Porphyrin - Based Supramolecular Nanotubes Generated by Aggregation Processes

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Porphyrins can form a variety of structures from linear head-to-tail or J-aggregates to fractal aggregates with different and specific photophysical properties. In this paper, the controlled aggregation of meso-5 ,10, 15, 20-sulfonato-phenyl porphyrin ($H_2TPPS_4^{4-}$) *was studied at room temperature. Structure of the aggregates was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV-visible spectroscopy. TEM and SEM results indicated the formation of organized nanostructures from the porphyrin derivative. UV-visible-NIR spectroscopic data showed broad red-shifted Soret band, indicating J-aggregation among the monomer units. Conjugate effect of lateral* π-π *interaction among the tetrapyrrole cores and hydrophobic interaction among the peripheral phenyl rings is believed to lead to the organized nanostructures. Such aggregates have the size of 5-6 nm in solution. The columnar structure formed by porphyrins has a length of 5 to 27 porphyrin unities.*

Keywords: porphyrin, aggregation, TEM, aggregates

In recent years, an increasing number of researchers have considered the possibility of using porphyrins as photosensitizer drugs in photodynamic therapy (PDT) [1,2]. PDT is based on the concept that photosensitizer (PS) molecules can be preferentially localized in tumor tissues upon systemic administration. Reactive oxygen species, such as singlet oxygen (${}^1O_2$), or free radicals are the main cytotoxic substances, which can irreversibly damage the treated tissues. It is generally accepted that singlet oxygen is the primary cytotoxic agent responsible for photobiological activity [3].

Porphyrins have been the preferred drugs used as a photosensitizing substances due to their high affinity for the tumor cell and their strong effect under irradiation with light. Among water soluble porphyrins, meso-5 ,10, 15, 20-sulfonato-phenyl porphyrin (H2TPPS4 $^{4-}$) as free base, is one of the best tumor localizer and killer [4-6].

Porphyrins can form a variety of structures from linear head-to-tail or J-aggregates to fractal aggregates grown under different regimes of aggregation, and can exhibit rich photophysical properties. Aggregates can break into their constituent parts which can be monomers or smaller aggregates. Meawhile, interaction between intraaggregate substructures (monomers or smaller aggregates) can be probed by transmission electron microscopy (TEM).

Structure of the aggregates was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV-visible spectroscopy. TEM results indicated the formation of organized nanostructures from the porphyrin derivative. XRD results showed that the bulk and nanostructured free porphyrin derivatives had the similar crystalline morphology. UV-visible-NIR spectroscopic data showed broad red-shifted Soret band, indicating J aggregation among the monomer units. Conjugate effect of lateral π-π interaction among the tetrapyrrole cores and hydrophobic interaction among the peripheral phenyl rings is believed to lead to the organized nanostructures. H and J-aggregates of some porphyrins are based on the intermolecular interactions of 3-5 Kcal/mol per porphyrin face. Such aggregates have the size of 5-6 nm in solution. The columnar structure formed by porphyrins has a length of 5 to 27 porphyrin unities. In this paper we focused on our own strategy based on coordination chemistry for the design and build-up of supermolecules and supramolecular structures porphyrin-based, are presented.

Experimental part

Materials and methods

5,10,15,20-tetra- *p*- sulphonatophenylporphyrin ($H_2TPPS_4{}^{4-}$) (fig. 1) has been prepared and purrified in the lab after a literature receipt [7].

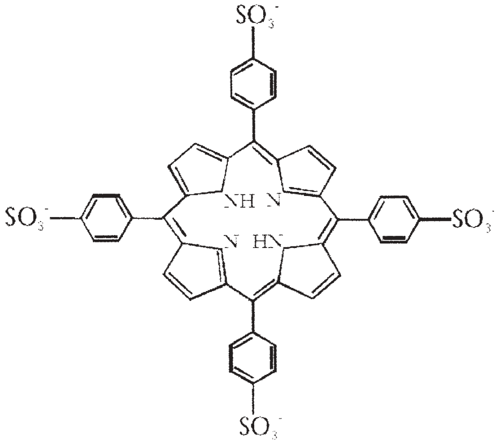

Fig. 1. Chemical structure of 5 ,10, 15, 20-sulfonato-phenyl porphyrin ($H_2TPPS_4{}^{4-}$)

The *J*-aggregate solutions were prepared by dissolving $H_2TPPS_4^{4-}$ in acidic aqueous medium (HCl was added to reach pH 1) at the concentration range $1 \, . \, 10^{-4}$ to $2 \, . \, 10^{-6}$ M. To stabilize the aggregates formation the solution was left at room temperature for aggregation for 10 days. The *J*-aggregates of $H_2TPPS_4^{4-}$ formed after solution preparation was confirmed by absorption spectra.

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Apparatus

Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a SPECORD M400 spectrometer. A Hitachi S-2700 electron microscope operating at 10 kV, was used to obtain TEM images.

SEM images have ben obtained with a scanning electron microscope Nikon T600 laser scanning microscope. The images were collected with an immersion objective and displayed on a charge-coupled device camera.

Results and discussions

5 ,10, 15, 20-sulfonato-phenyl porphyrin ($H_2TPPS_4^{4-}$) is a water-soluble tetrapyrrolic dye (fig.1). It has been shown that $H_2TPPS_4^{4-}$ can self-associate to form H- and J-aggregates depending on the dye concentration, pH and ionic strength [8-11]. In an acidic medium (pH < 5), the nitrogen atoms of $H_2TPPS_4^{4-}$ can be protonated resulting in a diprotonated form $H_4TPPS_4^{2-}$. The diprotonated tetraphenyl porphyrin shows, in contrast to its neutral form, a near to coplanar conformation of the phenyl rings to the tetrapyrrolic ring. This allows the approach of the sulfonato groups to the central part of the tetrapyrrolic ring thereby forming J-aggregates [12]. The formation of J-aggregates is indicated by the appearance of a sharp intense absorption band that is batochromically shifted with respect to the monomeric Soret band [13]. Figure 2 shows the ground state absorption spectra of $H_2TPPS_4^{4-}$ in aqueous solution buffered at *p*H 7.5, 3.4 and 1.2. The absorption spectrum of $H_2TPPS_4^{4-}$ at *p*H 7.5 is characteristic for the free-base porphyrins. It exhibits four Q bands located at 515, 553, 580 and 633 nm and an intense near-UV band (Soret band) with a maximum at around 414 nm [14].

The absorption spectrum changes in acidic environment (*p*H 3.4) exhibiting a bathocromic and slightly broadened Soret band at 433 nm, a narrow intense band at 490 nm, and two broad weaker bands at 642 and 707nm. The spectral bands at 433 and 642 nm can be attributed to the diprotonated ionic species $H_4TPPS_4^{2-}$, whereas the band at 490nm (B-band) and at 707nm (Q-band) are characteristic for J-aggregates [10]. A further decrease of the solution *p*H to 1.2 results in an increase in the intensity of the absorption bands at 490 and 706 nm, and in the disappearance of the absorption bands related to the neutral and diprotonated species of porphyrin $H_2TPPS_4^{4-}$ [15-18].

These changes in the absorption spectra have been assigned to the formation of the J-aggregates, derived from the dianionic $H_4TPPS_4^{2-}$, as indicated by the diminution of the absorption at 433 nm [19], with a heliptic structure, as have already been reported, (fig. 3).

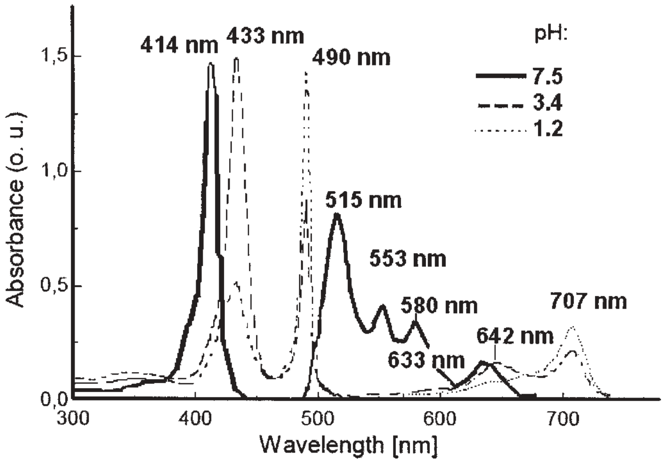

Fig. 2. The absorption spectra of $H_2TPPS_4^{4-}$ in aqueous solution buffered at *p*H 7.5, 3.4 and 1.2.

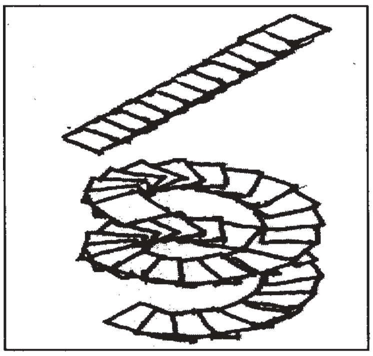

Fig.3. The $H_2TPPS_4^{4-}$ aggregates structure H (up) and J(down)

Assuming that the distance between molecules is ~5 Å, the aggregate length can be calculated to be ~10^{-6} cm. However, it has been proposed that J-aggregates of $H_2TPPS_4^{4-}$ tend to form large fractal-like structures or macroaggregates in organic solvents. Such aggregates have the size of 5-6 nm in solution. The columnar structure formed by porphyrins has a length of 5 to 27 porphyrin unities [20,21], as we determined from the TEM image obtained in figure 4.

If J-aggregates give different arrays depending on the meso-substitution pattern, the H-aggregates (face-to-face) are reported for porphyrin species with less than four sulfonic acid groups or phenyl rings.

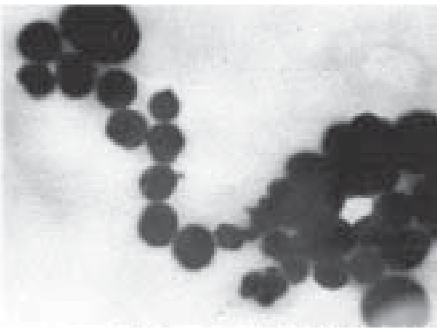

Fig.4.TEM Image of J agregate of $H_2TPPS_4^4$

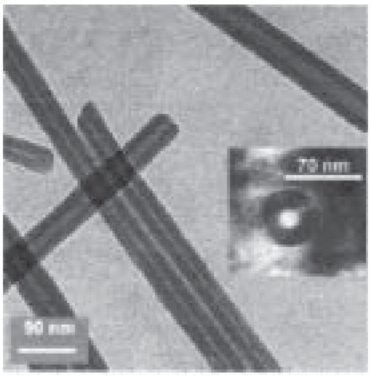

Fig.5. SEM image of J-aggregate hollow cyclinder of $H_2TPPS_4^{4-}$

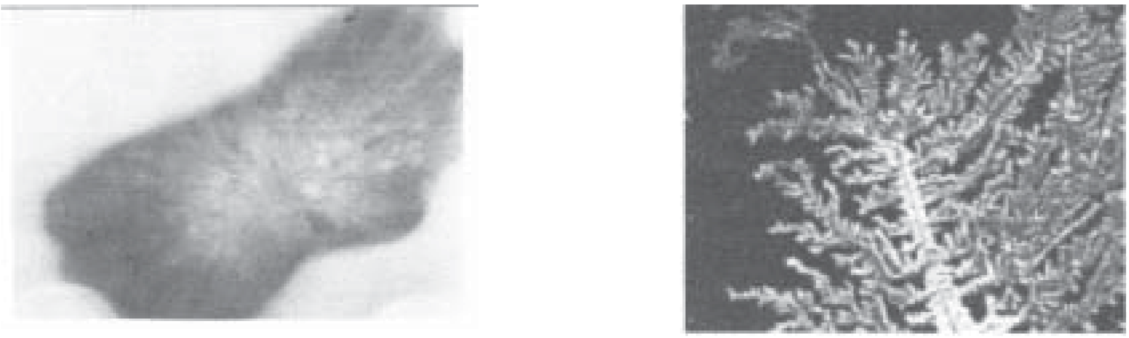

Fig.6. TEM images of the fractal H2TPPS4^{4-} aggregates: Bar = 10 µm

Preliminary measurements of the size of $H_2TPPS_4^{4-}$ indicate that $N \sim 10^4 - 10^5$ and aggregate is roughly a hollow cyclinder [22,23] with a radius corresponding to the radius TPP molecule (0.2 nm) and the length of the aggregate is 16 µM, as we detected by SEM image, (fig. 5).

From the analysis of the images it is noted that the $H_2TPPS_4^{4-}$ aggregation is a complex process occuring by fractal aggregation, as could be seen in SEM images, (fig. 6).

The nanostructure formed by ionic self-assembly, is observed in the nanotubes of $H_2TPPS_4^{4-}$ in solution.

Conclusions

In this paper, the controlled aggregation of meso-5 ,10, 15, 20-sulfonato-phenyl porphyrin ($H_2TPPS_4^{4-}$) was studied at room temperature. Structure of the aggregates was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV-visible spectroscopy. TEM and SEM results indicated the formation of organized nanostructures from the porphyrin derivative. UV-visible-NIR spectroscopic data showed broad red-shifted Soret band, indicating J-aggregation among the monomer units.

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