Influence of Surfactants on the Aggregation Behavior of Water-Soluble Dendritic Phthalocyanines

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ABSTRACT: The interactions of a series of water-soluble dendritic phthalocyanines containing terminal carboxylate functionality with a range of surfactants in aqueous media have been investigated. Cationic surfactants, as compared with neutral and anionic counterparts, are much more effective to disrupt the molecular aggregation of phthalocyanines, in particular for the first generation macrocycle, as demonstrated by the absorption and fluorescence spectroscopy. The interactions are mainly electrostatic in nature, arising from the cationic head of the surfactant and the anionic surface of the dendrimers which has been supported by the fluorescence quenching experiments using the cationic porphyrin $(TMePyP)^{4+}$ as the quencher. The complex formation between the first generation dendritic phthalocyanine and the cationic surfactant CTAB has also been monitored by dynamic laser light scattering in 0.01 mol dm^{-3} NaBr aqueous media. As the concentration of CTAB increases, the apparent average hydrodynamic radius of the aggregates decreases significantly from 14.1 to 3.2 nm, showing that the aggregation of phthalocyanines is greatly relieved by CTAB and eventually the anionic macrocycles, mainly in monomeric form, are adsorbed onto the cationic micelle surfaces in a sideways manner.

Introduction

Water-soluble phthalocyanines serve as an important class of photosensitizers which can be used in photodynamic therapy in the treatment of a range of cancers, macular degeneration, and infectious diseases.[1,2] One of the key factors determining their photosensitizing efficacy is related to the intrinsic aggregation tendency of these macrocycles which is usually significant, in particular in polar media such as water.[3] It has been well documented that this intermolecular association provides an efficient nonradiative energy relaxation pathway reducing the luminescence quantum yields and shortening the excited-state lifetimes.[4] Production of singlet oxygen, which is commonly believed to be the main active species responsible for cell death, is therefore greatly inhibited. Photophysical properties of several sulfonated and carboxylated phthalocyanines in micelle systems[5] and in different biological media such as vesicles,[4c] nucleoproteins,[4e] and human[5g,6] and bovine serum albumin[3b] have been investigated. The microheterogeneous systems, except the nucleoprotein histone,[4e] can usually prevent the formation of aggregates to a certain extent, giving phthalocyanines with a stronger emission and longer excited-state lifetimes when compared with the homogeneous aqueous media. The addition of the cationic surfactant *n*-hexadecyltrimethylammonium bromide (CTAB), for example, greatly increases the excited-state lifetime of zinc(II) tetrasulfonated phthalocyanine in water from <80 ps to >1 ns.[5g] This has been attributed to the formation of monomeric phthalocyanine resulting from the interactions between the macrocycle and the micelle surface.

An alternative strategy to develop water-soluble and nonaggregated phthalocyanines involves the incorporation of bulky hydrophilic substituents on the periphery of the macrocycles. Because of the unique structural features, dendritic substituents are of special importance.[7] Only a few dendritic phthalocyanines, however, have been reported so far.[8] Recently, we have reported a series of zinc(II) phthalocyanines substituted with four dendritic fragments containing terminal carboxylate functionality.[9] These compounds are soluble in water, and as expected, their aggregation tendency decreases as the size of the dendrons increases. According to the variable-concentration UV−vis spectroscopic studies, the second generation phthalocyanine exists mainly as a monomeric species even in highly polar aqueous media. The compound therefore gives a remarkably strong fluorescence emission and a relatively high singlet oxygen quantum yield in water. We report herein an extension of this work focusing on the effects of different surfactants on the aggregation behavior of these dendritic macrocycles in water, using absorption and fluorescence spectroscopy together with laser light scattering technique as the probes. Although numerous dendrimers have been known,[7] their interactions with surfactants have only been briefly examined previously.[10]

Experimental Section

The preparation of the dendritic phthalocyanines **1**−**3** was described previously (Scheme 1).[9] All other reagents including the surfactants and the quencher were used as received. Spectroscopic studies were performed in doubly distilled water on a Hitachi U-3300 spectrophotometer and a Hitachi F-4500 spectrofluorometer. The fluorescence quantum yields were determined from the equation $\Phi_{sample} = (F_{sample}/F_{ref})(A_{ref}/A_{sample})(n_{sample}^2/n_{ref}^2)\Phi_{ref}$,[11] where F_{sample} and F_{ref} are the measured fluorescence (area under the fluorescence spectra) of the sample and the reference, respectively, A_{sample} and A_{ref} are the absorbances of the sample and the reference, respectively, at

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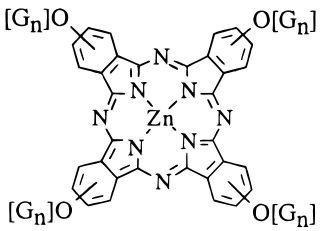
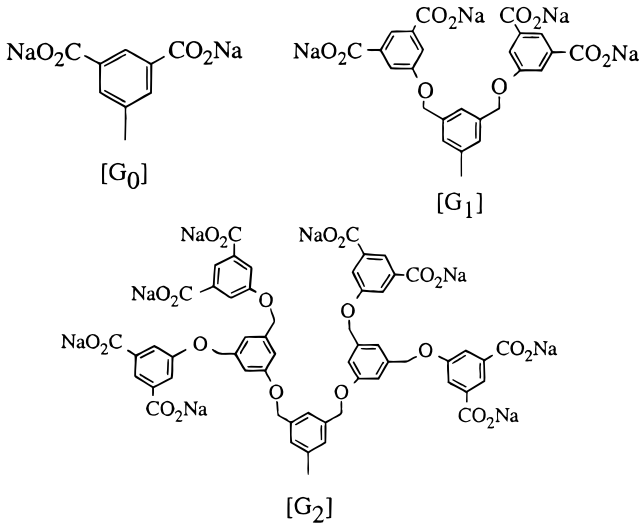
Scheme 1. Structure of the Dendritic Phthalocyanines



1 n = 0
2 n = 1
3 n = 2



the same excitation wavelength, n_{sample} and n_{ref} are the refractive index of the solvent used for the sample and the reference, respectively, and Φ_{ref} is the quantum yield of the reference which was taken as 0.30 for unsubstituted zinc(II) phthalocyanine in 1-chloronaphthalene.[12]

Dynamic laser light scattering (LLS) studies were performed on a modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlator (ALV-5000) and a solid-state diode laser (ADLAS DPY425II, output power $\approx$ 400 mW at $\lambda_0 = 532$ nm). The incident beam was vertically polarized with respect to the scattering plane. Details of the experimental setup can be found elsewhere.[13] The hydrodynamic radius $\langle R_h \rangle$ and the size distribution $[f(R_h)]$ were determined from the measured time correlation function.[14] All the LLS measurements were carried out at 25.0 $\pm$ 0.1 °C. All the solutions were clarified by 0.5 μm Millipore filters.

Results and Discussion

Figure 1 shows the UV−vis spectral changes of the first generation dendritic phthalocyanine **2** upon addition of CTAB in water. This macrocycle is significantly aggregated in water as shown by the broad and blue-shifted Q-band at 639 nm.[4b,f,15] With increasing concentration of CTAB, this band diminishes, and the band at 680 nm, which can be ascribed to the monomeric species, becomes more intense. When the concentration of CTAB reaches ca. 2×10^{-5} mol dm^{-3}, the spectrum is typical for monomeric phthalocyanines showing the B-band at 355 nm and the Q-band at 680 nm, together with a vibronic band at 611 nm. No significant changes were observed upon further addition of CTAB. Figure 2 plots the absorbance at 680 nm vs the concentration ratio of [CTAB]/[**2**]. For all the three concentrations of **2**, the absorbance increases rapidly and reaches a

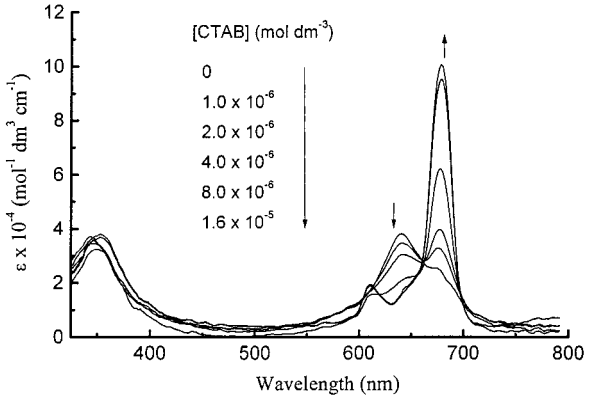


Figure 1. Absorption spectra of **2** in water (1.0×10^{-5} mol dm^{-3}) with different concentrations of CTAB.

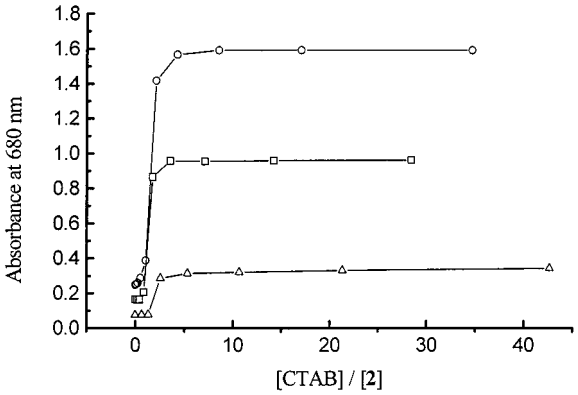


Figure 2. Plot of the absorbance at 680 nm for **2** vs the concentration ratio of [CTAB]/[**2**]. [**2**] = 3.0×10^{-6} (△), 9.0×10^{-6} (□), and 15×10^{-6} mol dm^{-3} (○).

saturated value at roughly the same value of [CTAB]/[**2**]. This observation suggested that the cationic surfactant can prevent the molecular aggregation of **2** favoring the formation of monomeric phthalocyanine. Similar effects of surfactants have also been reported for tetrasulfonated and carboxylated phthalocyanines in water,[5b,g,16] but a higher concentration of surfactant is required, indicating that the dendritic substituents themselves are able to inhibit aggregation of the phthalocyanine core.[9]

The fluorescence spectra of **2** were also susceptible to CTAB. Upon excitation at 615 nm, compound **2** exhibited a fluorescence emission at 686 nm, the intensity of which increased steadily with the concentration of CTAB. As dimeric or aggregated phthalocyanines are normally nonemissive,[4,17] the emission may arise mainly from the monomeric species. Figure 3 shows the variation of the emission peak area with the concentration of CTAB at three different concentrations of **2**. While the UV−vis spectra remained relatively unchanged when the concentration of CTAB was slightly higher than that of **2**, the fluorescence intensity was still increasing until the concentration of CTAB reached ca. 3×10^{-4} mol dm^{-3} in all the three cases. The results suggested again that the surfactant promotes the formation of monomer, and fluorescence, compared with electronic absorption of phthalocyanines, is much more sensitive to molecular aggregation, which depends largely on the concentration of CTAB. It is worth mentioning that although CTAB can also increase the fluorescence intensity of zinc(II) tetrasulfonated phthalocyanine, it happens only when the concentration of CTAB is well above its critical micelle concentration

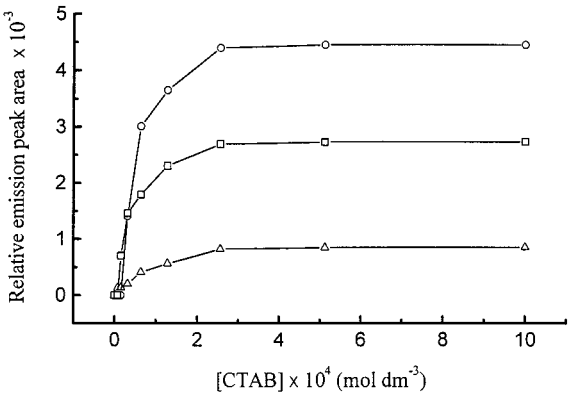


Figure 3. Plot of the relative emission peak area vs the concentration of CTAB at [**2**] = 3.0×10^{-6} (△), 9.0×10^{-6} (□), and 15×10^{-6} mol dm^{-3} (○).

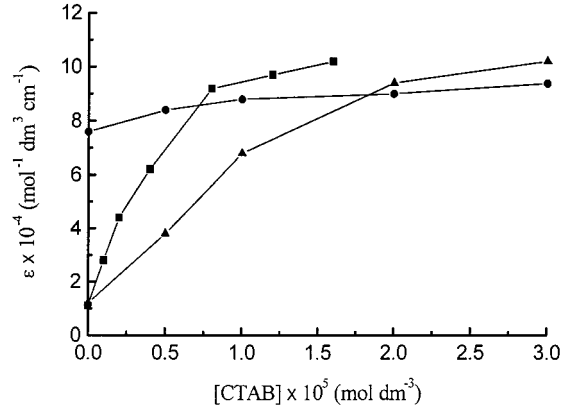


Figure 4. Variation of the molar absorptivity at 680 nm for **1** (▲), **2** (■), and **3** (●) (1.0×10^{-5} mol dm^{-3}) with concentration of CTAB.

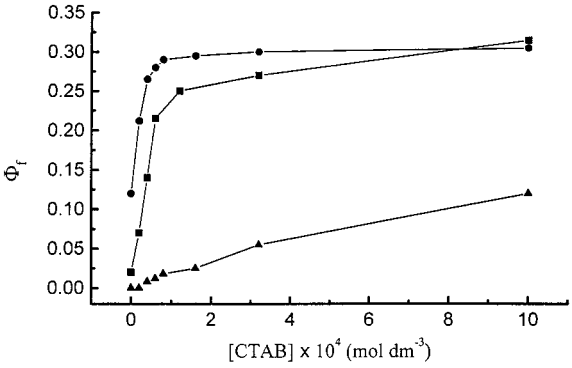


Figure 5. Variation of the fluorescence quantum yield of **1** (▲), **2** (■), and **3** (●) in water (2.0×10^{-5} mol dm^{-3}) with concentration of CTAB.

(cmc, ca. 1.0×10^{-3} mol dm^{-3}).[5g] This again demonstrated the supplementary effects due to the dendritic fragments on the aggregation process.

The absorption and emission properties of the zero and second generation analogues **1** and **3** were also studied in the presence of CTAB, and the results are depicted in Figures 4 and 5. It can be seen that the behavior of compound **1** is similar to that of **2**, but a larger amount of surfactant is needed to attain a similar effect, in particular for the fluorescence emission. Compound **3** is basically insensitive to CTAB, presumably due to the sterically hindered dendritic substituents and the additional negative charges which are able to disrupt the $\pi-\pi$ stacking of phthalocyanine even in the absence of surfactants.[9]

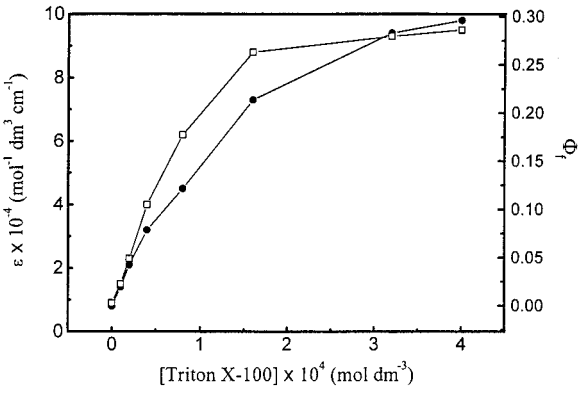


Figure 6. Change of the molar absorptivity at 680 nm (□) and fluorescence quantum yield (●) of **2** in water (2.0×10^{-5} mol dm^{-3}) with concentration of Triton X-100.

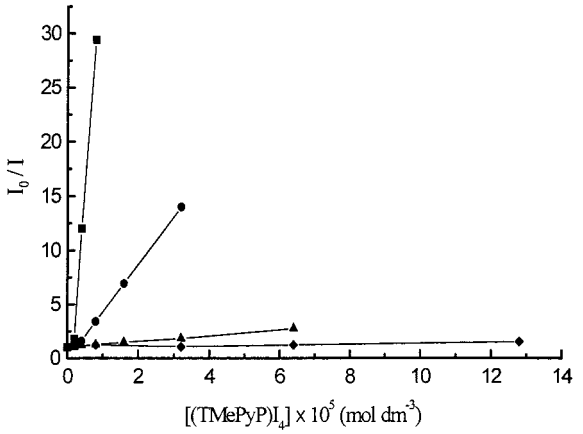


Figure 7. Stern−Volmer plots for the fluorescence quenching of **2** in water (2.0×10^{-5} mol dm^{-3}) by (TMePyP)I_4 in different concentration of CTAB: 2.0×10^{-5} (■), 4.0×10^{-5} (●), 8.0×10^{-5} (▲), and 32×10^{-5} mol dm^{-3} (◆).

The effects of neutral and anionic surfactants on the spectral properties of **2** were also investigated. The nonionic surfactant Triton X-100 could also relieve the extent of aggregation, giving monomer-like UV−vis spectra and a more intense fluorescence emission. Figure 6 shows the increase of molar absorptivity at 680 nm and the fluorescence quantum yield as the surfactant concentration increases. The effects, however, were weaker than those induced by the cationic CTAB, and a much more concentrated Triton X-100 solution was required. The anionic surfactants sodium dodecyl sulfate (SDS) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) virtually did not alter the spectral properties of **2**. This observation suggested that the electrostatic interactions between the anionic dendritic surface and the cationic head of CTAB play a crucial rule in promoting the monomer formation.

In our previous studies,[9] we found that the fluorescence of these dendritic phthalocyanines was effectively quenched by the cationic quencher *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin [$(TMePyP)^{4+}$], probably through a static quenching mechanism in which a dark complex is formed between the fluorophore and the quencher held by electrostatic forces. To examine the effects of surfactants on this quenching process, we repeated these experiments in the presence of various concentrations of CTAB. The results showed that the fluorescence quenching rate decreases remarkably with increasing concentration of CTAB (Figure 7), suggesting that there is a competition between $(TMePyP)^{4+}$ and

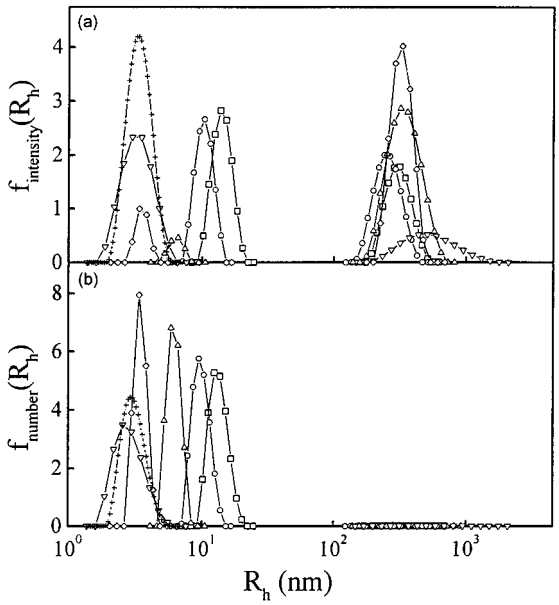


Figure 8. (a) Intensity- and (b) number-weighted distribution of the hydrodynamic radius of the **2**/CTAB complexes at a fixed concentration of **2** at 1.0×10^{-4} mol dm^{-3} in 0.01 mol dm^{-3} NaBr aqueous solutions. [**2**]:[CTAB] = 1:0 (□), 1:1 (○), 1:2.6 (△), 1:10 (◇), 1:32 (▽); + denotes pure CTAB.

CTAB for the anionic dendritic surface so that fewer molecules of the quencher are adsorbed on the dendritic surface, resulting in a slower fluorescence quenching. This observation provided evidence to support the static quenching mechanism between these dendritic phthalocyanines and $(TMePyP)^{4+}$ and the electrostatic nature of the interactions between **2** and CTAB.

The interactions of **2** and CTAB were also investigated by dynamic laser light scattering. Figure 8a shows the intensity-weighted distribution of the hydrodynamic radius of the **2**/CTAB complexes formed in various concentrations of CTAB in 0.01 mol dm^{-3} NaBr aqueous solutions. Two peaks were observed in all the cases, indicating that there exist two forms of aggregates. In the absence of CTAB, the two signals appeared at 14.1 and 305.6 nm which can be attributed to a phthalocyanine aggregate and a larger assembly of these aggregates, respectively. The formation of the smaller aggregates was in accord with the molecular modeling study[18] showing that the first generation dendritic substituents of **2** are not bulky enough to form a close shell to prevent molecular association. It is worth noting that the scattered light intensity is proportional to both the number (n) of scatterers and the square of the scatterer's mass (M), i.e., $I \propto M_w \propto nM^2$. As the dimension of the larger assemblies is at least 20 times larger than that of the smaller aggregates, the mass of the former is ca. 10^4 times higher than that of the latter, assuming their densities are similar. Since the light intensities scattered by these two types of particles differ by at most 1 order of magnitude, the actual number of the larger aggregates in NaBr aqueous solutions is extremely small in comparison with the number of the smaller aggregates (ca. $1-10^7$), showing that the latter is much more thermodynamically stable. This is well illustrated by the number-weighted distribution of the hydrodynamic radius shown in Figure 8b in which the contribution due to the larger assemblies is too weak to be observed. Similar results have been obtained previously for the system of CTAB and the dendrimer-like polyelectrolytes prepared by a condensation of Pentaerythritol and phthalic anhydride.[19]

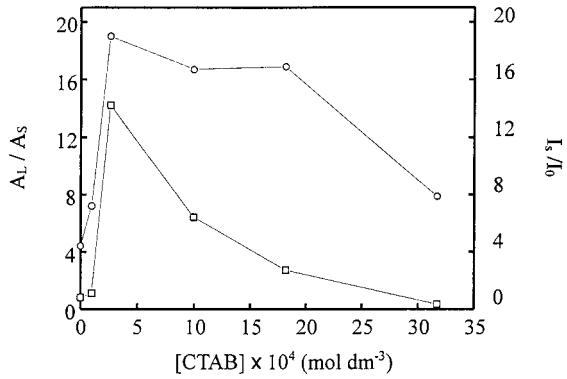


Figure 9. Plots of the peak area ratio (A_L/A_S) (□) and the normalized scattered light intensity (I_s/I_0) (○) vs the concentration of CTAB. [**2**] = 1.0×10^{-4} mol dm^{-3}.

As shown in Figure 8b, the average hydrodynamic radius of the smaller aggregates decreases significantly as the concentration of CTAB increases, indicating that CTAB is able to disrupt the phthalocyanine aggregates. Figure 9 displays the plots of A_L/A_S and I_s/I_0 vs the concentration of CTAB, where A_L and A_S represent the peak area for the larger and smaller aggregates (in Figure 8a), and I_s/I_0 is the normalized scattered light intensity, where I_0 is the reference intensity. It can be seen that both the plots give a sharp transition when the concentration of CTAB is around 2.6×10^{-4} mol dm^{-3}, which can be attributed to the cmc of CTAB under these conditions. It is worth noting that the cmc of CTAB in water has been reported to be 9.2×10^{-4} mol dm^{-3} at 25 °C.[20] The lowering of the cmc of CTAB in this case is related to the presence of NaBr and the anionic dendritic phthalocyanines, as it is well-known that the ionic strength of solution decreases the cmc.

According to the above results, we propose in Figure 10 a schematic representation of the structural changes for the **2**/CTAB system. Addition of a small amount of cationic CTAB partially disrupts, by electrostatic forces, the phthalocyanine aggregates which have an anionic surface. Smaller aggregates are thus formed in which the $\pi-\pi$ stacking tendency of phthalocyanine is relieved by the nonpolar tail of the surfactant. This results in a more monomer-like absorption spectrum and a more intense fluorescence signal due to phthalocyanine. When the concentration of CTAB reaches its cmc (ca. 2.6×10^{-4} mol dm^{-3}), micelles of CTAB are formed of which the surfaces are adsorbed by the anionic macrocycles. The average hydrodynamic radius of the aggregates (6.3 nm) measured under these conditions is in good agreement with the calculated value based on the radius of CTAB micelles (3.4 nm, measured in the absence of **2**) and the dimension of **2** (ca. 3.0 nm from a molecular modeling study).[18] According to Figure 9, this form of aggregate appears to have a higher tendency to form larger aggregates, probably due to the adsorbed molecules of **2**, which can act as the linking units. Upon further addition of CTAB, more CTAB micelles are formed, and the average number of phthalocyanine attached to each micelle decreases. This is in accord with the apparent size of the aggregates which is very close to that of CTAB micelles (Figure 8).

In summary, we have employed absorption and fluorescence spectroscopy along with a dynamic light scattering technique to study the influence of surfac-

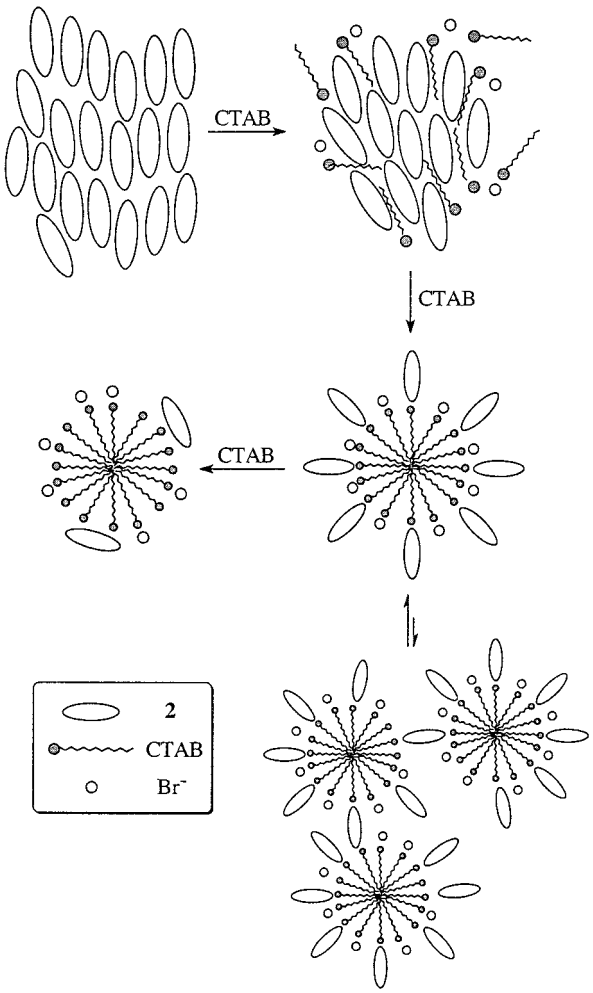


Figure 10. A schematic diagram showing the structural changes for the **2**/CTAB complexes upon addition of CTAB.

tants on the aggregation behavior of a series of water-soluble phthalocyanines with dendritic substituents. The cationic surfactant CTAB is very efficient to relieve the extent of aggregation of phthalocyanines in water, giving highly fluorescent monomeric phthalocyanines which are potentially useful for various photophysical and chemical applications.

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