
Synthesis and characterisation of porphyrin nanotubes obtained by ionic self-assembly

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Abstract: In this work, the porphyrin nanotubes were built by ionic self-assembly in acidic aqueous solution of two oppositely charged non-metal porphyrins, namely, the anionic meso-tetra (4-sulfonatophenyl) porphine dihydrochloride (TPPS₄) and cationic meso-tetra (4-pyridyl) porphine (T₄MPyP). The electrostatic forces between these porphyrin blocks contribute to the formation of porphyrin aggregates in the form of nanosheets and nanotubes, enhance the structural stability of these nanostructures. The nanosheets thickness approximately varies in the range of 3–15 nm and the sheets diameter up to 1 micron. Using the TEM and SEM, it was revealed that the mechanism of nanotubes formation is based on the wrapping of nanosheets in multiwall cigar-like structures. The porphyrin nanotubes obtained are hollow structures with a length from 200 nm up to 1,000 nm and have a diameter in the range of 50–140 nm with 20–40 nm thick walls. TEM images confirm a hollow tubular structure of the aggregates.

Keywords: nanotubes; nanosheets; porphyrin; self-assembly.

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1 Introduction

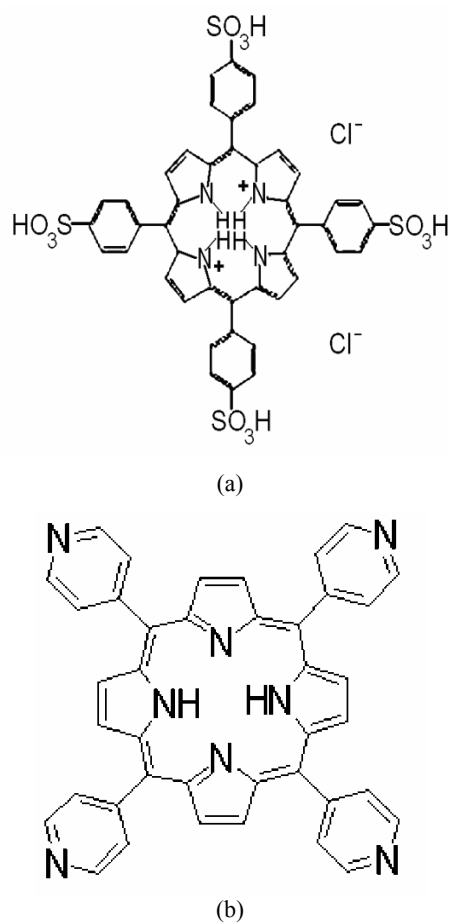
Organised self-assembly of molecules and self-organisation is the central issue to the utilisation of nanoscaled materials in the 'bottom-up' approach of nanotechnology for future manufacturing (Kosal and Suslick, 2000). Carbon nanotubes are interesting to the materials scientists for a variety of reasons, one of which is the nanotubes electronic behaviour. Depending on their structure, they can be either conductors or

semiconductors, so they have the potential to perform many different functions in miniaturised electronic technology. Carbon's natural ground-state structure is graphite, a layered material whose sheets, called graphene, form the basis for carbon-nanotube structures (Geim and MacDonald, 2007). The problem is that the structure cannot readily be controlled: Known methods of synthesis always yield a mixture of conducting and semiconducting nanotubes, which need to be separated before their electronic properties can be exploited in devices. That challenge, along with the quest for an even more diverse range of nanotube properties, has led researchers to turn their attention to nanotubes of other materials whose electronic properties may be both desirable and uniform. While nanotubes have been synthesised of many inorganic materials, including molybdenum disulfide, titanium dioxide and boron nitride, only few publications were devoted to organic nanotubes. Self-assembled, self-organised and covalent porphyrin arrays provide a versatile tool and are of fundamental importance as attractive building blocks for the modular construction of tailored field-responsive materials and potential applications in the design of sensors, catalysts, electronic and photonic devices, molecular sieves and solar energy conversion (Hofkens et al., 1997; Lin, 1999; Van der Boom et al., 2002; Balaban et al., 2003; Li et al., 2003; Doan et al., 2005). The design and construction of novel porphyrin architectures with well-defined 2D and 3D geometries is an area of increasing current interest because of their potential applications in electronic devices. This requires an accurate control of the molecular arrangements over a wide range of length-scales, spanning from micrometers down to the molecular size. Porphyrin can offer several remarkable features for molecular self-assembly (Doan et al., 2005). It has a large flat, conjugated central tetrapyrrole macrocycle, the peripheral of which can be decorated with both hydrophobic and hydrophilic groups and the non-covalent intermolecular forces can be used to engineer highly ordered three-dimensional (macro) molecular architectures where the single building blocks are held together by specific interactions, such as metal-ligand bonding, hydrogen bonding or π - π stacking. On the other hand, the self-assembly at the solid-liquid interface has been successfully used to control the molecular arrangement in two dimensions (Falk and Haase, 2002). In recent years, a wide variety of nanometer-sized self-assembly structures using porphyrin have been reported (Rotomskis et al., 2004; Snitka et al., 2005; Chirvony et al., 2007) and examples of hierarchical hetero-assembly have been presented (Ribo et al., 2000). More recently, a route to produce highly organised supramolecular materials from a variety of charged building blocks, by means of complexation with surfactants, was introduced in the work of Faul and Antonietti (2003). In general, ionic self-assembly (ISA) is a technique that organises multiple charged organic species by means of their association with oppositely charged counterions, with the latter being functionalised to have desirable properties. Hierarchical superstructures can then be generated in an ISA process, primarily through electrostatic interactions between charged surfactants and oppositely charged oligoelectrolytes. Hydrophobic and π - π interactions act as the secondary driving forces to promote self-organisation. Additional interactions, such as hydrogen bonding, can also be introduced to further stabilise and control the organisation of the assemblies (Camerel and Faul, 2003; Mammana et al., 2005). Nanotubes and in particular carbon nanotubes, are important functional materials for technological innovations. Nanotubular structures can be formed by the self-assembly of organic compounds (Camerel et al., 2007) and inorganic coordination compounds have also been known to generate tubular supramolecules by self-assembly through the coordination of bridging ligands to metal complexes as building blocks (Fenniri et al., 2002). The

application of ISA of distorted porphyrins as building blocks to construct self-assembled nanotubular structures and porphyrin nanotubes prepared by ISA of two oppositely charged metal porphyrins in aqueous solution were reported (Su et al., 2003; Harada et al., 2004). However, the mechanism of porphyrin nanotubes structure formation and relations between the structure and electrico-optical properties are still not understood and attempts are underway to understand how the porphyrin tectons are arranged and interact inside these nanostructures (Wang et al., 2004, 2006).

In the present work, the porphyrins nanoparticles were synthesised by ISA in aqueous solutions of two oppositely charged non-metal porphyrins, namely, the anionic meso-tetra (4-sulfonatophenyl) porphine dihydrochloride (TPPS₄) and cationic meso-tetra (4-pyridyl) porphine (T₄MPyP). We investigated in details the aggregate formation of TPPS₄ porphyrin and behaviours of aggregation induced by mixing an anionic TPPS₄ and cationic T₄MPyP acidic solutions by means of the UV-VIS spectroscopy and aggregates structure and morphology by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Figure 1 The structure of the porphyrins in acid (pH 2) aqueous solution: (a) anionic meso-tetra (4-sulfonatophenyl) porphine dihydrochloride; (b) cationic meso-tetra (4-pyridyl) porphine



2 Experimental

2.1 Synthesis of porphyrins nanotubes

The anionic meso-tetra (4-sulfonatophenyl) porphine dihydrochloride and cationic meso-tetra (4-pyridyl) porphine were obtained from Frontier Scientific (Lugan, UT) and were used without further purification. The solutions of different porphyrins were prepared by dissolving porphyrins in deionised water at room temperature under acidic aqueous medium (HCl was added to reach pH 2) at the concentration 1×10^{-5} M. The nanotubes of anionic meso-tetra (4-sulfonatophenyl) porphine dihydrochloride and cationic meso-tetra (4-pyridyl) porphine were fabricated by mixing aqueous solutions of the porphyrins. The structures of the porphyrins used in experiments are shown in Figure 1. In our experiments, 5 mL of $H_4TPPS_4^{2-}$ solution was mixed with 5 mL of tetrakis (4-pyridyl) porphyrin T_4MPyP^{2+} dichloride in water under stirring conditions. A greenish colloid was obtained after stirring $TPPS_4$ and T_4MPyP solutions for three minutes. The nanotubes formation was left in the dark and investigated by UV-VIS spectroscopy during five days.

2.2 Preparation of porphyrins films

Mica and microscopic glass cover slips were chosen as supporting substrates for the dry thin films investigation by AFM. Thin films of $TPPS_4$ were prepared by drop casting solutions and allowing the solvent to evaporate at room temperature in the dust-free environment, dipping substrate into solution or spin-coating technique at 100 rpm. Then the sample was dried in ambient air.

2.3 Characterisation of porphyrin nanotubes

TEM images were obtained with Hitachi S-4800 electron microscope in STEM mode. Acceleration voltage was 30 kV and emission current was 10 mA. Working distance was equal to 8 mm. Droplet of sample solution was placed onto the 200 mesh TEM grid with carbon film coating and was allowed to dry at ambient conditions. After that sample was directly imaged. AFM (NT-MDT Inc., Zelenograd, Moscow, Russia) measurements were made on the dry samples in the contact and tapping mode using commercial Si cantilevers NSG11 series (length 100 μm and width 35 μm) with a force constant of 11 Nm^{-1} and tip curvature of 10 nm and resonance frequency 178 kHz (NT-MDT). Solution and monolayer spectra on glass substrates for the UV-VIS experiments were obtained on an Ocean Optics diode array spectrophotometer to confirm the J-aggregates and nanotubes formation. A series of anionic meso-tetra (4-sulfonatophenyl) porphine dihydrochloride and cationic meso-tetra(4-pyridyl) porphine in acid aqueous solutions mixtures were prepared and were used for UV-VIS measurements. To obtain the monolayer absorption spectra, each glass cover slip was scanned before and after self-assembly of porphyrin film and the difference between the two spectra was the porphyrin monolayer absorption spectrum.

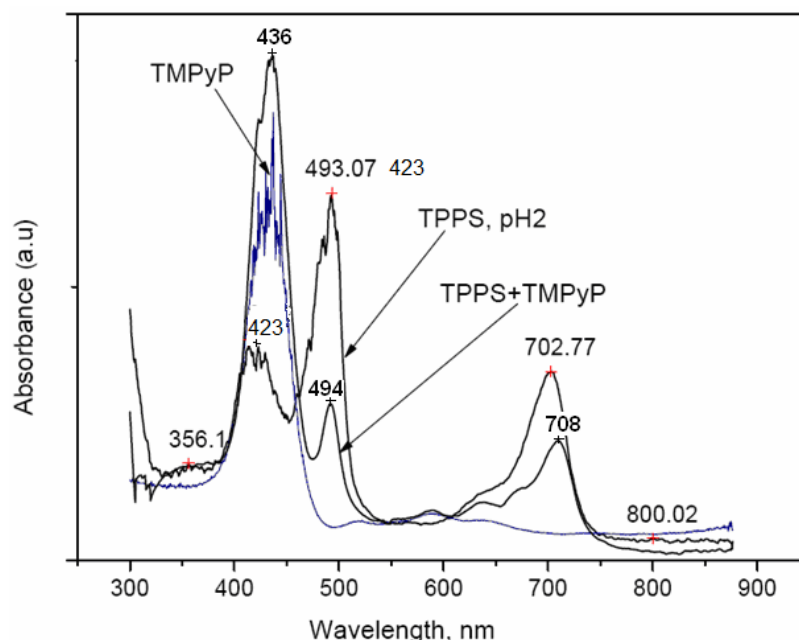
3 Results and discussion

3.1 Self-assembly of TPPS₄ J-aggregates in strip-like structures

In neutral media, TPPS is well-known as a tetraanion (H_2TPPS^{4-} species) and two nitrogen atoms of the macrocyclic ring of H_2TPPS^{4-} remain unprotonated. The protonation led to the diacid form H_4TPPS^{2-} , which exhibited a markedly different Soret band with respect to the neutral porphyrin (434 nm versus 412 nm). Consequently, acid-base equilibrium existed between unprotonated tetraanion (H_2TPPS^{4-}) and protonated dianion (H_4TPPS^{2-}) porphyrine forms. Due to the protonation of the two pyrrolic nitrogen atoms in porphyrin macrocycle, TPPS was characterised as the zwitterionic species. It was rationally speculated that any species with counter charges would be able to induce the formation of TPPS J- and/or H-aggregates by both electrostatic attracting force and hydrophobic effect in certain conditions. On the basis of the views above, initially, we investigated the effect of protonation on the absorption of the TPPS in acidic medium and investigated the self-assembly of J-aggregates into self-sustainable nanostructures.

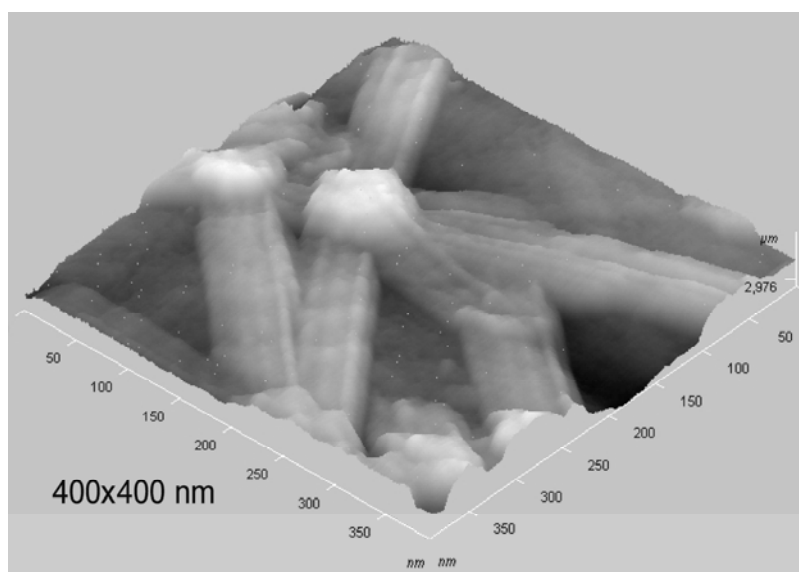
The measured UV-VIS spectrum of the monomeric acid solution (pH 2) of meso-tetra(4-sulfonatophenyl) porphine dihydrochloride has absorption maxima at 423 with overlapping bands at 413 and 433 nm, strong absorbance at 493,07 (J-band) and 702.77 nm (Q-band) (see Figure 2), which has to be attributed to the formation of J-aggregates (Rotomskis et al., 2004). The aggregates formation in solution is slow and takes hours.

Figure 2 UV-VIS absorption spectra of aqueous porphyrin solutions: (1) solution of TPPS₄ (pH 2, concentration 10^{-4} M) (2) solution of the TPyP (3) solution of the mixture of TPPS₄ and TPyP after five minutes (see online version for colours)



The formation of J-aggregates in solution leads to the further hierarchical aggregation to the nanorods and nanoribbons-like structures as it was revealed by AFM measurements (Figure 3).

Figure 3 AFM image of $H_4TPPS_4^{2-}$ self-assembled J-aggregates ribbon-like structures on glass substrate

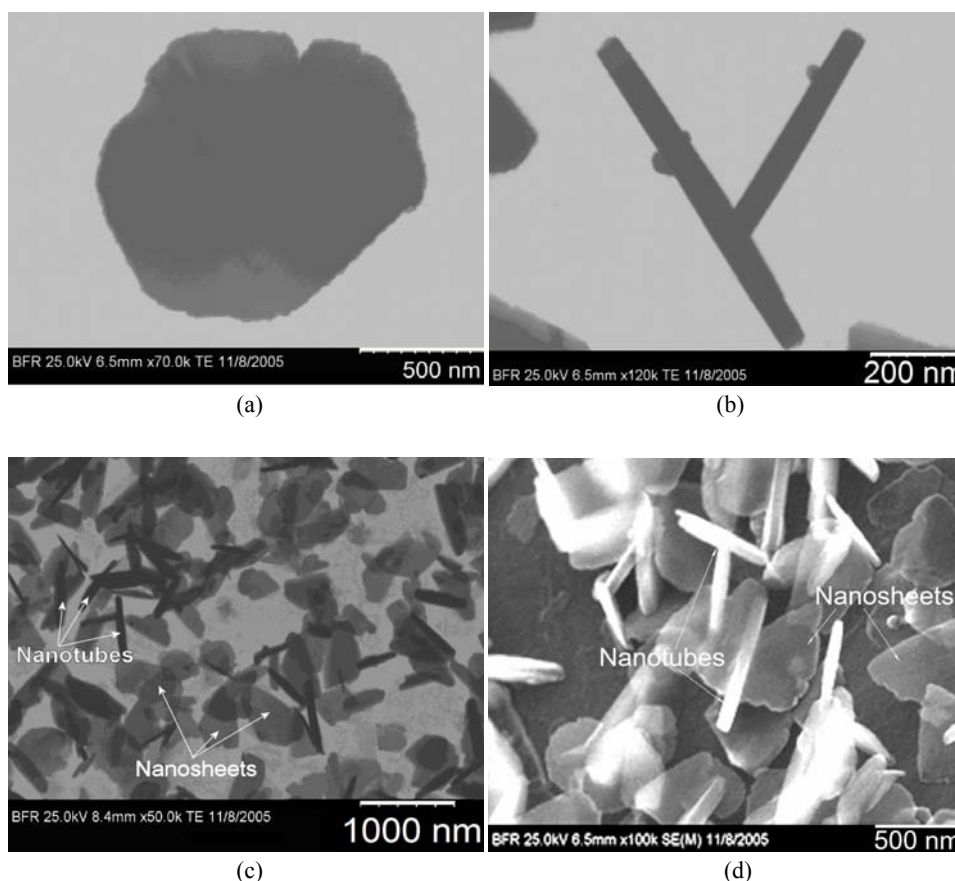


The ribbon-like structures have a width of about 80 nm and the thickness about 20 nm and the length up to microns.

3.2 *The self-assembly of protonated anionic TPPS and cationic TPyP porphyrins*

The mixture of anionic and cationic porphyrins immediately forms colloidal aggregates, in opposite to monomers solution. When the acidic solution of J-aggregated TPPS₄ monomers is mixed with cationic porphyrins solution, the UV-VIS absorption spectra changes significantly. The absorbance related to J-aggregates (493 nm) sharply decreased indicating the number of J-aggregates of TPPS vanished and Q-band (702 nm) was red-shifted (Figure 2). It was noteworthy here that the profile of the Soret band at 436 nm in absorption showed broaden with two bands at 422 nm and 436 nm and exhibited a blue shift (from 436 to 428 nm). However, the position of absorption of TPPS J-aggregates (494 nm) was in fact unchanged. It can be said that more complicated complexes were generated in this situation, namely, the heteroassociations of TPPS and TPyP J- and H-aggregates might be interpreted.

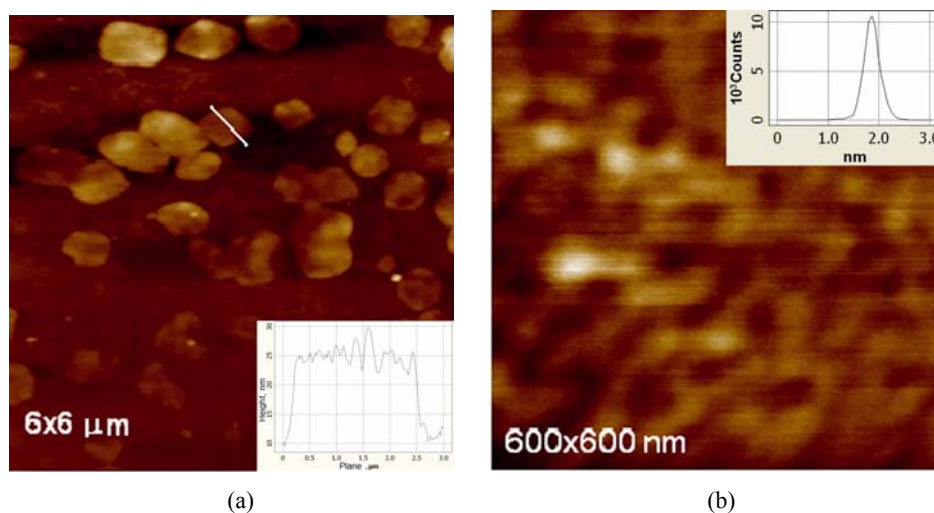
Figure 4 TEM and SEM images of porphyrin nanosheets and nanotubes, (a) TEM image of porphyrin nanosheet (b) TEM image of porphyrin nanotubes (c) TEM image of nanosheets and the wrapped nanosheets into nanotubes (d) SEM image of mixture of nanosheets and nanotubes



The two types of structure were revealed by TEM, SEM and AFM investigations. These new self-aggregated porphyrin structural forms, found by TEM imaging, are shown in Figure 4. Using the TEM, the primary structure of porphyrin aggregates was revealed to be a nanosheets and the secondary structure to be a hollow nanotubes. The mechanism of nanotubes formation revealed by TEM is a wrapping of nanosheets producing ‘cigar’ type multiwall porphyrin nanotubes. An individual nanosheet has a leaf shape with a diameter about 1 μm as is seen on TEM image in Figure 4(a). Aggregated particles consist of mixture of the nanosheets and nanotubes [Figure 4(c)] indicating that not all nanosheets are wrapping. The tubes have a length from 200 nm up to 1,000 nm and have diameter in the range of 50–140 nm with 20–40 nm thick walls. TEM images confirm a hollow tubular structure of the aggregates.

The molecular arrangement of the sheets was investigated by AFM imaging and measurements have shown that the thickness of different nanosheets vary in the range of 5–20 nm with the surface roughness of an individual sheet about 2 nm. The AFM image of nanosheets is presented in Figure 5.

Figure 5 AFM images of ISA nanosheets on glass, (a) nanosheets assemblies image (insert cross section profile) (b) nanosheet surface image (insert molecular roughness histogram) (see online version for colours)



The investigation of nanosheet surfaces revealed, that the nanosheets consist of circular structures built from porphyrin aggregates [Figure 5(b)]. The molecular ring-like structure diameter is typically about 60–80 nm and the height of the rings is about 1.8 nm, what corresponds with the size of porphyrins molecules and in agreement with the TPPS self-assembled structures revealed in the work (Falk and Haase, 2002).

The results of the investigation by TEM, SEM and AFM the nanosheets and nanotubes structure confirm the wrapping mechanism of nanosheets into multiwall nanotubes. The wrapping mechanism is not understood yet, but most likely it is related with the difference of mechanical stresses on the opposite surfaces of the nanosheet structures produced by non-symmetrical molecular arrangements. The nanosheets consist of several layers of porphyrin molecules arranged into circular structures by ISA mechanism as it was confirmed by TEM and AFM imaging. The imaging experiments of synthesised nanostructures by TEM revealed that the nanotubes are open-ended hollow cigar-like structures built from molecular nanosheets.

4 Conclusions

Porphyrin nanosheets and nanotubes have been synthesised using ISA technique. Using the TEM and SEM, it was revealed that the mechanism of nanotubes formation is based on the wrapping of nanosheets. The nanosheets thickness depends on the nanosheet size and approximately varies in the range from 3–15 nm and in diameter from tenths of nanometers up to 1 micron. The porphyrin nanotubes obtained are hollow structures with the length up to 1 μm and diameter 50–100 nm. The nanotube wall thickness varies from 10 to 40 nanometers. The nanosheets and nanotubes demonstrate the unique morphology, they are catalytically active and they can find applications in sensing devices, electronics and optics.

In summary, a circular porphyrin nanosheets with high aspect ratios and the wrapped nanotubes have been synthesised by ISA of non-metallic porphyrins. The mechanism of nanotubes formation was investigated and for the first time the self-aggregated non-metal porphyrin nanosheets wrapping into nanotubes are demonstrated.

Their unique morphology, photocatalytic properties and large surface area suggest that they may find a wide range of applications in electronics, photonics and catalytic systems. Currently, we are working on investigation of electrical and optical properties of the synthesised nanostructures.

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