PORPHYRIN-PHTHALOCYANINE NANORODS (P-PCNR) FORMED BY ELECTROSTATIC SELF-ASSEMBLY

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ABSTRACT

Porphyrin-Phthalocyanine nanorods had been formed by electrostatic self-assembly of two oppositely charged complexes. The negatively charged complex was *meso-tetra-4-phenylsulfonated porphyrin* ($H_2TPPS_4^{4-}$) and the two positively charged complex were tin and indium complexes of tetra {2,(3)-(2-mercaptopyridine) phthalocyaninato}(MTSPyPc). The transmission electron microscope (TEM) images of the colloid suspension of the aggregate confirmed formation of nanorods while their electron spectra showed that the molecules formed J-aggregation.

Keywords: Porphyrin, Phthalocyanine, Nanorods, Electronic Spectra, Aggregates.

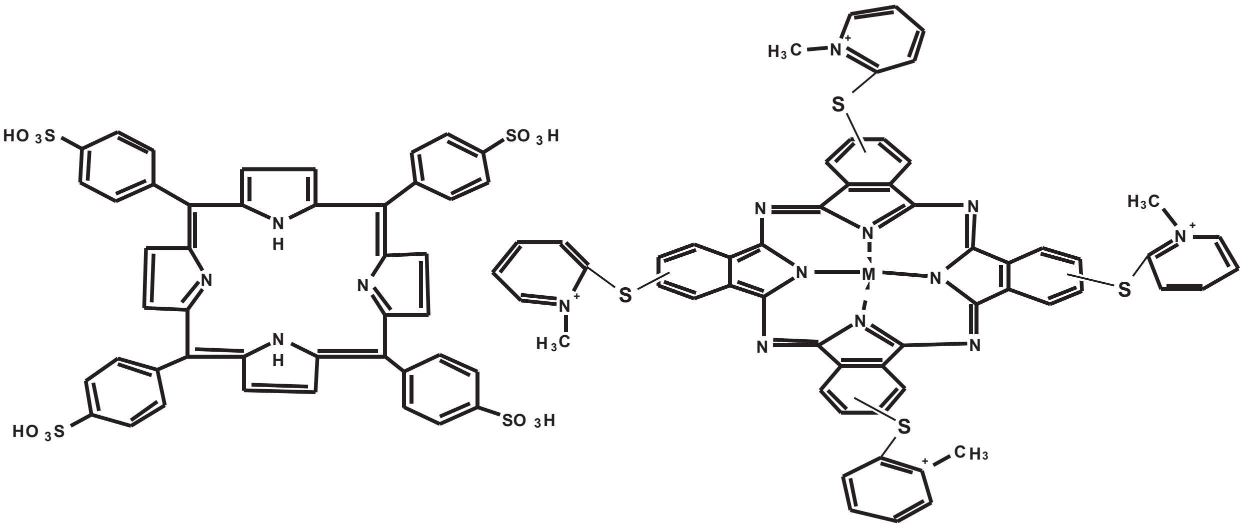
INTRODUCTION

A Porphyrin is a heterocyclic compound consisting of four pyrrole rings joined together by the methylene bridges. It has 22 π electrons of which only 18 are delocalized and obey the Huckel's theory of aromaticity. Phthalocyanines belong to the porphyrin family having the meso carbons of porphyrins replaced by aza linkages and a benzene ring fused onto each pyrrole ring. These classes of compounds are dyes due to their extensive conjugated π-bond systems and have a lot of plausible applications as a result of their tunability (Camerin *et al.,* 2005; Chang *et al.,* 2000; Chou *et al.,* 2000; Dolmans *et al.,* 2003; Wamser *et al.,* 2002). Tuning of these compounds is achieved by inserting various metals ions into the central cavity of the dianionic ligand, axial ligation of these metals, introducing several substituents at various positions on the macrocycle which extends the π-bond system, and or form several macrocyclic dye assemblies (Anderson 1999; Chang *et al.,* 2005).

One of plausible applications of these compounds is their role as light harvesters in dye sensitized solar cells (DSSC) (Barea *et al.,* 2011; Mozer *et al.,* 2009; Giribuba *et al.,* 2012; Nagata *et al.,* 2008). This is because both molecules absorb strongly in the UV-Vis region, and are thermally stable. They can also be modified to have anchoring groups which would bind on the surface of the semiconductors used in the solar cells. Porphyrin has its Soret band around 400 – 430 nm and weak Q-bands 550 nm – 650 nm. While phthalocyanines have strong Q-bands at 650 nm – 700 nm and weak Soret band around 350 nm – 420 nm. This paper reports fabrication porphyrin-phthalocyanine nanorods (P-PcNR) through electrostatic self-assembly of two oppositely charged complexes.

EXPERIMENTAL

The negatively charged molecules was meso-tetra-(4-sulfonatephenyl) porphyrin ($H_2TPPS_4^{4-}$) (10.5 x 10^{-6} M, Fig. 1a) and the positively charged complexes used were tin and indium complexes of tetra-{2, (3)-(2-mercaptopyridine) phthalocyaninato} (MTSPyPc) (3.5 x 10^{-6} M, Fig. 1b). Free base meso tetra-(4-phenyl) porphyrin (H_2TPP) was first synthesized according to an earlier method described by Nascimento *et al.* (2007) and then sulphonated to free base meso-tetra-(4-sulphonatephenyl) porphyrin ($H_2TPPS_4^{4-}$), according to the process described by Srivastava and Tsutsui (1973). Tin and indium complexes of tetra {2,(3)-(2-mercaptopyridine) phthalocyaninato (MTMPyPc) were synthesized by Moeno and Nyokong (2008).



ms-Tertra-4-phenylsulfonated porphyrin ($H_2TPPS_4^{4-}$)

Tetra{2,(3)-(2-mecaptopyridine) phthalocyaninato} (MTSPyPc) M= Sn,In

1a

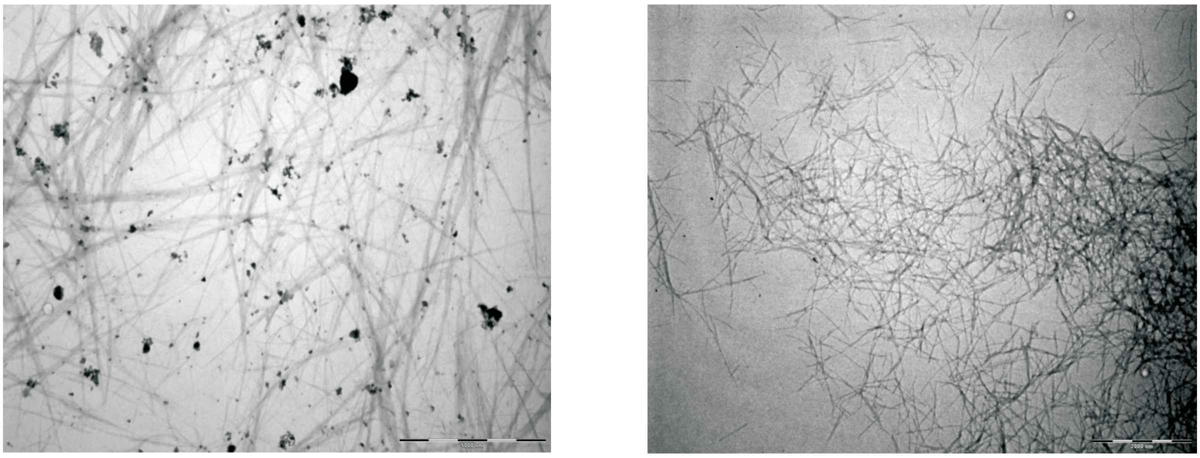
1b

Figure 1 (a) Meso-tetra-(4-sulfonatephenyl) Porphyrin ($H_2TPPS_4^{4-}$) (b) Quaternized Tin and Indium Complexes of Tetra-{2, (3)-(2-mercaptopyridine) Phthalocyaninato} (MTSPyPc; M = Sn, In).

$H_4TTPS_4^{2-}$ (10.5 x 10^{-6} M) was first prepared in an acidic solution (HCl 0.02 M) so as to protonate the central cavity. Protonation creates electrostatic interactions between the peripheral negative sulphonate group of one molecule and the positive central cavity of another (Pasternack *et al.,*1972; Maiti *et al.,* 1998; Ribó *et al.*, 1994). $H_4TTPS_4^{2-}$ (10.5 x 10^{-6}M, 6 ml) was mixed with solution of each of the positively charged molecules $SnTMPyPc^{4+}$ and $InTMPyPc^{4+}$ (3.5 x 10^{-6}M, 6 ml) and left in the dark for 72 hours (Wang *et al.*, 2004). At the end of the duration a green colored colloidal suspension of the aggregates as observed. The aggregates formed were investigated using TEM and UV-Vis spectroscopy. UV/Vis spectra were recorded on a Cary 500 UV-Vis-NIR spectrometer and TEM images were obtained using with JEOL 1210 (80KV). 10 μl of the colloidal suspension of P-PcNR were deposited onto carbon coated grids and air dried before imaging.

RESULTS AND DISCUSSION

The mixing of the porphyrin and the phthalocyanines produced elongated nanorods as seen in the TEM images Figure 2 and from UV-Vis spectra of P-PcNR, the presence of absorption bands at 493 nm and 709 nm in Figure 3 show that the molecules have J-aggregation.



a

b

Figure 2: TEM Images of (a) $H_4TPPS_4^{2-}$-SnTSPyPc (b) $H_4TPPS_4^{2-}$-InTSPyPc

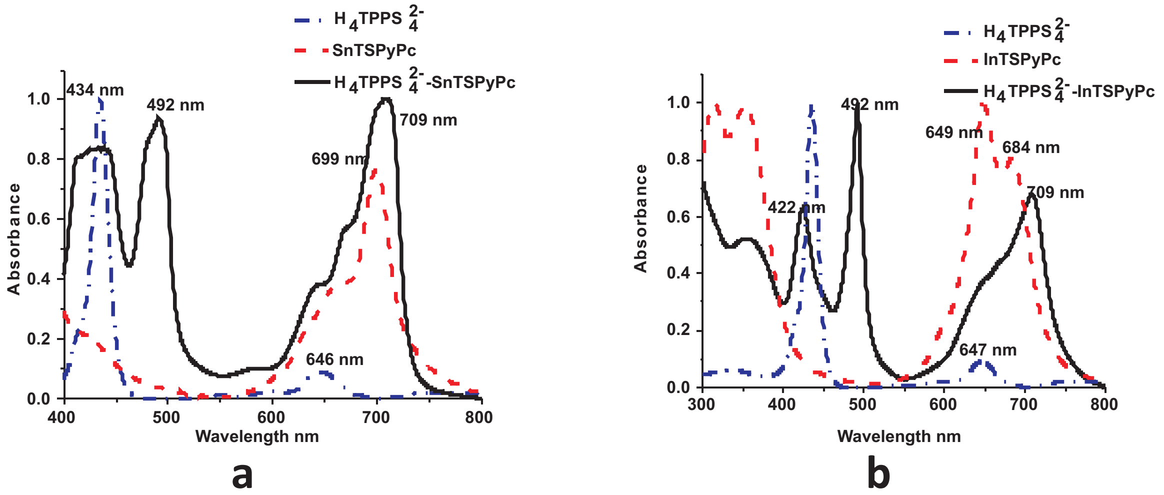


Figure 3: Electronic Spectra of (a) $H_4TPPS_4^{2-}$-SnTSPyPc (b) $H_4TPPS_4^{2-}$-InTSPyPc

These spectra are different from the J-aggregate spectra of homoaggregates of $H_4TPPS_4^{4-}$ (> 10^{-5} M) which has narrow band 490 nm known a Q-band at 706 nm (Pasternack *et al.,*1972; Maiti *et al.,*1998; Ribó *et al.,*1994). Another remarkable difference is the presence of an intense Q-band which is due to electronic properties of the phthalocyanine as this is a weak band in porphyrin nanorods (Wang *et al.*, 2004; George *et al.,* 2010).

It was reported that the fabrication of phthalocyanine nanorods (PcNR) by electrostatic self-assembly, two oppositely charged metallated Pc complexes, produced leaf-like and short rod-like nanostructures. The electronic spectra of these structures where blue shifted compared to the respective monomers and this indicates the formation of H-aggregation (George *et al.,* 2009). They also reported that homoaggregates of tetrasulphonate phthalocyanine $H_4TPcS_4^{2-}$ under similar conditions did not self-aggregate into well defined structures like $H_4TPPS_4^{2-}$. Furthermore their electronic spectra are typical of water soluble phthalocyanine usually very broad and blue shifted showing formation of non specific H-aggregation (van-Lier and Spikes, 1989). Since Pc-Pc heteroaggregates did not form elongated nanorods or nanotubes like the porphyrin-porphyrin aggregation, it can inferred that the ability of $H_4TPPS_4^{2-}$ to form J-aggregates is the driving force of the heteroaggregation of porphyrin and phthalocyanine complexes to form P-PcNR nanorods.

CONCLUSION

The fact that porphyrins absorb strongly in the UV region and phthalocyanine in the visible region give an added advantage over other forms of nanostructures formed by molecules as P-PcNRs absorbs strongly in both regions. Secondly phthalocyanines can be structurally modified to absorb further into the IR region. In addition, J-aggregation produces highly delocalized excitons, which constitute a major requirement for DSSC.

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