

TIME DEPENDENCY ON THE FABRICATION OF $H_4TPPS_4^{2-}$ - $SnTPyP^{2+}$ PORPHYRIN NANORODS*

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Abstract

Meso-tetra(4-phenylsulfonic acid)porphyrin ($H_4TPPS_4^{2-}$) and tin(IV) meso-tetra(4-pyridyl)porphyrin dichloride ($SnTPyP^{2+}$) porphyrin nanorods were prepared at room temperature by ionic self-assembly of these two oppositely charged porphyrins. The UV-VIS absorption spectra of the samples were measured hourly for the first six hours (after mixing the two porphyrin compounds) and then on a 24 hourly basis for 96 hour period. The spectra show a decrease in absorbance accompanied by a broadening of the absorption bands especially the J-aggregate bands with a red shift. This phenomenon was more pronounced after 24 hours, and no significant decrease in absorbance was observed after 72 hours. Transmission Electron Microscope (TEM) images of the product confirm the formation of the nanorods.

Key words: Porphyrins, nanorods, J-aggregates, ionic self-assembly.

1. Introduction

The ability of biological systems in light-harvesting, energy and electron transfer functions has been of great interest to researchers (Suslik *et al.*, 2000). For this reason a lot of work is being done on artificial systems in order to study their properties. Compounds that are often used for these artificial systems are porphyrins and other tetrapyrroles. The unique properties of these compounds are largely due to the fact that they have extensive conjugative systems. They can also be metallated or demetallated. Furthermore, they have the outstanding ability to aggregate to dimers, trimers, oligomers and polymers. This they do through various non-covalent interactions such as hydrophobic interaction, electrostatic interaction, hydrogen bonding, co-ordative interaction, and δ - δ stacking interaction (You, 2005; Smith, 2006). These systems have found applications in electronics, photonics, light-energy conversion and in catalysis (Wang *et al.*, 2005). Another example of growing importance of the use of porphyrins is in photodynamic therapy (PDT) for cancer treatment (Andreoni and Cubeddu, 1984). Porphyrins and their derivatives are known to be interesting photonic materials in view of their large third-order optical non-linearity and optical limiting properties (Sendhil, Vijayan and Kothiyal, 2005). Studies have also shown that porphyrins and metalloporphyrins possess interesting photosensitization and photo-redox properties (Suslick and Waston, 1992).

Furthermore, a lot of materials at the nanoscale exhibit properties which are far different from what has been reported all through the centuries. For example, macroscopic gold is chemically inert, whereas at nanoscale gold becomes extremely reactive and catalytic and even melts at a lower temperature (Britannica, 2006).

The aggregates of porphyrins also possess interesting optical and electronic properties which are good building blocks for nanostructures. However, in some cases these aggregates are in less useful forms such as nanoparticles, sheets or fractal objects (Wang *et al.*, 2004). Wang *et al.*, (2004) have prepared well-defined shapes and dimensions by mixing two oppositely charged porphyrin compounds

We have reported that the application of heat results in the formation of nanotubes instead of nanorods (George *et al.*, 2007). Nanotubes of greater dimension and population are also produced due to the catalytic properties of tin-based porphyrin (George *et al.*, 2007). Here we report the time dependency as a requirement for the preparation of these structures.

2. Materials and Methods

The negatively charged porphyrin used in this work was meso-tetra(4-phenylsulfonic acid)porphyrin (10.5 μ M, $H_4TPPS_4^{2-}$ in 0.02 M HCl $H_4TPPS_4^{2-}$) while the positively charged porphyrin was tin(IV) meso-tetra(4-pyridyl)porphyrin dichloride (3.5 μ M

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$SnTPyP^{2+}$ in ultra pure water). All porphyrin precursors were purchased from Frontier Scientific and no further purification was done and all solutions were prepared in ultrapure water. Hydrochloric acid (98%) was purchased from Sigma-Aldrich and prepared with ultra pure water. The solutions (9 ml each) were mixed together and kept in the dark at 25 °C for 96 hours.

Transmission Electron Microscope (TEM) images of the products were obtained using LEO Omega 912 (120 keV). The sample for the TEM was prepared by pipetting 10 μ l of the sample unto carbon-coated copper grid and allowed to dry in air. The time dependency for the formation of aggregates was monitored by measuring the UV-VIS absorbance. This was taken hourly for the first six hours after mixing, then every 24 hours till the 96th hour. Absorption studies were done using GB UV/VIS 920 Spectrophotometer, (1 cm path length quartz cell).

3. Results and Discussion

The electronic absorption of porphyrins usually occurs within the porphyrin ligand involving the excitation of the electrons from the π to π^* porphyrin orbitals. Using the Gouterman four-orbital model; the π -orbitals are the two highest occupied molecular orbitals (HOMOs) of a_{1u} and a_{2u} symmetries and the two lowest unoccupied molecular orbitals (LUMOs) of e_g symmetry (Gouterman, 1978). The spectra generally consist of the Soret bands (**B**-bands) which are strong transition to the second excited state ($S_0 \rightarrow S_2$) occurring between 400 nm – 450 nm and a second one, the Q-bands (550 nm - 750 nm) which is the transition to the first excited state, ($S_0 \rightarrow S_1$) (Suslick and Waston, 1992). The $a_{1u}(\pi) \rightarrow e_g(\pi^*)$ and the $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ transitions mix together by configurational interaction, producing these two bands. Constructive interference leads to the high intense Soret bands while the weak Q-bands arise from destructive combination (Fig. 1)

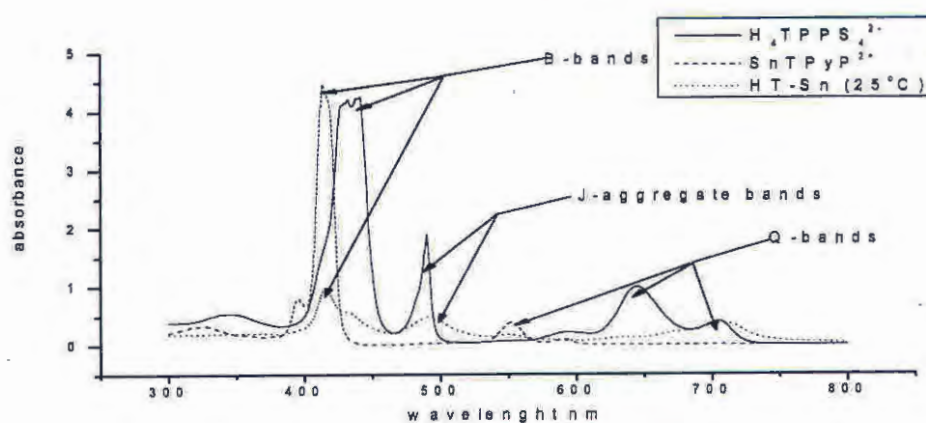


Fig. 1: UV-VIS absorption spectra of HT-Sn nanotubes

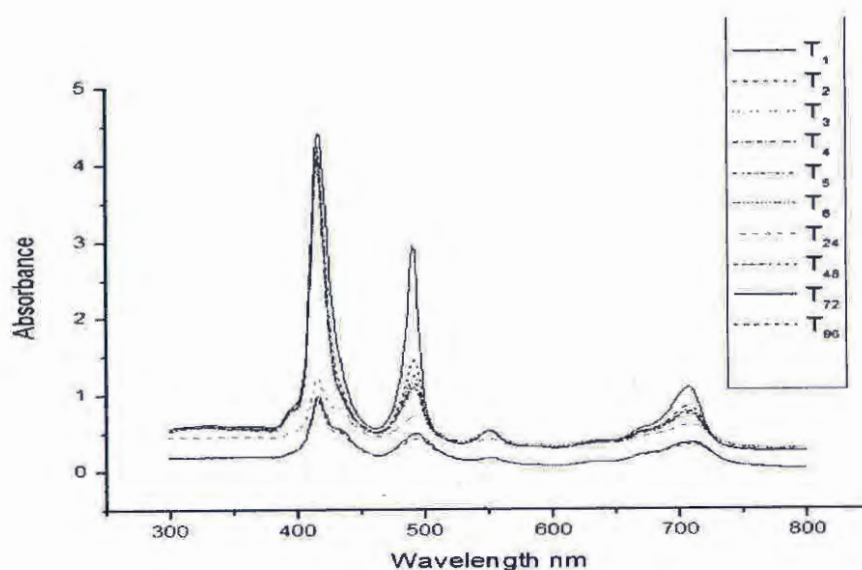
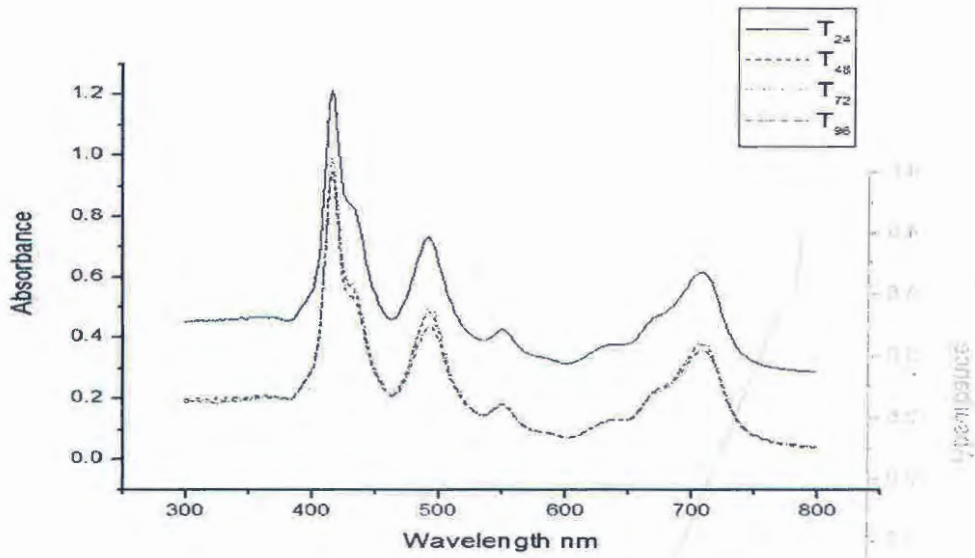


Fig. 2: UV-VIS absorbance measured with time for T_1 - T_{96} .

a.



b.

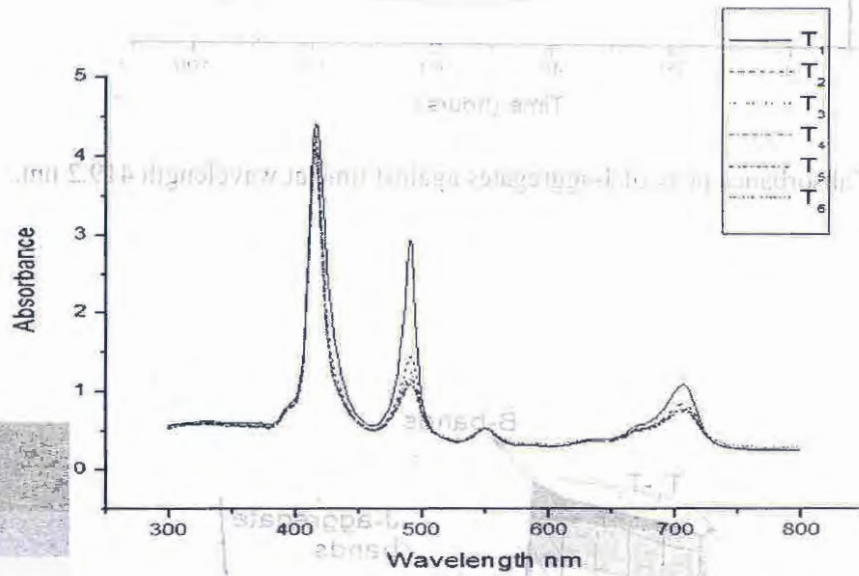


Fig. 3: UV-VIS absorbance measured with time for (a) T_{24} - T_{96} , (b) T_1 - T_6 .

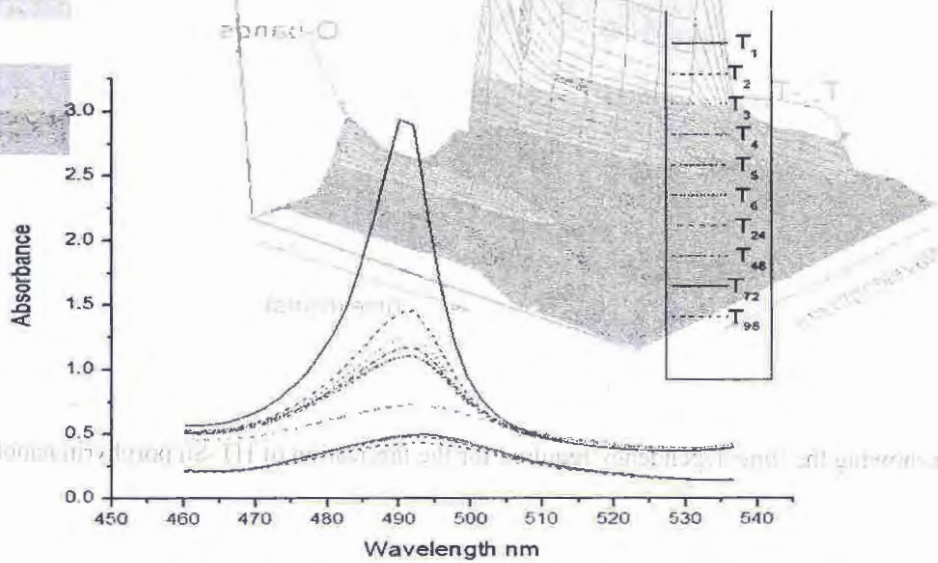


Fig. 4: UV-VIS absorbance spectra of J-aggregate bands from time T_1 - T_{96}

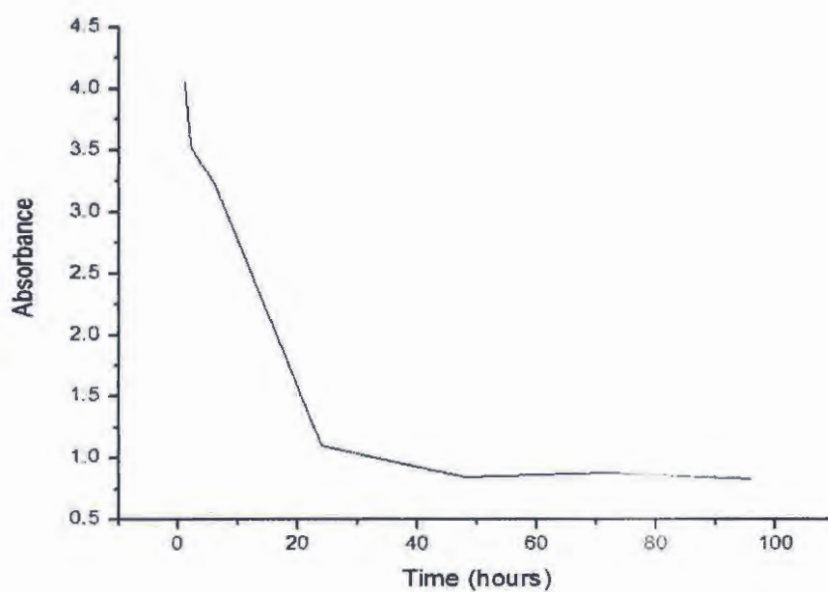


Fig. 5: Plot of absorbance peak of J-aggregates against time at wavelength 419.2 nm.

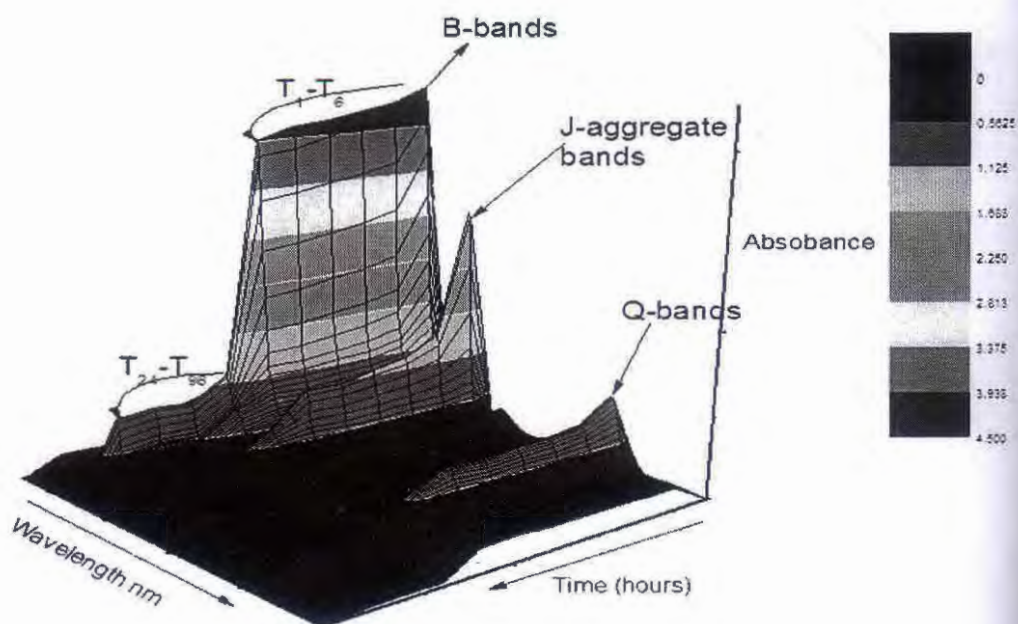
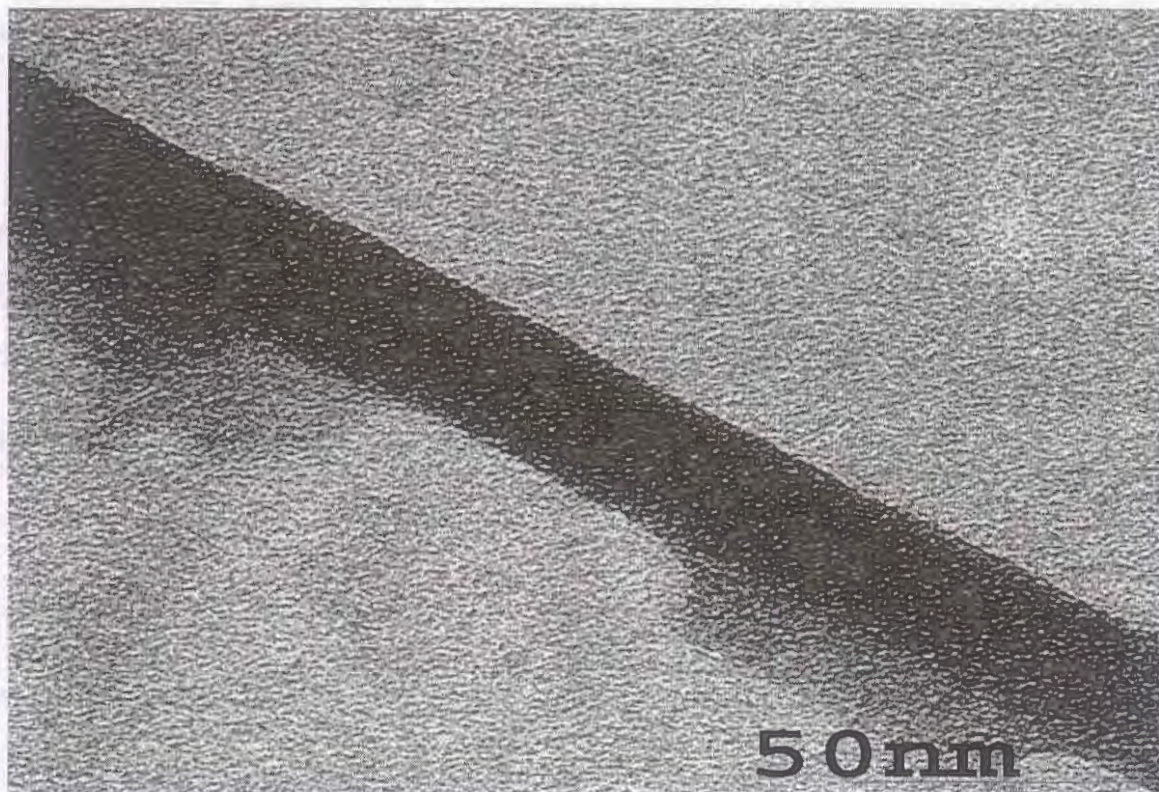


Fig. 6: 3-D graph showing the time dependency required for the fabrication of HT-Sn porphyrin nanotubes.

a.



b.

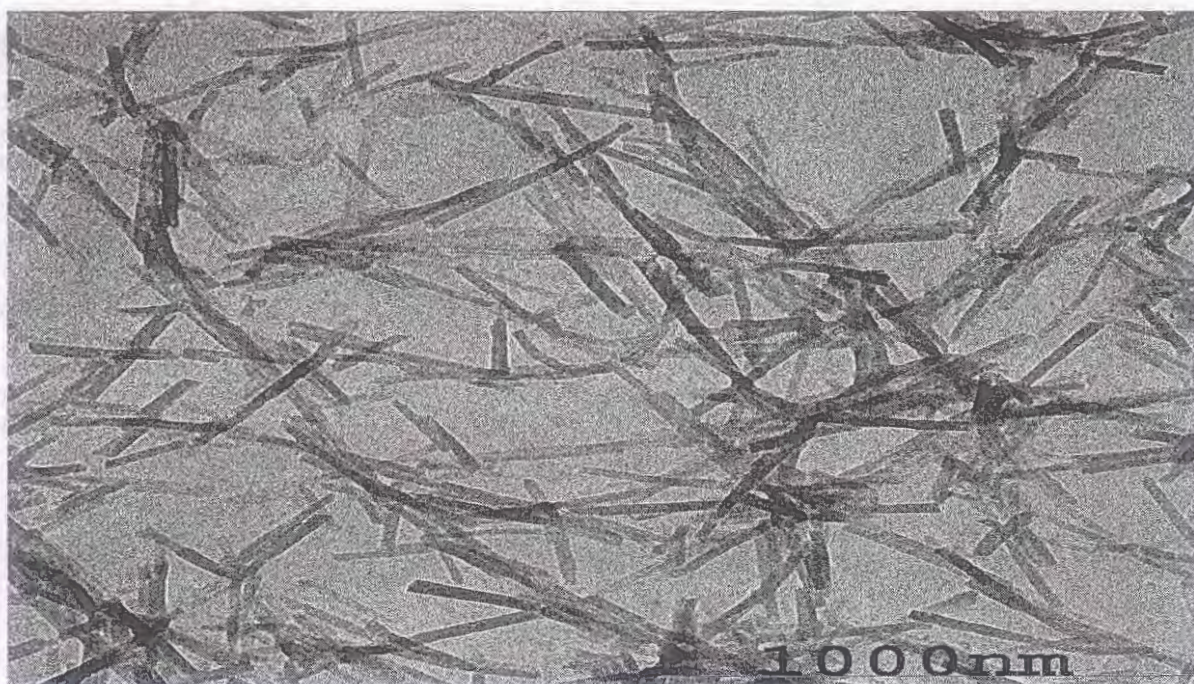


Fig. 7: TEM images (a) a single HT-Sn nanorod, (b) a collection of HT-Sn nanorods.

(Anderson, 1999). Some porphyrins, such as the precursor $H_4TPPS_4^{2-}$, form aggregates in solution. This feature is evident in the spectra (Fig. 1) occurring somewhere between 450 nm – 500 nm called the J-aggregate band (J-band) (Snitka, Rackaitis and Rodiate, 2005). These bands suggest a coherent coupling of transition dipoles of parent porphyrins i.e. a transition from the HOMOs of one parent to the LUMOs of the other parent (Wang *et al.*, 2004).

The UV-VIS spectra (Fig. 1) of the precursor porphyrin ($H_4TPPS_4^{2-}$) and the product (after 72 hours) revealed that with the formation of nanorods the absorbance generally decreases and bands broaden, accompanied by a red shift. From Fig. 2 it can be seen that the intensity of the bands decrease and broaden with time. This decrease is more pronounced from time T_{24} – T_{72} (Fig. 3a) when compared to those measured in the first six hours (Fig. 3b), after which no significant change was observed. A closer inspection of the J-aggregate bands shows that T_1 has its absorbance as high as that of the parent porphyrin, $H_4TPPS_4^{2-}$ with sharp decline to T_2 , and then a progressive decline in absorbance and band broadening with time from T_2 – T_{96} (Fig. 4). This decrease with time was further demonstrated in Fig. 5, which is a plot of the various absorbance peaks of the J-aggregate bands (i.e. at 419.2 nm) versus time and in Fig. 6, a 3-dimensional graph of absorbance, wavelength and time.

The key driving force for aggregation is the electrostatic force of attraction between the oppositely charged porphyrins. This force of attraction brings the molecular orbitals closer, thereby decreasing the energy gap between the HOMOs and the LUMOs. This reduction in energy accounts for the red shift. According to Rousseau *et al.* (2002) who worked with cyanine dyes, an increase in absorbance and any small shift (broadening) to a longer wavelength is an indication of regular growth in dye layers. In retrospect, from the absorbance spectra, the broadening of the J-aggregate band indicates the large number of porphyrin molecules participating in the aggregate formation. TEM images in Fig. 7a and b show the cylindrical shapes of the nanorod products.

4. Conclusion

The role of porphyrin in the future of nanoscience and nanotechnology cannot be over emphasized. This work was designed to take a look at the importance of time in the preparation of nanostructures. From

the investigation, time was found to be a relevant condition for complete formation of nanostructures of well defined shapes. The time duration for the formation of porphyrin nanostructures by ionic self-assembly of two oppositely charged porphyrins was found to be 72 hours.

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