−NIR spectrophotometer using the same reversed micellar system in the absence of the phthalocyanine as the reference. Steady-state fluorescence

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† Dedicated to Professor Suk-Ping So on the occasion of his retirement.

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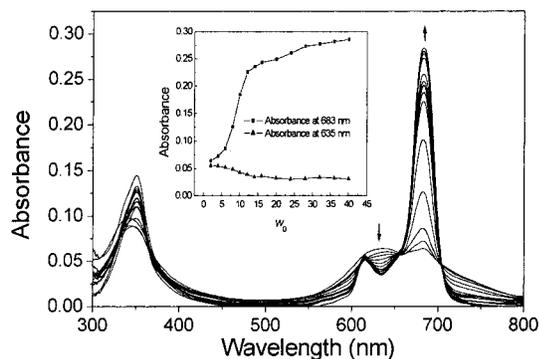
Figure 1. Absorption spectra of **1** in water/AOT/*n*-heptane with different water-to-AOT molar ratios ($w_0 = 2-40$), where $[AOT] = 0.1$ mol dm^{-3} and $[\mathbf{1}] = 2.2 \times 10^{-6}$ mol dm^{-3}. The inset shows the variation of the absorbance at 683 and 635 nm for **1** with w_0.

spectra were recorded on a Hitachi F-4500 spectrofluorometer. To minimize the re-absorption of radiation by ground-state species, the emission spectra were obtained by exciting very diluted solutions of **1** (ca. 2×10^{-6} mol dm^{-3}) at 615 nm, where the absorbance ≤ 0.05.

Preparation of Reversed Micelles. According to the water-to-AOT molar ratio ($w_0 = [water]/[AOT]$), an appropriate amount of an aqueous solution of **1** was mixed with a solution of AOT in *n*-heptane ($0.05-0.40$ mol dm^{-3}). The solution was shaken gently by hand until it became optically transparent. The CTAB reversed micelles with different w_0 values were prepared similarly by mixing an aqueous solution of **1** with a solution of CTAB in 12% (v/v) *n*-hexanol/isooctane (0.2 mol dm^{-3}).[14]

Results and Discussion

Figure 1 shows the UV−vis spectral changes of the cationic phthalocyanine **1** in water/AOT/*n*-heptane microemulsions as the water-to-AOT molar ratio ($w_0 = [water]/[AOT]$) increases from 2 to 40. In neat water[13] or when the water concentration is low ($w_0 < 6$), the macrocycle is highly aggregated as shown by the broad and blue-shifted Q-band at 635 nm.[15] This band diminishes while the band at 683 nm, which can be attributed to the Q-band of the monomeric species, becomes more intense when the w_0 value increases. The weak vibronic band at 615 nm can also be easily recognized in these cases. The inset of Figure 1 shows the variation of the absorbance of the two Q-bands at 635 and 683 nm with the w_0 value. It can be seen that the absorbance of the monomeric Q-band (683 nm) increases steadily with w_0 from 2 to 6, then it increases rapidly until $w_0 \approx 14$, where the increase becomes steady again. A reverse trend is observed for the Q-band due to the aggregated species (635 nm), but the effect of water content is much less pronounced in this case. All these observations indicate that the aggregation tendency of **1** can be greatly reduced in AOT reversed micelles having a sufficiently large water pool.[16] Surprisingly, a similar monomerization process was not observed for the tetrasulfonated aluminum(III) phthalocyanine in cationic reversed micelles of benzyldimethyl-*n*-hexadecylammonium chloride, in which the phthalocyanine tends
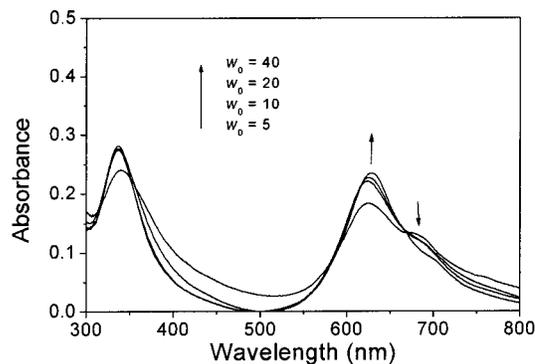
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Figure 2. Absorption spectra of **1** in water/CTAB/*n*-hexanol/isooctane with different water-to-CTAB molar ratios ($w_0 = 5-40$), where $[CTAB] = 0.2$ mol dm^{-3} and $[\mathbf{1}] = 6.5 \times 10^{-6}$ mol dm^{-3}.
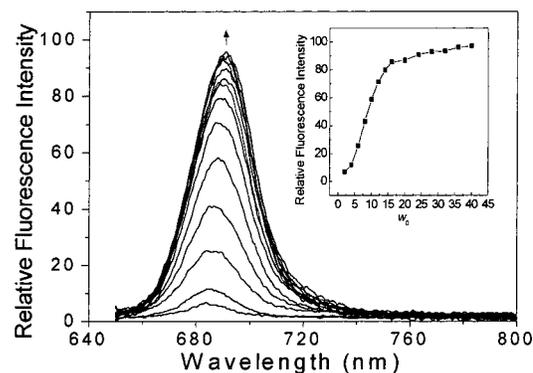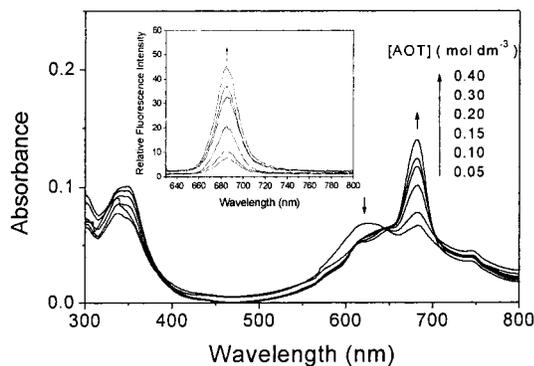

Figure 3. Fluorescence spectra of **1** in water/AOT/*n*-heptane with different water-to-AOT molar ratios ($w_0 = 2-40$), where $[AOT] = 0.1$ mol dm^{-3} and $[\mathbf{1}] = 2.2 \times 10^{-6}$ mol dm^{-3}. The inset shows the variation of the relative fluorescence intensity for **1** with w_0.

to be more aggregated as the water concentration increases.[10f]

For comparison, the behavior of **1** in cationic CTAB reversed micelles was also examined. As shown in Figure 2, when the w_0 value (=[water]/[CTAB]) increases from 5 to 40, the Q-band due to the aggregated species (ca. 625 nm) is slightly red-shifted and intensified, while the shoulder at ca. 680 nm (the monomeric Q-band) disappears gradually. This suggests that compound **1** becomes more aggregated as the size of the water pool increases. For all the w_0 values, the compound remains highly aggregated, which is in contrast to the **1**/AOT system, showing that the electrostatic interactions between the cationic groups of **1** and the anionic head of AOT play a crucial role in reducing the aggregation tendency. A similar situation was observed for the tetrasulfonated nickel(II) phthalocyanine/AOT system, in which the anionic phthalocyanine remains significantly aggregated in the anionic reversed micelles with a w_0 value from 10 to 60.[10g]

The fluorescence spectra of **1** in AOT reversed micelles are also susceptible to the water-to-AOT molar ratio. Upon excitation at 615 nm, compound **1** exhibits a fluorescence emission at ca. 690 nm, the intensity of which increases with w_0, in particular when the value ranges from 4 to 16 (Figure 3). This trend is similar to that observed for the monomeric Q-band absorption (Figure 1). As aggregated phthalocyanines are normally nonemissive,[6] the emission arises mainly from the monomeric species. This again indicates that the anionic AOT reversed micelles promote the monomerization of the cationic phthalocyanine **1**. It is also worth noting that the emission position shifts

Figure 4. Absorption spectra of **1** in water/AOT/*n*-heptane with different AOT concentrations, where $w_o = 8$ and $[\mathbf{1}] = 8.8 \times 10^{-7}$ mol dm^{-3}. The inset shows the change in fluorescence spectrum of **1** with the AOT concentration.

slightly to the red (by ca. 5 nm) as w_o increases, which suggests that the fluorescence probe **1** is gradually displaced to a more polar microenvironment as the size of the water pool increases.[17]

The influence of the concentration of AOT and **1** on the aggregation behavior of **1** was also investigated. Figure 4 shows the changes in UV–vis and fluorescence spectra of **1** in AOT reversed micelles with $w_o = 8$, where the effects are expected to be more remarkable according to the trend observed in Figures 1 (inset) and 3. It can be seen that a higher concentration of AOT also promotes the formation of monomeric phthalocyanine, giving a more intense Q-band absorption and fluorescence emission. Figure 5 shows the UV–vis spectra of **1** with a concentration ranging from 5.0×10^{-7} to 3.0×10^{-6} mol dm^{-3}. On

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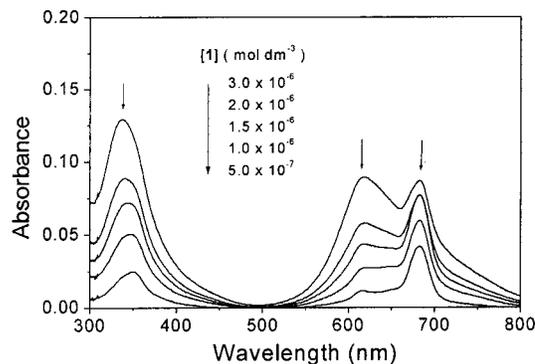

Figure 5. Absorption spectra of **1** in water/AOT/*n*-heptane with different concentrations of **1**, where $w_o = 12$ and [AOT] = 0.1 mol dm^{-3}.

the basis of the relative intensity of the two Q-bands attributed to the monomeric (682 nm) and aggregated (618 nm) species, it can be concluded that the relative population of monomer increases as the concentration of **1** decreases.

In summary, we have incorporated a cationic phthalocyanine into AOT reversed micelles. As shown by absorption and fluorescence spectroscopy, the reversed micellar system very effectively inhibits the aggregation of phthalocyanine, promoting the formation of a photoactive monomeric species, which may serve as a good photosensitizer for various applications.