SUMMARY AND CONCLUSION

The phenomenon of aggregation plays a significant role in photophysical behaviour of porphyrins. Many biological structures either exist as self-assembling forms or are able to form aggregates and superaggregates. It is intended in the present work to study the influence of aggregation on the spectral properties of the composite species formed from water soluble free base and metallated mesotetrakis(p-sulfonatophenyl)porphyrin (H$_2$TPPS/MTPPS) and mesotetrakis(4 N-methylpyridiniumyl)porphyrin (H$_2$TMePyP/MTMePyP).

Free-base as well as metallated tetrasulphonated phenyl porphyrins (MTPPS) and tetra 4 methylpyridylporphyrins (MTMePyP) were synthesized from the present study. The former is anionically functionalised and the latter is cationically functionalised. The aggregated species of these cationic and anionic porphyrins were developed by reacting them in 1:1 molar aqueous solution. The various 1:1 aggregated systems developed are CuTPPS:ZnTMePyP, CuTPPS:H$_2$TMePyP, AgTPPS:ZnTMePyP, AgTPPS:H$_2$TMePyP, CoTPPS:ZnTMePyP, CoTPPS: H$_2$TMePyP, ZnTPPS:CuTMePyP, ZnTPPS:AgTMePyP and ZnTPPS:CoTMePyP. The aggregated species were characterized by spectral (electronic and EPR) measurements. Noticeable changes in the electronic properties have been found for the porphyrins on aggregation. Their electronic spectral absorption (both Q and B bands) are found to be shifted to a higher wavelength region (red shift) compared to the monomeric porphyrins. The red shift can be attributed to the electrostatic bonding between the two types of porphyrins and associated electronic charge distribution.
EPR studies have been carried out to find out the extent of electronic modulation occurring on these strongly interacting aggregates. Simple 1:1 combinations like CuTPPS:H₂TMePyP, H₂TPPS:CuTMePyP, AgTPPS:H₂TMePyP, etc. gave only broad peaks from which no useful spin-Hamiltonian parameters could be derived because of strong dipolar coupling. So appropriate dilution (to the extent of 5% or less) of the magnetic species was achieved in solid state (taking care of the charge compensation also) to get the fine structure. Compared to the monomeric species in dilute solution, these magnetically diluted coulombic aggregates exhibited interesting trend in their various spin-Hamiltonian parameters. This could be explained in terms of strong π-π interaction between the oppositely charged porphyrin systems.

Since the aggregation of cationic and anionic porphyrins is polymeric-like system made up of porphyrin units, we extended our studies about the effect of polymeric environments on the porphyrin systems. Studies on the nature of the porphyrin units in polymer network are interesting. Several works have been reported in polymer incorporated porphyrin structure. So we developed a system in which pyridyl porphyrin is bonded to PVC chain. Electronic modulation of the porphyrin structure was investigated and it was found that the porphyrin bounded to PVC was more electronically modulated than in the aggregated systems. On aggregation, there is only a marginal shift in the electronic peak value but when the pyridyl porphyrin was incorporated in PVC, a blue shift is seen which could be explained in terms of their structural modulation.

It is of interest to investigate the properties of porphyrin ligand systems containing more than one porphyrin center especially in view of isolating any special features such as intra and intermolecular energy-transfer, electron-transfer and other properties. In view of close structural resemblance, the synthetically developed porphyrins with natural systems like chlorophylls, studies on porphyrin systems have been the subject of numerous investigations.
These studies involve dimerization reactions of porphyrins. The dimers can be accomplished by diverse methods, such as concentration changes, specific complexation behaviour and intentional synthetic methods.

In the present work, we developed a method for the facile synthesis of diporphyrins with two different linking groups. The synthetic strategy employed here was to couple the monohydroxyporphyrin (MTOPP) with the acid chloride (adipoylchloride/sebacoylchloride) under high dilution reaction conditions.

The various homo-type dimers developed in the present work are the dimers of MTOPP (where M = H₂, Cu(II) and Zn(II)) with adipoyl chloride/sebacoyl chloride. All the dimeric porphyrins prepared were characterized by spectral methods (electronic, NMR, EPR and fluorescence).

The electronic absorption spectra of the dimers exhibit characteristic spectra with the appearance of an intense soret band (B band) in the region 410-425 nm followed by Q bands. There is a marginal shift in the soret band relative to that observed for the monomer. The magnitude of shift in the bands in different porphyrins shows the relative strength of π-π* interaction brought about by dimerisation.

The ¹H NMR spectra of dimers are highly characteristic and the assignment of proton resonances is based on the position of the resonances and their integrated intensity. The position of the resonance and its nature of the multiplet often furnish the details about the proton position of the dimers. In general, all the proton resonances of diporphyrins occur in a shielded region relative to the manner indicative of the presence of ring current effect induced by the proximal disposition of the two porphyrin units¹⁰-¹¹. The details are discussed.
EPR spectroscopy of the diporphyrins bearing Cu(II) centers were informative in identifying the extent of interaction between the Cu(II) centers. The g and A tensors were calculated from the spectra. These Cu(II) dimers exhibit two sets of (parallel and perpendicular) lines corresponding to $g_{||}$ and $g_{\perp}$ tensors with superhyperfine interaction with the pyrrolic nitrogens. The existence of two porphyrins in proximity to one another permits interaction between the metal centres.

The fluorescence spectra of the dimers exhibit two emissions corresponding to $Q(0,0)$ and $Q(0,1)$ bands. The emission spectra of the free base dimers and those of Zn(II) derivatives are recorded. It is seen that the free-base diporphyrins and Zn(II) derivatives exhibit fluorescence with large decrease in intensity and quantum yield relative to that of corresponding monomer. The free-base dimers exhibit a reduction in the emission intensity relative to that observed for the monomer free-base. The Zn(II) dimers show a substantial decrease in quantum yield relative to the corresponding Zn(II) monomer.

Since most of the catalytic activities aided by metalloporphyrins occur at relatively higher temperatures, the thermal stability of metalloporphyrins is a crucial factor in terms of their catalytic function and efficiency. Also the method of thermal analysis is now considered to be a highly useful technique for studying the overall structure, nature and extent of bonding of many coordination compounds. Hence the phenomenological and kinetic aspects of thermal decomposition of five different metallotetraphenyl porphyrins were studied in the present investigation. The kinetic parameters of the major stages of thermal decomposition were calculated, their significance explained and mechanisms were assigned to these decomposition stages using the nine mechanism-based equation proposed by Satava. The thermodynamic parameters show interesting trend which could be explained. Correlation could also be made between the various kinetic and thermodynamic parameters and ionic radii of the metal ions.
The present investigation throws light on various aggregated porphyrins synthesised by different techniques. Several covalently linked dimers were also prepared by the condensation method using two different acid chlorides as their linking groups. The characterisation of these dimers, aggregated and monomer species were done by analytical, thermal and spectroscopic (electronic, NMR, EPR and fluorescent) methods. Noticeable changes are observed on the electronic modulation of these samples compared to their monomers. These are explained. It was found that the formation of dimers and aggregates are dependent on various factors like nature of the central metal ion, nature of the solvent used during the reaction, temperature of the reaction etc. Electronic absorption studies of PVC incorporated porphyrin systems were also done. Thermal studies of the metalloderivatives of tetraphenyl porphyrins show their thermal stability and also the mechanism and modes of thermal decomposition.