

Chapter

7

Summary and Conclusion

The protein envelope around the natural porphyrins is known to play a crucial role (by way of specificity and efficiency) in many biological systems like the heme enzymes and photosystems. A great deal of information about the effect of proximal groups on porphyrin system in the protein pocket has come to light, thanks to concerted efforts due to chemists, biologists and physicists. However, the overall nature and effect of protein matrix on the enzyme core is still not fully understood. The present study is aimed at investigating the fine-tuning property of the (both electronic and redox) surrounding protein network on the porphyrin π -framework by developing synthetic models based on polymer-grafted/encapsulated porphyrins. A variety of suitably functionalised polymer systems are developed and employed for incorporating modified porphyrins for this purpose. The polymer grafted/dispersed porphyrin systems developed in this work were characterised by electronic, EPR and cyclic voltametric methods. The enzyme-like (catalase and peroxidase) activities of a few such polymer-porphyrin systems were investigated in detail. A few singlet emitting polymer-bound metalloporphyrins were also developed and their efficiency for generating $^1\text{O}_2$ species were also monitored in brief. A novel binary porphyrin system anchored on polymer surface was also developed in the present study.

The basic porphyrin systems selected for the studies were mesotetraphenylporphyrins (H_2TPP) and their mesotetrapyrrolyl analogues (H_2TPyP). These were further derivatised to get either anionic (H_2TPPS) or cationic ($H_2TMPPyP$) porphyrins. All the free-base (metal-free) porphyrins were complexed with various of metal ion/carriers to synthesise their metalloderivatives— $MTPP/MTPPS/MTPyP/MTMPyP$ ($M = Mn, Fe, Co, Zn, Ag, Cu, Cd$). All porphyrins/metalloporphyrins synthesised in the present work were characterised by spectral measurements.

One of the polymer supports employed was divinylbenzene (DVB)-crosslinked polystyrene (in bead form) after functionalisation with chloromethylmethyl ether. This chloromethylated resin was further functionalised by reacting with pyridine. The resulting polymer (PS) with N-alkyl pyridinium functions (having cationic centres) was used as an effective polymer support for immobilising anionic $MTPPS$ by anion exchange method to get various PS- $MTPPS$ systems.

The anionic polymer support(PA) was prepared by controlled sulphonation of polystyrene (either linear or cross-linked) with conc. H_2SO_4 using Ag_2SO_4 as the catalyst. The cationic porphyrins, $H_2TMPPyP/MTMPyP$ were grafted on this polymeric surface by cation exchange method, which yielded various PA- $MTMPyPs$.

The ability of pyridine moiety to coordinate to some of the metalloporphyrins was made use of in developing poly(4-vinylpyridine) (PVP)-grafted metalloporphyrins. Various grafted systems synthesised were PVP-MP where MP = $CoTPPS$, $CoTM4PyP$, $MnTPPS$, $MnTM4PyP$, $FeTPPS$ and $CuTPPS$.

In order to mimic certain encapsulated heme systems, a few metalloporphyrins, $MTPPS(M = Fe, Co, Mn, Ag, Cu)$ were made to disperse within polymeric systems like polyethyleneglycol(PEG) and Bovine albumin serum(BSA). It was found that the above porphyrins get immobilised (encapsulated) within the polymeric matrix accompanied by property changes.

The various polymer–porphyrin systems developed were characterised by spectral (IR, electronic and EPR) measurements and their redox tuning monitored by cyclic voltammograms. Noticeable changes in electronic properties were found for the MPs on polymer grafting. Their electronic spectral absorptions (both Q and B–bands) of supported MTPPS are found to be shifted to a higher wavelength region (red shift) compared to the unsupported porphyrins. Generally, MTPPS grafted on polymer support with chemical bonds exhibited higher red shift compared to porphyrins simply dispersed in polymer matrix without any chemical interactions. These observations could be explained in terms of molecular distortions and variation in electronic charge brought about by steric interaction of polymer matrix on the porphyrin moieties. The coordinating ability of some of the functional groups presented in the polymer network was also seen to be modulating the electronic properties of these supported MTPPS moieties. At the same time, cationic MTMPyP systems did not show considerable shift in absorption peaks when incorporated within polymer matrices. These are also explained.

Similarly, the half wave potential of Fe(III)/Fe(II) redox couple of FeTPPS was found to be shifted towards more negative potential due to polymer immobilisation. This was compared with other M(III)/M(II) couples and the trend explained in conjunction with their electronic spectra by considering the ordering of orbitals and electron occupancy in them. The EPR parameters calculated for Cu- and Ag-porphyrins, incorporated in various polymer supports were also found to be slightly different when compared to their unsupported porphyrins. This is also explained in terms of electronic modifications brought about on these metalloporphyrins during polymer grafting.

The catalase– and peroxidase–like activities of some PS–MTPPS systems were studied in the present work. Since Fe(III), Mn(III) and Co(III) porphyrins are known for their catalytic efficiencies, MTPPS involving these metal ions were employed for enzyme model studies. These immobilised metalloporphyrins were found to exhibit these enzyme actions quite effectively.

It was found that the three metalloderivatives MTPPS[M=Fe(III), Mn(III) and Co(III)] exhibit varying efficiency with respect to the catalase-like reaction. In acidic pH, the order of efficiency of the metalloderivatives was Fe(III) > Mn(III) > Co(III) while in basic as well as in neutral pH, the order gets changed to Mn(III) > Co(III) > Fe(III). The maximum efficiency was found to be around pH 10.0 in all the cases. The possible mechanism involved in these reactions is discussed. While the Fe(III) derivatives showed greater sensitivity to temperature, Mn(III) showed the least sensitivity. This is explained in terms of the temperature-dependent spin-crossover possible within FeTPPS system. The recyclability/reusability of the polymer supported porphyrin system was also investigated by carrying out the reaction for several cycles. The results showed a very high degree of recyclability in all the cases.

It was found that the peroxidase activity of these PS-MTPPS systems depends greatly on the pH of the reaction medium. In order to have an appreciable activity, the pH of the medium should be between 7.9 and 8.6. In this pH range the PS-CoTPPS system is found to be exhibiting the highest activity and PS-FeTPPS the least. PS-MnTPPS showed intermediate activity. The catalytic efficiency of all the supported MTPPS system is found to be enhanced as the temperature was increased. The reusability of the PS-MTPPS systems for peroxidase like activity was also studied and found that they exhibited a high degree of recyclability without getting poisoned much.

In the present work, some attempts were made to explore the photo-sensitisation properties of selected singlet emitting PS-MTPPS[M=Zn(II), Cd(II) and 2H] systems especially their ability to photogenerate singlet oxygen. For comparison, polystyrene anchored Rose-bengal(RB) was also employed for the purpose. It was found that the binding of porphyrin to polymer has decreased its efficiency of singlet oxygen generation. The observed lowering has been attributed to structural modifications on porphyrin moieties due to the polymer network.

In the present work, attempts were also made to develop some ionically bound novel porphyrin moieties. Two different classes of 'dimers' were prepared by employing appropriate strategies. Tetra(4-pyridyl)porphyrins were reacted with chloromethylated polystyrene beads to get covalently bound (through quaternisation of one of the pyridine moieties) porphyrins on the polymer support (PS-H₂T4PyP¹⁺/PS-MT4PyP¹⁺). This mono-cationic porphyrin has exchangeable chloride function which could be replaced with anionic H₂TPPS or MTPPS. Several 'dimers' (both homo and hetero) of this type were prepared and characterised using electronic spectroscopy. The monocationic porphyrin moieties on the polymer surface could be further converted to their tetra-cationic porphyrins (PS-MTM4PyP⁴⁺) through exhaustive quaternisation by reacting with CH₃I. These solid immobilised porphyrins were made to react with MTPPS/H₂TPPS in aqueous condition. Spectrophotometric estimation showed that PS-MTM4PyP⁴⁺ take up tetraanionic MTPPS (in solution) very effectively and the overall porphyrin stoichiometry corresponded to 1:1 (MTM4PyP⁴⁺ : MTPPS⁴⁻). This was confirmed by electronic spectra of the final product. A series of hetero- and homo-dimers could be synthesised by this strategy. The compounds isolated by this method were PS-M₁TM4PyP⁴⁺-M₂TPPS⁴⁻ with the following combinations, M₁= 2H, Mn(III), Ag(II) and Cu(II); M₂ = 2H, Mn(III), Co(III), Fe(III), Cu(II), Ag(II), Zn(II) and Cd(II). Characterisation of these monomers and dimers were carried out by electronic and EPR studies.

The possible catalytic (enzyme-like and industrial) applications of these polymer supported porphyrins (both monomeric and binary) systems offer a promising field of study for future. It is intended to look into some of these in details along with more interesting biological model reaction as an extension of this work. The photocatalytic activities of various polymer bound systems can also be actively investigated in the context of their antibacterial and antiviral characteristics, along with some of their electron-transfer and energy-transfer properties.

The work presented in the thesis was published or is in the process of publication as detailed below:

- (i) Studies on Catalase Model Systems Based on Immobilised Metalloporphyrins on Modified Solid Polystyrene Support.: M. V. Vinodu and M. Padmanabhan., *Proc. Indian Acad. Sci (Chem. Sci)*, **110**, 1998, 461– 470.
- (ii) Efficient Enzyme Model Systems Based on Metalloporphyrins of Fe(III), Mn(III) and Co(III) Grafted on Solid Polystyrene Support.: M. V. Vinodu and M. Padmanabhan., *Proc. Kerala Science Congress*, 1999, 49–52.
- (iii) Studies on Catalase-like Activities of Polymer-Supported Metalloporphyrin Catalysts.: M. V. Vinodu and M. Padmanabhan., *Proceedings of National Workshop on Catalysis*, 1997, 43–44.
- (iv) Photosensitizing Properties of Ionic Porphyrins Immobilised on Functionalised Solid Polystyrene Support.: M. V. Vinodu, J. J. Inbaraj, R. Gandhidasan, R. Murugesan and M. Padmanabhan., *Photochem. Photobiol.*, (communicated).
- (v) Electronic and Redox Modulation of Metalloporphyrins Grafted on Polymer Matrices, (under publication).
- (vi) Studies on Metalloporphyrins Encapsulated on Natural Proteins, (under publication).
- (vii) Peroxidase-like Activity of Polymer-Supported Metalloporphyrins, (under publication).
- (viii) Synthesis and Characterisation of Novel Mono-and Tetra-Cationic Metalloporphyrins Covalently Bonded to Functionalised Solid Polymer, (under publication).
- (ix) Ionically Bonded Binary Metalloporphyrin Systems on Solid Polymer Support, (to be communicated).

