

Photophysical Properties and Aggregation Behavior of Transition Metal Tetraphenylporphyrin Tetrasulfonate Complexes in Microheterogeneous Media

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This paper considers the influence of various surfactants and polyelectrolytes on the photophysical properties and the aggregation state of transition metal complexes of meso-5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin (MeTPPS). Porphyrin transition metal complex aggregation stability in acidic medium is also compared for a number of metal cations. The mechanism of J-aggregate formation and the nature of porphyrin-surfactant interactions in microorganized systems are discussed in details.

Keywords: Transition metal porphyrin complexes, ZnTPPS, J-aggregates, ionic associates.

Фотофизические свойства и агрегационная устойчивость металлокомплексов тетрасульфофенилпорфирина в микрогетерогенных средах

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Изучено влияние различных полиэлектролитов и сурфактантов на агрегационное поведение в водных растворах металлокомплексов тетрасульфофенилпорфирина.

Ключевые слова: Порфирины, комплексы с переходными металлами, ZnTPPS, J-агрегаты, ионные ассоциаты.

Introduction

Porphyrin based supramolecular assemblies in recent years have been considered as novel mesoscopic materials with tunable electronic and optical properties, useful as photosensitizers, optical switches, molecular sensors, artificial light-harvesting systems and photovoltaic device components.^[1-3] Such smart materials can include either homoporphyrin aggregates (*H*- or *J*-type ones) or multiporphyrin assemblies,^[4] as well as heteroaggregates^[5] and ionic associates with various non-porphyrin compounds.^[6] Since both photophysical and photochemical properties of various porphyrin derivatives strongly depend on the chromophore aggregation state determined predominantly

by the medium acidity, ionic strength and the presence of template molecules, controlled reversible aggregation of porphyrin supramolecular assemblies is still of great research interest.

To date among the known water-soluble porphyrin derivatives the most well-studied one is *meso*-5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin (TPPS). During the past decade much work has been done on TPPS interactions with surfactants,^[7-11] polyelectrolytes^[12-15] and especially biomacromolecules.^[16-18] The increasing research interest in porphyrin behavior within microorganized systems is due to their possible application as photosensitizers in photodynamic therapy (PDT),^[19] since the microheterogeneous medium is known to favor supramolecular ionic associate and

heteroaggregate formation, especially at low pH abundant in cancer cells.^[20-22] Despite the large amount of available experimental data, we still lack a unified detailed description of the mechanism of porphyrin aggregate formation in microorganized biomembrane-mimetic media.

The main aim of this work was to compare the photophysical properties and the aggregation state of water soluble transition metal complexes of tetraphenylporphyrin tetrasulfonate in various microheterogeneous systems, such as surfactant (SDS, CTAB, TX-100) and polyelectrolyte (PDDA, PVP, PEG) solutions with different surface charge. We especially focused on influence of the cation nature on the porphyrin metal complex stability in acidic medium, *J*-type aggregate formation and their morphology.

Experimental

Transition metal complexes of cobalt, nickel and zinc with anionic *meso*-5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin were synthesized in Ivanovo State University of Chemistry and Technology (Ivanovo, Russia) and used without any further treatment. The stock solutions with $5 \cdot 10^{-5}$ M chromophore concentration in 1 M sulfuric acid were prepared using bidistilled water. The acidified solutions were stored in a darkness at room temperature for at least 3 days in order to allow full precipitation of aggregated species. Then the stock solutions were centrifuged at 8000 rev/min and the precipitate morphology was studied using optical microscopy.

The surfactant and polyelectrolyte solutions were prepared from analytical grade chemicals in an appropriate concentration just before the experiment. The surfactants used included: anionic sodium dodecyl sulfate, SDS (Scharlau, Germany), cationic cetyltrimethylammonium bromide, CTAB (BioChemica & AppliChem, Germany) and neutral Triton X-100, TX-100 (Lab-Scan, Poland). Polydiallyldimethylammonium chloride, PDDA was kindly provided by Prof. Shapiro B.I. (Lomonosov Moscow State University of Fine Chemical Technologies).

The absorption spectra were obtained using Shimadzu UV-Vis 3100 (Japan) and the emission spectroscopic measurements were performed with Shimadzu RF-5000 (Japan) in a 1 cm quartz cell. Data processing and visualization were performed using Origin 6.1 and ChemSite software, respectively.

Results and Discussion

According to the known mechanism^[23] (Figure 1), ZnTPPS dissolution in a strongly acidic medium with $\text{pH} < 2$ results in a rapid demetallization of the metal complex (1) and protonation of the imine nitrogen atoms within the macrocycle (2), accompanied by further aggregation of a neutral zwitterionic precursor H_4TPPSH_2 into ladder-type *J*-aggregates (3):



Some workers suggest the initial formation of less ordered *H*-aggregates, which eventually transform into *J*-aggregates during the induction time.^[24]

The metal porphyrin absorption spectrum changes upon the decreasing pH from a typical monomer TPPS with the absorption maxima at 422 and 556 nm to the light-green solution which shows a gradual absorbance increase at 490 and 710 nm, characteristic for *J*-type aggregated species, with the decreasing extinction in the diprotonated monomeric bands at 434 and 590 nm (Figure 2). The spectral changes observed in the long wavelength spectral region corresponding to *J*-aggregate formation without any electrolytes or surfactants require several hours to occur. Monitoring of the aggregation kinetics at characteristic absorption bands reveals the limiting step of the neutral precursor aggregation requiring an appropriate orientation of the monomer building blocks (Figure 1,c).

After three days' storage in the dark place at room temperature amorphous green microparticles precipitate out of the solution. The optical microscopy allowed to reveal the average size of the visible particles in the precipitate of 1-10 μm , while the individual particles were about 30 μm (Figure 3). Since the tetrasulfonatophenyl porphyrin molecule diameter is about 2 nm and the typical size of *J*-aggregates is below a hundred nanometers,^[25] the observed microstructures are the products of secondary *J*-aggregate association.

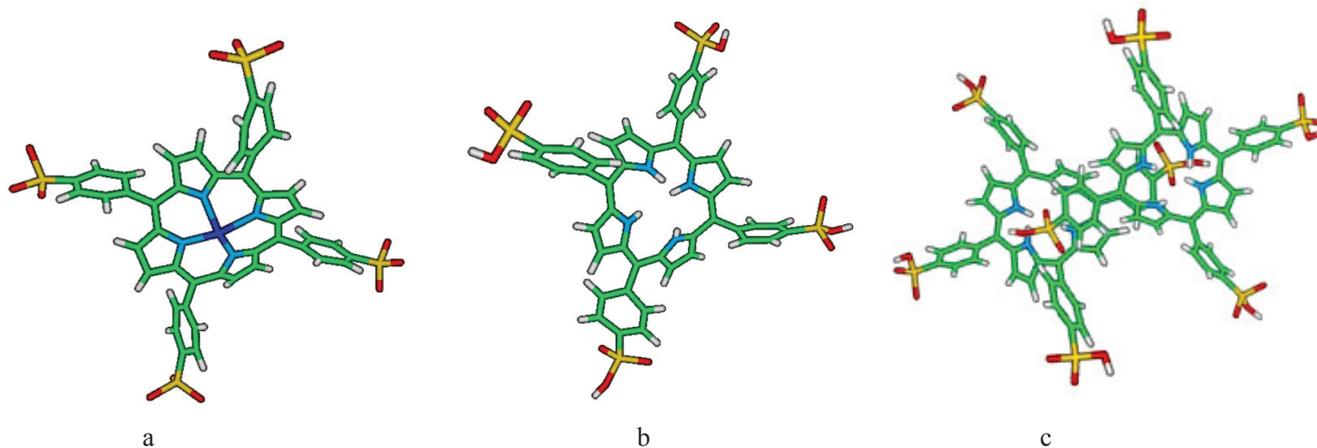


Figure 1. TPPS species at the major stages of *J*-aggregate formation in acidic medium: *a* - monomeric metal porphyrin, *b* - protonated zwitterion, *c* - *J*-type dimer.

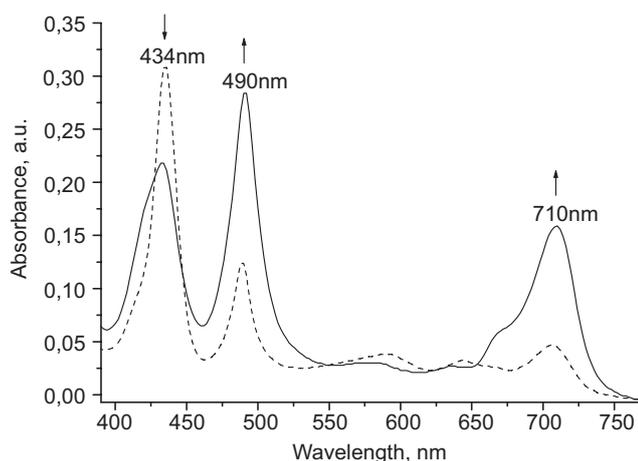


Figure 2. Absorption spectra of ZnTPPS in the course of *J*-aggregate formation.

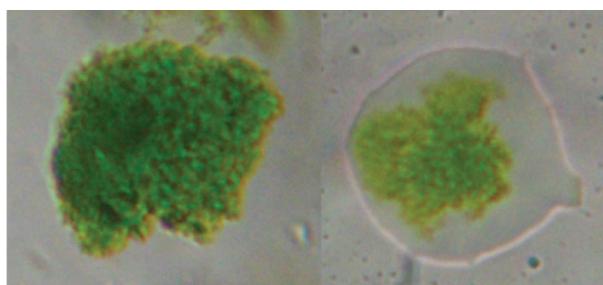


Figure 3. The optical images of the microparticles after *J*-aggregate precipitation (1 cm = 10 μm).

The excess of 0.1 M NaOH added to the initial acidic solution caused a blue shift of the porphyrin's Soret band from 434 nm to 412 nm and a strong fluorescence quenching due to *H*-aggregate formation. Thus, the alkaline medium inhibits *J*-type aggregate formation due to electrostatic repulsion between peripheral sulfonic groups, which is compensated in acidic medium by protonation. Even after the addition of small amounts of alkaline the aggregation equilibrium shifts towards the monomeric porphyrin species (Table 1). The presence of an inorganic salt increasing the ionic strength also leads to a significant broadening of the porphyrin Soret band due to *H*-aggregate formation, which is consistent with the known data.^[26]

Table 1. The influence of medium acidity on the TPPS monomer to aggregate ratio.

$A_{\text{monomer}}/A_{\text{aggregate}}$	Acidic	Neutral	Alkaline
A_{435}/A_{491}	1.20	1.30	3.76
A_{435}/A_{700}	2.97	3.53	7.23
A_{644}/A_{700}	0.59	0.56	1.12

For other transition metal complexes in the strongly acidic medium ($pH < 1$) the dynamic equilibrium between the coexisting porphyrin species with a various degree of protonation is strongly dependent on the nature of the metal ion.^[27] In the case of NiTPPS and CoTPPS the emergence of fluorescence in 662–664 nm region at low pH , which is not characteristic for transition metal porphyrin complexes with

an incomplete *d*- sub-shell due to self-quenching, reveals the presence of metal-free protonated species H_4TPPS^{2-} . Thus, the mechanism of *J*-aggregate formation in this case includes the same steps of demetallization and protonation of the initial complex, accompanied by further aggregation, as known for ZnTPPS. But the aggregation rate and monomer to aggregate ratio in each case strongly depend on the nature of the metal ion (Figure 4.) After a week-storage in acidic solution the nickel complex produced *J*-aggregates, while the cobalt one mostly remained in a metal-coordinated form with a minor amount of aggregated species. The observed difference in porphyrin metal complex stability to demetallization can be probably attributed to the difference in the metal ionic radii.

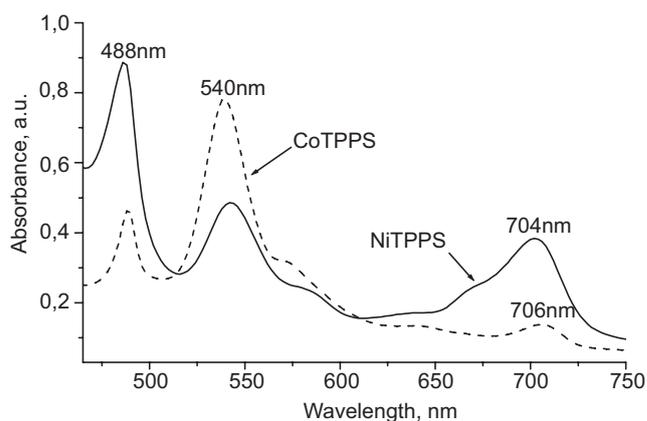


Figure 4. The comparison of CoTPPS and NiTPPS absorption spectra (*Q*-band region) in acidic solution ($pH = 1$) after a week-storage in darkness at room temperature.

The presence of surfactants and polyelectrolytes in the stock solution strongly affects the porphyrin aggregation process. In the case of ZnTPPS both cationic (CTAB) and nonionic (TX-100) surfactants after being added to the metal porphyrin solution cause a *B*-band bathochromic shift of about 5 nm and effectively prevent ZnTPPS from demetallization and protonation in acidic medium, while the anionic one, namely SDS, does not influence the Soret band position and failed to protect ZnTPPS (Figure 5). This fact indicates the importance of electrostatic nature of porphyrin interactions with the micellar surface at the first steps of the solubilization process.

It was also shown that cationic polyelectrolytes, namely PDDA, and pre-micellar cationic surfactant solutions (CTAB) promote *J*-aggregate formation from demetallized protonated H_4TPPS^{2-} species, while cationic micelles provide a hypsochromic shift of H_4TPPS^{2-} absorption maximum from 434 to 418 nm, resulting from predominant micellization of deprotonated monomeric H_2TPPS^{4-} species.^[28] The above findings are in a good agreement with the results obtained under similar experimental conditions earlier.^[7,9,10,26]

A special type of ionic associate formation was observed for CoTPPS in presence of PDDA. Unlike the bulk water CoTPPS solution, a freshly prepared PDDA-containing system exhibited significant fluorescence at 609 nm, resulting from the possible heteroaggregate formation (Figure 6,a). After a week-storage at room

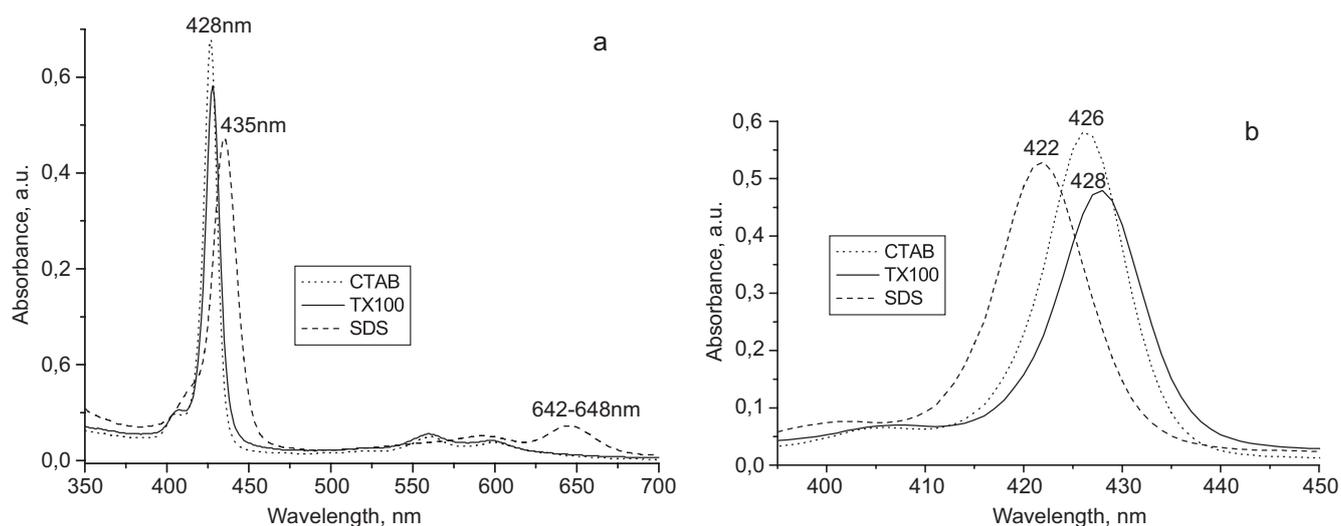


Figure 5. *a* – The absorption spectra of ZnTPPS in acidic medium in presence of various surfactants; *b* - the same for ZnTPPS neutral aqueous solution (for comparison).

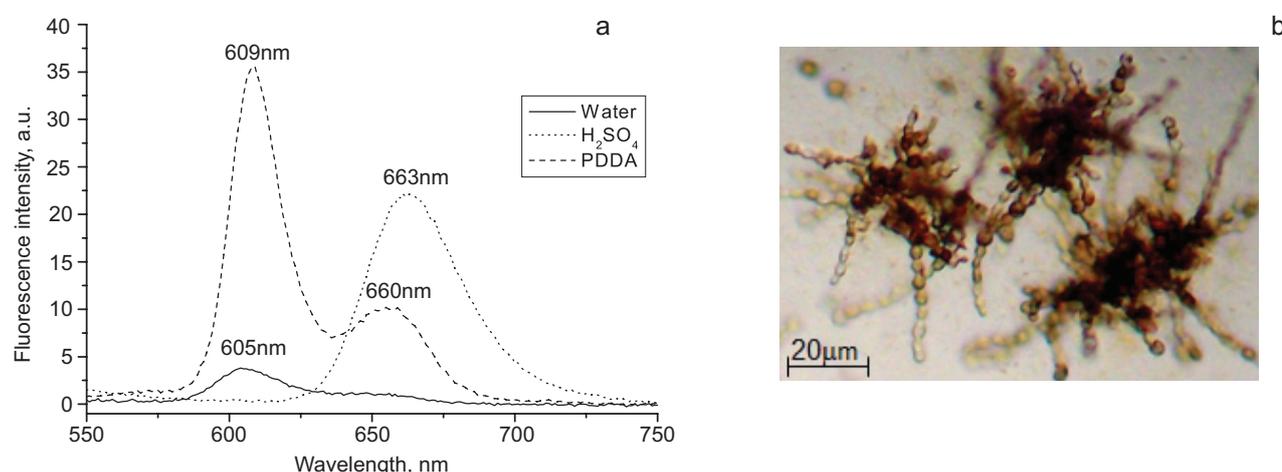


Figure 6. *a* - Emission spectra of CoTPPS in various media; *b* - the optical image of CoTPPS-PDDA heteroaggregates.

temperature the latter system produced a large amount of well-organized brown amorphous species of about 10 μm in size (Figure 6,b), which appeared to be stable enough for at least two months.

Conclusions

Water soluble tetrasulfophenylporphyrin transition metal complexes were found to possess different aggregation stability in acidic medium, depending on the metal ion parameters (*e.g.* ionic radius), as well as on the presence of cationic template surfaces. According to fluorescence spectroscopy, cationic polyelectrolytes and especially surfactants significantly decrease ZnTPPS fluorescence intensity due to electrostatic attraction between their cationic surface and sulfonic acid residues of the macrocycle, providing fluorescence self-quenching by the porphyrin aggregated species. Thus, the latter are the most appropriate precursors for *J*-aggregate formation, and their ionic interactions with cationic polyelectrolyte and micellar

surface provide novel approaches for supramolecular design based on *pH*-controlled reversible porphyrin self-assembly in microheterogeneous media.

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