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5,10,15,20-Tetra(4-carboxyphenyl)porphyrin J-aggregate self-assembly in submicellar aqueous sodium dodecylsulfate solutions

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meso-Tetra(4-carboxyphenyl)porphyrin J-aggregate self-assembly in submicellar acidic aqueous solutions of the anionic surfactant sodium dodecylsulfate due to hybrid porphyrin–surfactant ionic associate formation has been observed.

The porphyrin–surfactant interactions are of great interest both for the biomedical practice allowing one to model and predict the aggregation behavior with the directly related photophysical properties and photochemical activity of the potential biocompatible photosensitizers and diagnostic agents[1] in aqueous microheterogeneous systems that mimic an intracellular medium and for the study of porphyrin self-assembly mechanisms aimed at the development of porphyrin-based supramolecular structures[2] with unusual electronic and optical properties.[3,4] Most of the authors considered the pigment localization and equilibria between various chromophore species in micellar surfactant solutions,[5–8] while some of them described submicellar porphyrin–surfactant ionic associate formation between the oppositely charged porphyrin monomers and surfactant molecules for both charged[9–13] and neutral[14] porphyrin species with the final products being often amorphous irregular heterogeneous assemblies. However, in several cases well-defined highly ordered supramolecular structures[14–18] with the ladder-type monomer arrangement and strong π–π-conjugation between chromophore aromatic systems known as J-aggregates were obtained.[19] A rearrangement between J- and H-aggregates, which are formed spontaneously due to hydrophobic interactions in polar solvents, was also reported.[5]

This work provides evidence for the surfactant-induced self-assembly of the *meso*-tetra(4-carboxyphenyl)porphyrin (TCPP) J-aggregates in submicellar acidic aqueous solutions of sodium *n*-dodecylsulfate (SDS) within a concentration range of 0.1–0.01 cmc.

In a neutral aqueous solution, TCPP exists as the anionic monomer H_2TCPP^{4-} with an intense Soret band at 414 nm and four Q-bands in the red spectral region corresponding to the D_{2h} chromophore symmetry group [Figure 1(*a*)]. The bulk solution acidification causes the peripheral carboxylic group protonation leading to the formation of neutral $H_2TCPPH_4^0$, which, under strongly acidic conditions (pH < 1), undergoes further pyrrole nitrogen atom diprotonation in the macrocycle core resulting in the dicationic $H_4TCPPH_4^{2+}$ form with a higher D_{4h} symmetry and a coplanar arrangement of the *meso*-aryl rings with the macrocycle plane, providing a 20 nm Soret band batochromic shift and the reduction in the Q-band number in the absorption spectrum.[20] In the presence of counterions capable of coordination with dicationic porphyrin monomers reducing the electrostatic repulsion, one can usually observe the formation of J-aggregates which are characterized by a narrow red-shifted Soret band and a new excitonic J-aggregate band at about 690 nm and by strong fluorescence self-quenching [Figure 1(*b*)].† This seems to be the reason for the earlier reported counterion dependence of both the TCPP J-aggregate structure and its aggregation kinetics in aqueous solutions.[21,22] Comparing TCPP aggregation behavior

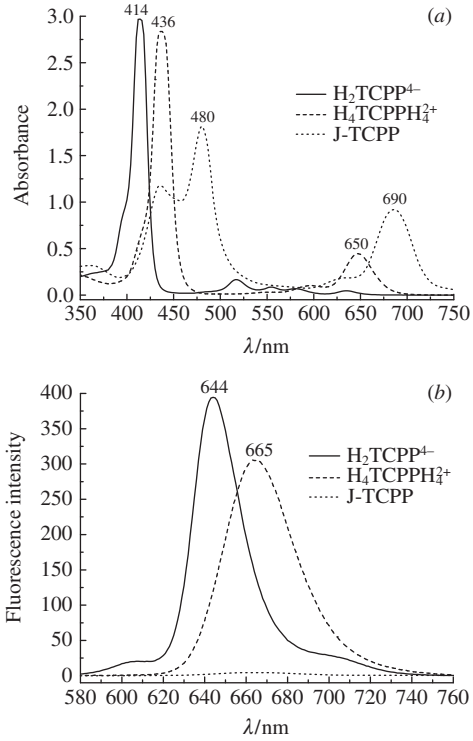

Figure 1 (*a*) Absorption and (*b*) fluorescence spectra of TCPP forms.

in nitric and hydrochloric acid solutions, Choi *et al.*[21] reported a greater efficiency of the nitrate anion compared to that of the chloride anion in TCPP J-aggregate formation with absorption maxima at 467 and 662 nm. Using sulfuric acid, we managed to obtain TCPP J-aggregates‡ with a more significant batochromic shift of aggregate absorption bands relative to those of the monomeric diprotonated form up to 480 and 690 nm and a higher degree of aggregation, which is assumed to be due to the greater coordinating potential of the sulfate anion.

In addition to the simple inorganic counterions, anionic polyelectrolytes can also promote TCPP J-aggregation and serve as templates for stable highly ordered supramolecular porphyrin-

† The excitation wavelength corresponded to the Soret absorption band of the porphyrin species: 414 nm for the neutral monomer, 434 nm for the diprotonated $H_4TCPPH_4^{2+}$ form and 480 nm for the J-aggregated TCPP.

‡ TCPP J-aggregates with the absorption bands at 480 and 690 nm were obtained in H_2SO_4 (2 mol dm^{-3}) without any electrolytes at room temperature with a TCPP concentration of 10 μmol dm^{-3}.

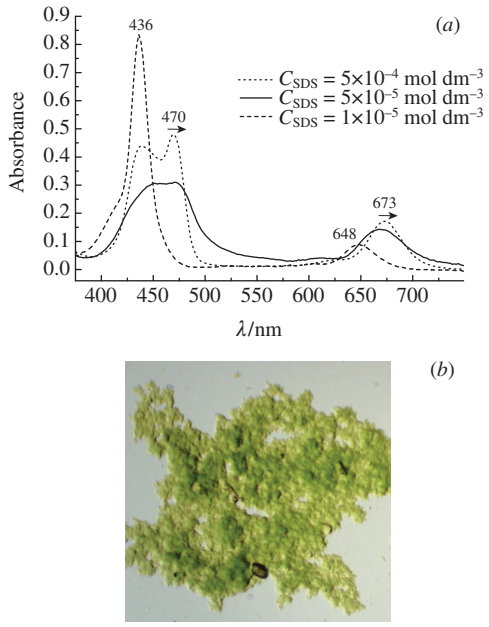

Figure 2 (*a*) Absorption spectra of $H_4TCPPH_4^{2+}$. (*b*) A micrograph of the TCPP J-aggregate microparticle (1000×) obtained from the acidic aqueous SDS solution at C_{SDS} = 5×10^{-4} mol dm^{-3}.

based assemblies. In our experiments, the above function appeared to be performed by the anionic dodecyl sulfate or its 2.37 nm dimers,[23] which are abundant in the premicellar surfactant solutions of 0.1–0.01 cmc and responsible for the self-assembly of the TCPP–SDS ionic associates, which can be attributed to the TCPP J-aggregates according to their morphology and spectral features (Figure 2).[§]

The minimal surfactant concentration required for the TCPP–SDS ionic associate formation is 5×10^{-5} mol dm^{-3}, while the maximum of the TCPP aggregate-to-monomer ratio is observed at 5×10^{-4} mol dm^{-3}, which corresponds to the same values obtained earlier for the tetraphenylporphyrin J-aggregate self-assembly in submicellar aqueous-organic SDS solutions (unpublished data). This similarity suggests the key role of the electrostatic interactions between the diprotonated porphyrin monomers and the oppositely charged surfactant sulfonic head groups, resulting in macrocycle charge neutralization followed by surfactant-mediated chromophore aggregation. In addition to the charge compensation, the surfactant headgroups can also serve as bridging groups between neighboring macrocycles owing to hydrogen bonding. Though the strong interchromophore π–π interactions contribute to the resulting aggregate structure stabilization, the building block orientation and, hence, the highly ordered chromophore arrangement seem to be due to the ionic contribution.

For single surfactant molecules, the required porphyrin : surfactant molar ratio for minimal neutral building block formation should be at least 1 : 2, which is five times lower than the observed complex formation threshold. In this regard, we propose to consider the linear SDS dimers with oppositely directed headgroups as possible linkers between the neighboring porphyrin rings (Figure 3).

Since the premicellar SDS solutions demonstrate a kind of supramolecular chirality in the course of the premicellar aggregate self-assembly,[24] one should obtain the CD spectra of the porphyrin–surfactant ionic associates in order to reveal the possibility of the surfactant-induced chirality of the TCPP J-aggregates. Thus,

[§] The absorption spectra were obtained at a given surfactant concentration in aqueous sulfuric acid solution with pH 0.55 containing 3 μmol dm^{-3} TCPP at room temperature. The aggregation time was about 30 min.

The final precipitate morphology was studied after two-day storage with the subsequent centrifugation of the suspension at 8000 rpm for 15 min.

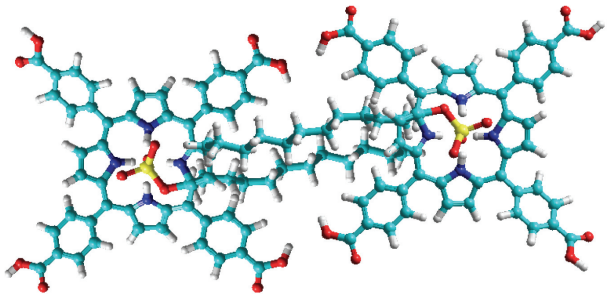

Figure 3 TCPP J-aggregate structure fragment with the SDS dimer.

our preliminary data suggest that in the studies of the premicellar dye–surfactant interactions it is necessary to consider not only chromophore aggregation but also the aggregation state of the surfactant.

The above system is also expected to depend on the surfactant molecular structure, so it would be useful to examine interactions between the cationic diprotonated porphyrins with anionic surfactants with different alkyl chain lengths and hydrophilic–lipophilic balance, including gemini surfactants and binary surfactant mixtures as the promising candidates for the water-soluble porphyrin J-aggregation promoting agents.

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