UV-VIS SPECTROSCOPY STUDY ON PORPHYRIN NANOSTRUCTURES FORMED BY ELECTROSTATIC INTERACTION

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ABSTRACT

Porphyrin nanostructure were fabricated by ordinary electrostatic self - assembly and phase transfer electrostatic self–assembly and characterized using ultraviolet-visible spectrophotometry only. For ordinary electrostatic self-assembly, aqueous solution of the negatively-charged porphyrins - meso-tetra(4-phenylsulphonic) porphyrin ($TPPS_4^+$) and meso-tetra(4-carboxyphenyl) porphyrin ($TCPP^+$) (TPPS/TCPP) was mixed with aqueous solution of the positively-charged metalloporphyrins - meso-tetra(4-pyridyl) porphyrin [MTPyP (M=Zn, Ni, Co and Mn)]. In the case of phase transfer technique, the aqueous solutions of the negatively-charged porphyrins were (TPPS/TCPP) added to dichloromethane solution of MTPyP. The aqueous and organic phases were studied separately. The electronic spectra of TPPS-MTPyP using ordinary electrostatic self-assembly technique showed the typical J-aggregation influenced by TPPS with bands around 492 nm and 708 nm. These bands were absent in the case of TCPP-MTPyP instead, there was a shift of the absorption bands to shorter wavelength, indicating H-aggregation. For the phase-transfer electrostatic self-assembly technique, the electronic spectra were quite complex and bands were narrower than expected for aggregation. This was indicative of very weak or no aggregation occurring.

Keywords: Porphyrin, Electronic, Spectra, Absorbance, Nanostructures

INTRODUCTION

Porphyrin nanostructures are created by aggregation of porphyrin molecules to form large clusters which are of great interest in chemistry, physics and biology. In nature, self-association of these class of molecules play a very important role; an example is given by molecular aggregates of chlorophyll that have been found to mediate the primary light harvesting and charge-transfer processes in photosynthetic complexes (Creighton *et al.*, 1988; Kuhlbrandt, 1995). In fact, light-harvesting and the primary charge-separation steps in photosynthesis are facilitated by these aggregated species. An increasing interest in recent years in supramolecular assemblies of π-conjugated systems is due to their potential applications in optoelectronic, photovoltaic, non-linear optical device as well as fuel cells (Schenning and Meijer, 2005).

Formation of self-assembled aggregates of macrocyclic compounds like porphyrin into supramolecular assemblies can be achieved via electrostatic interaction, hydrophobic and hydrophilic interactions, hydrogen bonding, π-π interaction and through the axial ligands (Pasternack *et al.*, 1972). Based on the relative orientation of molecules, orderly aggregates are

classified into two; H-aggregation and J-aggregation. H-aggregate is a face to face arrangement and J-aggregate is side to side. H-aggregates are not known to have sharp spectra like the J-aggregates; nevertheless, there are many examples where the spectroscopic blue shift, evident for formation of H-aggregates, was observed. In addition to having narrower band width, and a red shift in absorption peak, J-aggregation sometimes produce new spectra bands (Pasternack *et al.*, 1972).

Recent techniques used in the fabrication of porphyrin nanostructure are by ordinary electrostatic self-assembly and phase-transfer electrostatic self-assembly. These are done by combining different porphyrin building blocks (charge tectons) via electrostatic interaction. Wang *et al.*, (2004) reported the fabrication of porphyrin nanotubes by ordinary electrostatic self-assembly of two oppositely charged porphyrins both in aqueous solution. The negatively charge molecule was of meso-tetra(4-phenylsulphonic) porphyrin (TPPS) and Sn(IV) tetra(4-pyridyl) porphyrin (SnTPyP) was made positively charged via protonation of the nitrogen atoms of the pyridine ring. Phase-transfer electrostatic self-assembly of water-soluble porphyrins with water-insoluble

porphyrins (Wang *et al.*, 2006). This group used aqueous solution of meso-tetra(4-phenylsulphonic) porphyrin (TPPS) and dichloromethane solution of antimony (IV) oxide meso-tetraphenyl porphyrin (SbOTPP) in which positive charged was on antimony. Well-defined shapes and sizes porphyrin nanostructure which are of great importance particularly for applications in electronic, photonics, light-energy conversion and catalyst are obtained.

The diverse chemical and photophysical properties of porphyrins are in many cases due to their different aggregation mode and, as a result of interchromophoric interactions, perturbations in the electronic absorption spectra of these dyes occur. These in turn influences their efficacy in several applications thus, it is very important to take on detailed informations about the formation dynamic and on the typology of aggregates.The aim of this work is to fabricate porphyrin nanostructures using two different types of negatively charged porphyrin and several metallated porphyrins which serve as the positively charged species and apply both ordinary and phase-transfer electrostatic self-assembly and to furthermore investigate their electronic properties using UV-Vis spectroscopy.

EXPERIMENTAL

The negatively charged molecules were meso-tetra(4-phenylsulphonic) porphyrin (TPPS$_4^+$) and meso-tetra(4-carbonxyphenyl) porphyrin (TCPP$^+$) while zinc, nickel, cobalt and manganese meso-tetra(4-pyridyl) porphyrin (ZnTPyP^{4+}, NiTPyP^{4+}, CoTPyP^{4+} and MnTPyP^{4+}) were protonated to generate the positively charged species. The structures of these molecules are shown in Figure 1. They were synthesized and characterized following standard synthetic methods (Alder *et al.*, 1967; Srivastava and Tsutsu, 1972; Herman *et al.*, 1978; Hambright *et al.,* 1985; Gonslave *et al.,* 1991 and Hong *et al.*, 1996). The four metalloporphyrins (MTPyP, M = Zn, Ni, Co, Mn) were protonated by dissolving (0.025 g) of MTPyP in 0.02 M HCL.
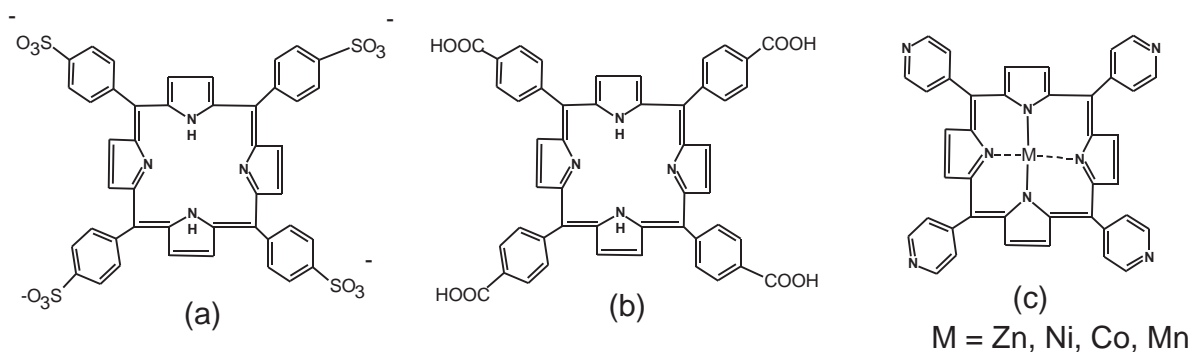

Figure 1: Porphyrin used in study (a) were meso-tetra (4-phenylsulphonic) porphyrin (TPPS) (b) meso-tetra (4-carbonxyphenyl) porphyrin (TCPP) (c) zinc, nickel, cobalt and manganese meso-tetra (4-pyridyl) porphyrin (ZnTPyP, NiTPyP, CoTPyP and MnTPyP).

For ordinary electrostatic self-assembly, about 6 mL of 10.5 x 10-4 M solution of the negatively-charged porphyrins (TPPS) dissolved in 0.02 M HCl, pH   2) was mixed with 6 ml of 3.5 x 10-5 M solution of the positively-charged metalloporphyrins [(MTPyP) dissolved in 0.02 M HCl]. In the case of TCPP, it was first dissolved in 0.002 M NaOH solution and then 0.02 M solution of HCl was added. This was then mixed with 6 ml of 3.5 x 10-5 M solution of MTPyP (dissolved in 0.02 M HCl). These mixtures were left in the dark for 72 hours for the formation of the nanostructures. In the case of phase transfer technique, 10 mL of the solutions of TPPS/TCPP prepared above was added to 10 mL of dichloromethane solution of MTPyP (3.5 x 10-5 M) in a glass vial. The mixture was shaken vigorously and rapidly stirred for 1 h. The liquid/liquid interface becomes re-established with the formation of nanostructures. The aqueous phase and organic phases were studied separately. Ultraviolet/Visible (UV/Vis) spectra were recorded on a Shimadzu UV-200 spectrophotometer (path length 1 cm, quartz cell).

Transmission electron microscope (TEM) pictures were obtained using a ZEISS LIBRA 120C transmission electron microscope at a 90 kV accelerating voltage. The TEM samples were prepared by drop coating of nanoparticles dispersed onto a copper grid.

RESULTS AND DISCUSSION

The electronic spectra presented in Figure 3a were typically for TPPS-MTPyP using ordinary electrostatic self-assembly technique. Previous studies have reported broadness of the bands compared to monomers indicative of aggregation (Koti *et al.*, 2003). But most importantly, the appearance of the J-aggregate bands occurring around 492 nm and 708 nm is characteristic of aggregation involving TPPS (Wang *et al.*, 2004, George *et al.*, 2010) (Figure 2a). J-aggregation of TPPS is unique because under acidic condition and with an increase in concentration of TPPS gave a characteristic band at 490 nm accompanied by a band at 706 nm. These bands are referred to as J-aggregate bands arising predominantly from the electrostatic interactions between the sulphonate groups TPPS and the positively charged protonated central cavity of another TPPS (Ribó *et al.*, 1994). A unit cell of J-aggregates of TPPS consists of 4 molecules in which 2 parallel dimers are at an angle to each

other (El-Hachemi *et al.*, 2013). These 1-dimensional unit cells aggregate further into 2-dimensional structures. In the presence of the positively charged species, electrostatic interactions, H-bonding between the central NH and SO_3^- groups and π-stacking of the phenyl groups and the porphyrin ring results in the formation of 3-dimensional supramolecular structures such as nanorods or nanotubes (El-Hachemi *et al.*, 2013).

In the case of TCPP-MTPyP, J-aggregate bands were absent and there was a shift of the absorptions band to shorter wavelength compared to the monomers (Figure 2b). This is due to H-aggregations. Several interactions occurred during aggregation but predominantly are electrostatic interaction and π-π interactions. For TCPP in acidic media the centre nitrogen does get protonated and this is observed with a change in the electronic spectra (Ribó *et al.*, 1994) but the dissociation of hydrogen from carboxylic acid group to generate $CO.O^-$ group is inhibited due to the presence of the stronger acid (HCl). For this reason it was first dissolved in NaOH before addition of HCl hence for TCPP, π-π interactions are the predominant and this promotes H-aggregation which is face-to-face.

Ordinary Electrostatic Self-Assembly(TPPS-based)

(a)
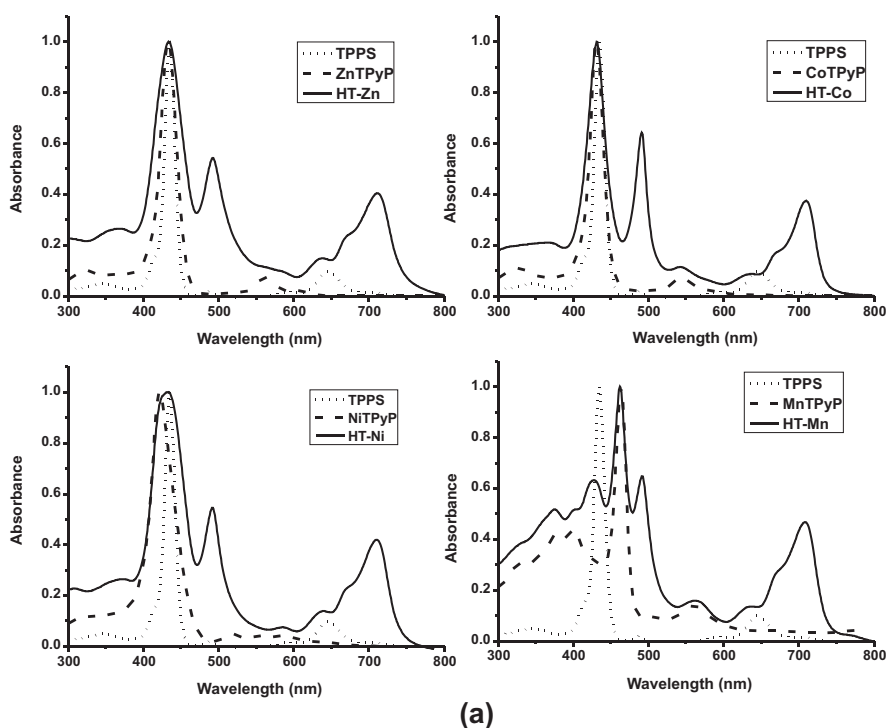
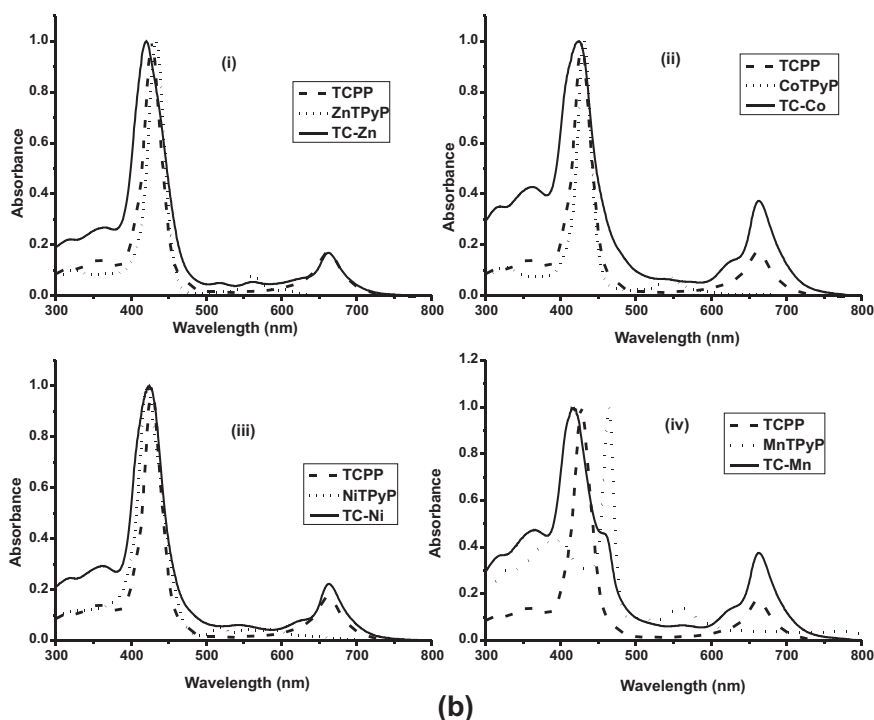## Ordinary Electrostastic Self-Assembly (TCPP-based)

Figure 2: Electronic spectra of ordinary electrostatic self -assembly (a) TPPS-based) (b) TCPP-based.

The electronic spectra of porphyrin aggregates have been explained using the Molecular Exciton Model (Kasha *et al.*, 1965). According to this model, absorption of light by single porphyrin molecule will cause the molecule to move from the ground state, G to an excited state, E. However due to the van der Waals interactions between the molecules in aggregation, the excited state split to E' and E'' and excitation generates transition dipole moment (f) in the individual molecules. There are two possible arrangements of these transition dipoles and these are out-of-phase and in-phase and the sum of these dipole moments (M) determines the allowed excited state of the aggregate.

For the H-type, the transition dipole moments are perpendicular to the line connecting the centers of the molecules as shown in (Figure 3a). The out-of-phase dipole moment interaction is an attractive state which that has the lower energy E' but it is forbidden because $M=0$. The in-phase interactions are repulsive having high energy exciton state E″ but is it allowed $(M=2f)$. This is the reason for the hypsochromic shift (blue shift) of the electronic spectra when H-aggregates are formed by the molecules. In case of J-aggregate, since the transition dipole is parallel (Figure 3b), the in-phase dipole interaction is attractive producing the lower exciton energy state E' which is allowed because $M=2f$ while the out-of-phase is repulsive raising the energy level of the exciton state E'' and is forbidden $(M=0)$. Therefore, the electronic spectrum of J-aggregate is bathochromic shift (red shift) (Kasha *et al.*, 1965).
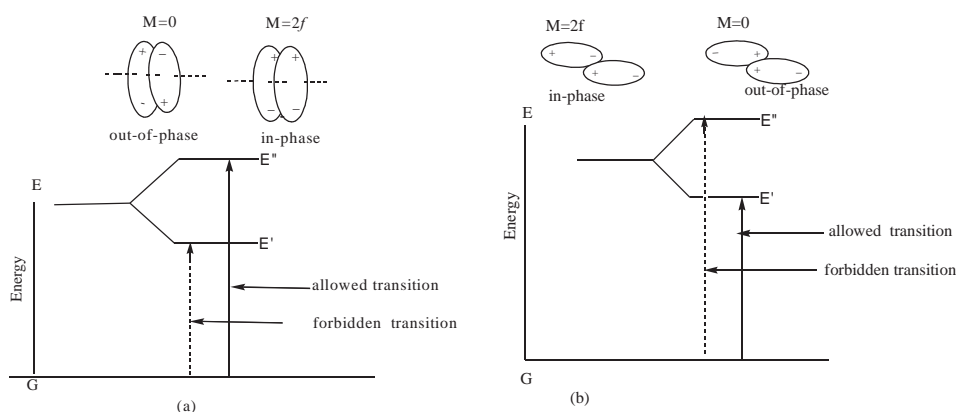
Figure 3: An illustration of the exciton model (a) H-aggregate (b) J-aggregate.

TEM images (Figure 4) of both the TPPS-MTPyP and TCPP-MTPyP of showed the formation of nanorods structures and this was not expected for TCPP-MTPyP. This is because J-aggregation in TPPS has been previously been reported to be the probable drive force for the formation of these cylindrical nanostructures (George *et al.*, 2014). This study contradicts that theory and therefore presumes that the formation of these nanorods is more likely driven by electrostatic interactions and the flexibility of the porphyrin molecule which enables it adopt various conformations hence the molecules can roll up into cylindrically shaped nanostructures (Figure 5).
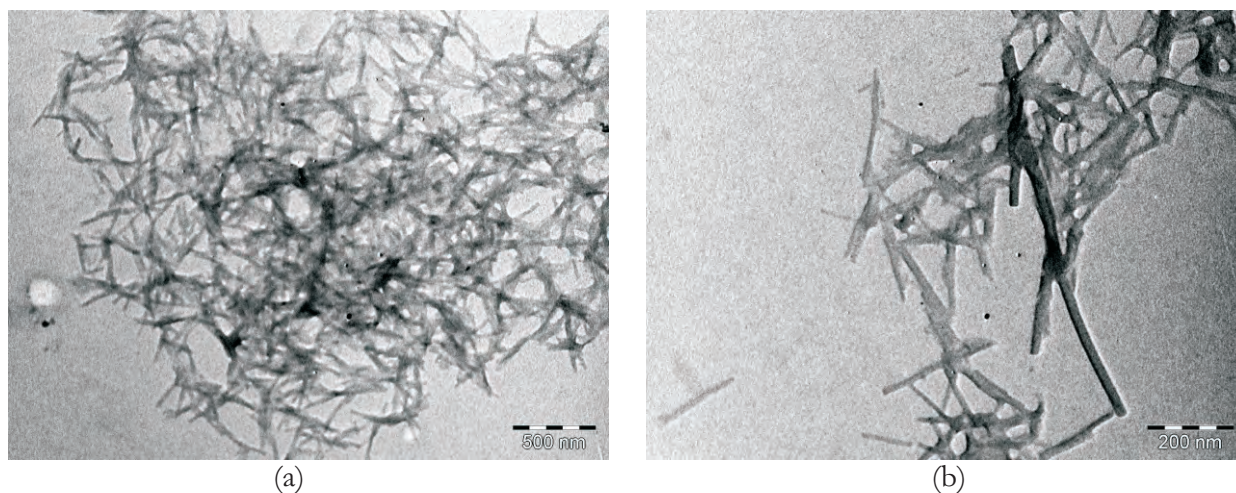

Figure 4: TEM images of (a) HT-Co and (b) TC-Co formed by ordinary electrostatic self-assembly.
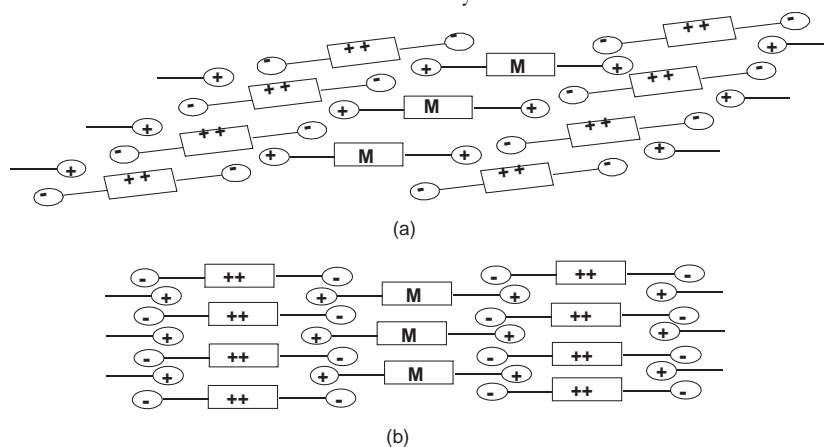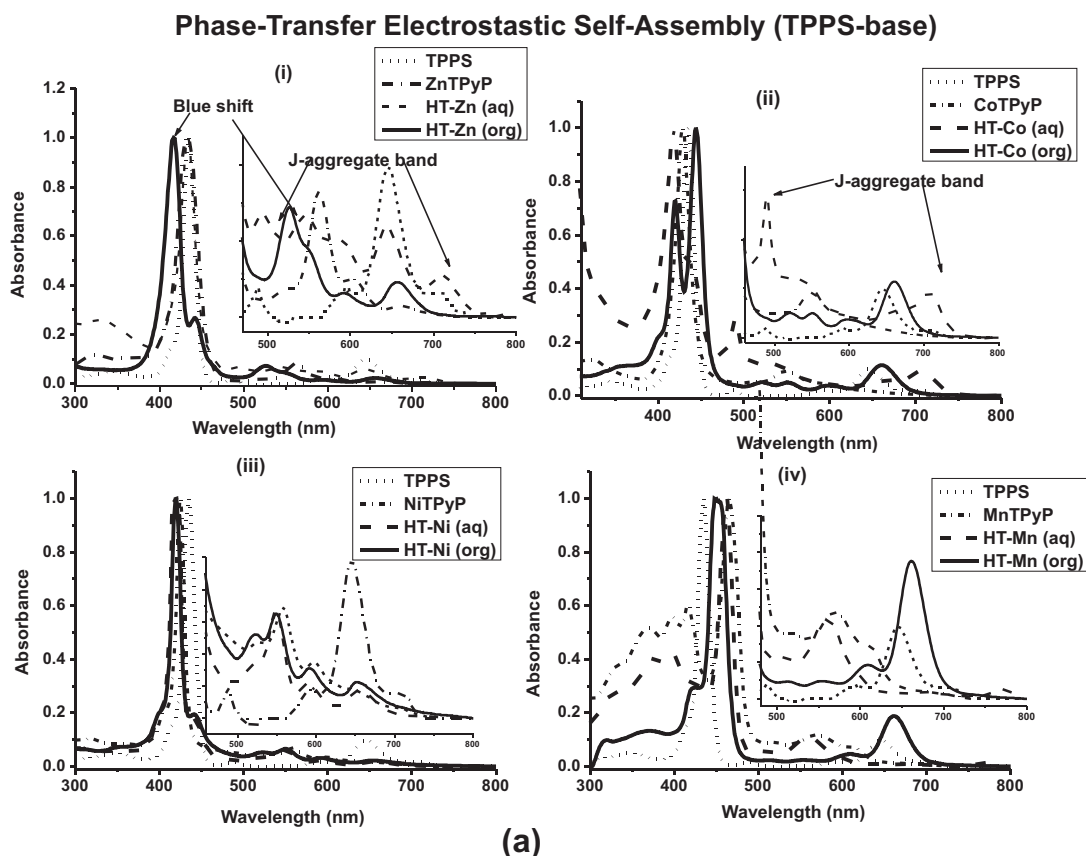

Figure 5: Illustration of the proposed arrangement of molecules in (a) J-aggregation of TSPP-MTPyP (b) H-aggregation of TCPP-MTPyP.

In phase-transfer electrostatic self-assembly technique, it was assumed that with vigorous stirring the negatively charge porphyrins and the metalloporphyrins though in different phases would come in contact and aggregate. The electronic spectra produced from this technique were quite complex. Generally for the TPPS-based, the electronic spectra had narrower bands and this was prominent in HT-Ni and HT-Mn (Figure 6a (iii) and (iv)). This narrow band indicate very weak or no aggregation, particularly for HT-Ni. In the organic phase of HT-Mn the charge transfer band were quenched.

HT-Zn and HT-Co appeared to have very weak J-aggregation bands in aqueous phase which were completely absent in the organic phase (Figure 6a (i) and (ii)). The bands of organic phase of HT-Zn were generally shifted to shorter wavelength from 434 nm to 416 nm and from 564 nm to 526 nm arising from ZnTPyP (Figure 6a (i)). In these spectra as well the shoulder at 440 nm and the band at 658 are similar to the TPPS band (434 and 645 nm). These characteristic bands of the individual molecules confirm little or no interactions between these molecules. This is clearly observed in the electronic spectra of the organic phase of HT-Co, there are two B-band peaks (419 nm and 443 nm) (Figure 6a (ii)). The band at 419 nm is assigned to CoTPyP and the high shoulder at 443 nm to TPPS.

For the TCPP based samples, generally the bands were broader indicative of stronger interactions between these molecules (Figure 6b). The organic phase of TC-Co is similar to that of HT-Co (Figure 6b (ii)) having spilt B-band. For TC-Zn in the aqueous phase were two peaks at 428 and 488 nm (Figure 6b (i)). The band at 428 nm is assigned to ZnTPyP. It is not clear what is responsible for the band at 488 nm but this could be as a result of a different kind of interaction created under these conditions. Although this band does appear close to the J-aggregate band influenced by TPPS (at 490 nm), for now it is assumed that it is not the case as it has been established that TCPP cannot achieve the same kind of arrangement.

Phase-Transfer Electrostastic Self-Assembly (TPPS-base)

(a)

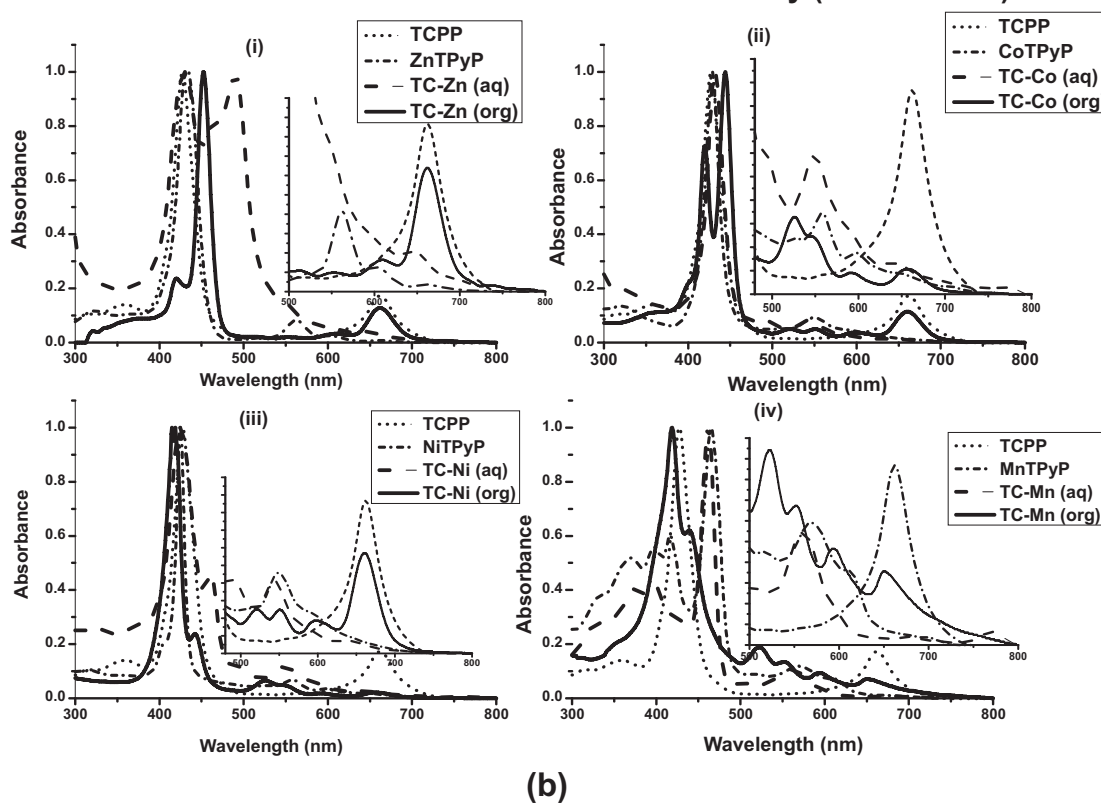**Phase-Transfer Electrostatic Self -Assembly (TCPP-based)**

(b)

Figure 6: Electronic spectra of phase-transfer electrostatic self-assembly (a) TPPS- based (b) TCPP-based

The broadness of the TC-Ni bands confirmed stronger interaction between TCPP and NiTPyP in the two phase systems (Figure 6b (iii)). The band around 463 nm could also be as a result of similar interaction occurring in TC-Zn. Again in Figure 6a (iv), the quenching of the charge transfer band of MnTPyP in organic solvent occurred. It appears as though the presence of other species in the organic phase prevents the ligand to metal charge transfer.

TEM images of these samples were not obtained due to poor results of the electronic spectra. The possible challenge is that with the two phases, solubility and other interactions such as hydrophobic and hydrophilic interactions come into play and would influence the electronic properties of the aggregates. As a result of these interactions there could co-exist the following species: homoaggregates of TCPP/TPPS + homoaggregates of MTPyP + heteroaggregates TCPP/TPPS and MTPyP. These would account for the multiple peaks in the electronic spectra of phase-transfer technique.

CONCLUSION

This study concluded that ordinary electrostatic self-assembly was a more effective method for the fabrication of nanostructure than the phase transfer method in producing robust and well-defined porphyrin nanorods. For TCPP-based, π-π interactions are predominant and these promote H-aggregation which is face-to-face. For TPPS-based, electrostatic interactions tend to promote J-aggregation being a side-to-side arrangement.

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