

Optical spectroscopic studies on porphyrin nanorods/tubes for solar radiation harvesting

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Abstract. Porphyrins are macro-cycles often organized into nano-scale structures which perform many of the essential light-harvesting-, electron- and energy-transfer functions in various natural and synthetic systems. In addition to the sub-picoseconds charge generation and transfer, they exhibit various shapes and functional properties that make them useful for the construction of ultrafast nanodevices and more specifically as effective components in solar cells. This latter case would require to expand their specific J, S and Q absorption bands; a task of this research work. They are related to chlorophyll molecules found in natural systems that carry out light harvesting, charge separation and energy conversion. Using the free base and diacid forms of tetrakis (4-sulfonatophenyl) porphyrin and by varying the ionic strength of aqueous solutions used, Schwab et al were able to form single and bundled nanorods, whereas Wang et al used the mixture of tetrakis (4-sulfonatophenyl) porphyrin and Sn (IV) tetrakis (4-pyridyl) porphyrin to form a mixture of nanotubes and nanorods. Once synthesized, the incorporation of such nanostructures into a functional device presents its own set of unique problems, but one promising approach is to incorporate the nanotubes/rods onto a support to obtain an array that can be directly used as a device. Understanding the sizes and optical properties of nanorods is essential for the successful implementation in solar cells hybrid systems. This contribution reports on the synthesis of nanorods/tubes of the self assembled above mentioned porphyrins, their UV-VIS, fluorescence and light scattering properties at room temperature. This study demonstrates the potential for using different solvents to influence the physical and optical properties of porphyrin based nanorods.

1. Introduction

Self assembled organic nanostructures offer new opportunities for mimicking the processes that occur in nature, like biological photosynthesis to produce fuels or electrical energy in organic solar cells. This possibility is especially valid when the subunits of these nanostructures are chlorophyll related porphyrins. Indeed, the porphyrins are related to chlorophyll molecules found in natural systems that carry out light harvesting, charge separation and energy conversion [1]. These are macro-cycles often organized into nano-scaled structures which perform many of the essential light-

harvesting, electron and energy ultrafast transfer functions in various natural and synthetic systems. The structure of organized porphyrins in nanostructures and formation of delocalized excitons that give rise to additional absorption bands (J-aggregate) may alter the nanomaterials optical, electronic, mechanical and physical properties of the nanorods [2]. The ionic self-assembly/molecular recognition is one potential synthetic method available for the production porphyrin based nanostructures [3,4]. As aforementioned and because of their desirable functional properties, porphyrins and other tetrapyrroles are attractive building blocks for the engineering of synthetic functional nanostructures. As recently confirmed, Wang et al. [5] reported the first synthesis of porphyrin nanotubes using ionic self-assembly of two oppositely charged porphyrins in aqueous solution. The electrostatic forces between the porphyrins' tectons, in addition to the van der Waals, hydrogen bonding, axial coordination, and other weak intermolecular interactions contribute to the formation of porphyrin aggregates and enhance the structural stability of these nanostructures [5]. Molecular recognition between the complementary arrangements of opposite charges and H-bonds on the porphyrins' tectons also contributes to the ionic self-assembly process. Using the free base and diacid forms of tetrakis (4-sulfonatophenyl) porphyrin and by varying the ionic strength of aqueous solutions used, Schwab et al were able to form single and bundled nanorods, whereas Wang et al [3] used the mixture of tetrakis (4-sulfonatophenyl) porphyrin and Sn (IV) tetrakis (4-pyridyl) porphyrin to form a mixture of nanotubes and nanorods. In the present study, we report on the synthesis, morphological and optical properties of porphyrin-based nanotubes/rods in different acidic media.

2. Experimental

2.1. *Porphyrin nanorods synthesis*

The porphyrin nanorods were synthesized via an ionic self-assembly technique. This was carried out by mixing aqueous solutions of two porphyrins similar to procedures developed by Wang et al, [5] and reproduced by Mongwaketsi et al, [6]. For the synthesis of porphyrin nanorods: an acidic aqueous solution (HCl 0.02 mol/l) of 5, 10, 15, 20-tetrakis-(4-sulfonatophenyl) porphyrin [H₂TSPP] with a concentration of 10.5 μM was mixed an aqueous solution of the tin complex of 5,10,15,20-tetrakis-(4-pyridyl)-porphyrin [SnTPyPCl₂] with a concentration of 3.5 μM. Equal volumes of the two aqueous solutions were blended, obtaining a final solution with pH 2. The solutions were then stored in the dark at room temperature for 72 hours, until a greenish precipitate was formed. Another set of porphyrin nanorods were synthesized by using a procedure slightly modified from the one described previously [5]. Nitric acid, sulfuric acid, phosphoric acid and oxalic acid with lower solution concentrations: (10.5 μM H₄TPPS₄²⁻, 0.01M HNO₃: 3.5 μM SnTPyP²⁺), (10.5 μM H₄TPPS₄²⁻, 0.01M H₂SO₄: 3.5 μM SnTPyP²⁺), (10.5 μM H₄TPPS₄²⁻, 0.01M H₃PO₄: 3.5 μM SnTPyP²⁺) and (10.5 μM H₄TPPS₄²⁻, 0.01M H₂C₂O₄: 3.5 μM SnTPyP²⁺) were used for porphyrin nanorods self-assembly.

2.2. *Porphyrin nanorods: characterization*

The transmission electron microscopy images were obtained using LEO Omega 912 (120 KeV). For TEM observations, a few drops of solutions were drop-dried onto a 200 mesh carbon coated copper grid and then examined. The optical absorption spectra of the porphyrin nanorods solutions were collected with UV/VIS spectroscopy (CECIL 2021 UV-VIS spectrophotometer, scanned from 250nm – 1100 nm, using scan rate of 200nm/minute, slit width of 0.2nm, path length of 10mm). Fluorescence excitation spectra were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer with a 150 W xenon lamp. Diffuse light scattering (DLS) measurements were conducted using Beckman Coulter®, Delsa™ Nano C TM particle analyzer.

3. Results and discussion

3.1. Porphyrin nanorods: Transmission electron microscopy

Porphyrin nanorods formation in solution was confirmed by transmission electron microscopy (TEM). Experimental methods used in this study were similar to those used by Wang et al. and thus favours the formation of nanorods/tubes. However, the TEM images show solid cylindrical shapes with diameters ranging between 40 and 75 nm, and lengths in micrometers (figure 1). The difference in diameters and lengths is attributed to the light sensitivity of these structures and the ease of the nanostructure's transition from nanotubes to nanorods when exposed to light [3]. For all solvents used we were able to form nanorods by self-assembly with differences in both the nanorods diameters and lengths. figure 1 (a)-(d), revealed that; the average diameter of nanorods formed using H_2SO_4 was 36.40nm, 31.6nm for H_3PO_4 , 29.8nm for $H_2C_2O_4$ and 27.0nm for HNO_3 solvent. With H_2SO_4 solvent, the majority of the nanorods in solution had longer lengths than those of other solvents, followed by those of H_3PO_4 , $H_2C_2O_4$ and HNO_3 in order of decrease in lengths respectively. Likewise, close TEM investigations showed that H_3PO_4 produced highly aggregated nanorods as compared to other solvents, see figure 29 (b) whereas with $H_2C_2O_4$ most of the nanorods appeared to be broken, figure 1(c).

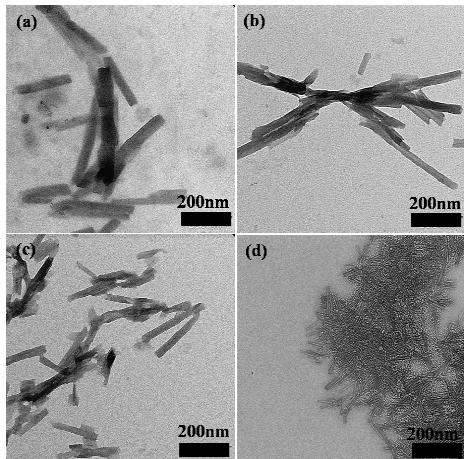


Figure 1. TEM micrograph of porphyrin nanorods in the various acidic solutions.

3.2. Porphyrin nanorods: UV-VIS-NIR optical absorption

The UV-VIS-NIR absorption bands of the porphyrin result from electronic transitions from ground state (S_0), to the two lowest singlet excited states S_1 (Q state) and S_2 (S state) [10,11]. In the case of such macro-cycles, the exciton theory states that when molecules lie in a head-to-tail arrangement (J-aggregation), the allowed state is lower in energy, producing a red-shift to the monomer [8], and since the S band of $[H^4TPPS_4]^{2-}$ is red-shifted upon aggregation (J-aggregate), it implies that the planar porphyrin molecules are stacked in an arrangement where individual porphyrin units are not positioned directly one on top of the other [4]. Figure 2 shows the spectra of the precursors and the resulting nanorods in the various acidic solutions. The nanorods composed of $[H^4TPPS_4]^{2-}$ J-aggregates are photoconductive, hence the higher absorbance peak of $[H^4TPPS_4]^{2-}$ in near UV region (400-460 nm). The decrease in the main absorbance peaks of the precursors and the several peaks identified in the spectrum for the nanorods —417, 434.5, 495.5, 711 and 974 nm — are similar to what has been reported before so far [3,4,9].

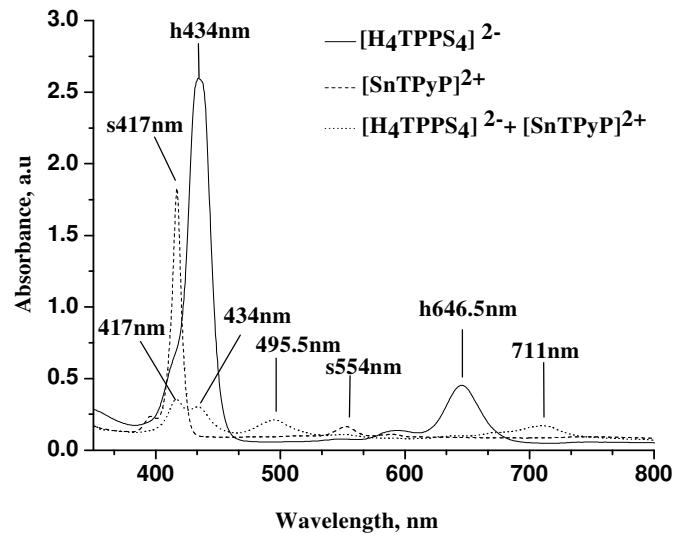


Figure 2: UV-VIS absorbance spectra of the precursors and porphyrin nanorods formed after mixing of the precursors. Peak labels with the letter ‘s’ are for the SnTPyP^{2+} monomer, the values with an ‘h’ are for the $\text{H}_4\text{TPPS}_4^{2-}$ monomer, and the remaining values are for the porphyrin nanorods formed.

3.3. Porphyrin nanorods fluorescence spectroscopy

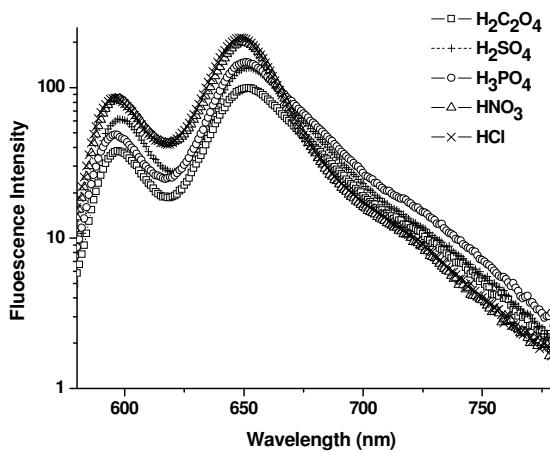


Figure 3: Spectra illustrating the fluorescence intensities versus the wavelengths measured for porphyrin nanorods in solutions of different acidic solvents.

Once the photon energy has been absorbed by a porphyrin molecule in order to induce the excited singlet state, the electrons distribution is altered from the ground state and the molecule posses more total energy. The molecule can dissipate its excitation energy by fluorescence mode in which electronically excited molecule decays to its ground state by emitting a photon. Four main bands in the fluorescence spectra were observed, with two sharp bands assigned to the excitation sources at 400 nm and 800 nm. As shown in figure 3, all the porphyrin nanorods in different solvents emitted similar in trend fluorescence profiles, with the main emission bands situated at 596 and 652 nm. It is worth noting that the two bands are attributed to the porphyrin molecules and not the type of solvent used or the porphyrins-solvent interface. The order of the fluorescence intensity of the porphyrin nanorods with respect to the type of solvents used was HCl > HNO₃ > H₃PO₄ > H₂SO₄ > H₂C₂O₄.

3.4. Porphyrin nanorods: Light scattering

The nature of the aggregate in the solution was studied by diffuse light scattering technique. It should be noted that the lengths as measured by dynamic light scattering experiments are not very different from each other. These studies showed that the particle lengths vary from 296.56 nm to 16,324 μm. The particle size distribution was in the range of 2683.5 nm for H₃PO₄ solvent with HCl, HNO₃ and H₂SO₄ in the range of ~2260 and in 1535 for H₂C₂O₄, as in figure 4(a)-(e). This may be explained in terms of the strengths of the acids whereby the highest size distribution was in the range 2683.5 nm for H₃PO₄. The produced nanorods are amorphous for all solvents and in the case of H₂C₂O₄ they were the least agglomerated. Higher differential intensity was observed for the H₃PO₄ and less for H₂C₂O₄. These results are comparable with the TEM (figure 1) which showed that some nanorods had lengths as small as 214 nm for H₂C₂O₄, figure 4(c) and the longest rods were observed for nanorods in H₃PO₄ solvent figure 4(e).

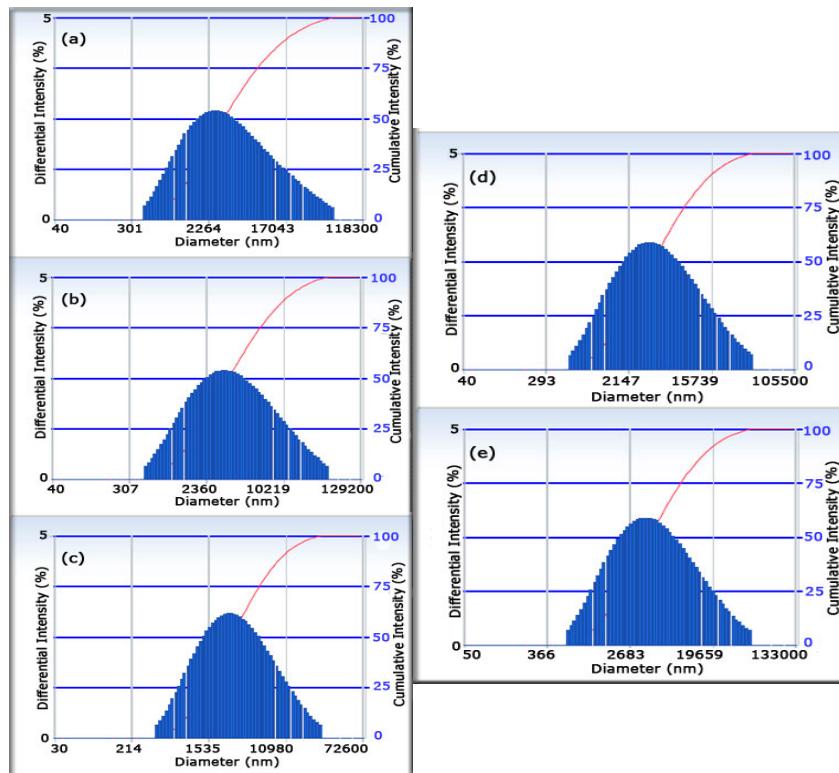


Figure 4 Size distribution graphs as a function of solvent determined by diffuse light scattering, (a) HCl, (b) HNO₃, (c) H₂C₂O₄, (d) H₂SO₄, and (e) H₃PO₄ solvents respectively

Conclusion

We investigated the effect of preparing porphyrin nanorods using different solvents and the results showed that using HNO_3 , H_3PO_4 , H_2SO_4 and $\text{H}_2\text{C}_2\text{O}_4$ also resulted in the successful ionic self assembly of porphyrin nanorods but of different sizes. The DLS results not only provided important structural information, but it is clear that the average size of the aggregates depends also on the type of solvent used.

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