

# Chapter

# 6

## Binary Porphyrin Systems Grafted on Polymer Supports

### 6.1 Introduction

Both the molecular environment (protein globule) and the nature of metalloporphyrins are important factors which decide the specificity and efficiency of the porphyrin-bearing biological systems (as discussed in Chapter 1). A closer look at some of the biosystems, however, reveals that another important factor which is vital is the necessity of having one or more of additional porphyrin moieties in the vicinity of the metalloporphyrins. This is quite evident in the reaction centre of photosystems<sup>1</sup>. Hemoglobin, catalase and cytochrome-c-oxidase are also other well-known examples the chemistry of which are remarkably different from the corresponding monomers<sup>2-5</sup>. For example the oxygen binding property and the functional aspects of hemoglobin is significantly different from that of myoglobin, its monomeric analogue. This variation in property to a great extent is due to the molecular placement (cooperative effect) and the specific action of the surrounding proteins. The electronic interactions between the adjacent porphyrin moieties are also expected to play a crucial role in the unique behaviour of such biosystems.

A great deal of efforts have been, therefore, made in the synthesis, characterisation and exploring the catalytic role and utility of metalloporphyrin dimers. These include face-to-face porphyrin dimers, slipped dimers or dimers

separated by spacers<sup>6-17</sup>. The electronic and redox properties of such porphyrin dimers are seen quite different from that of the corresponding monomers. It has been demonstrated that a great deal of specificity and efficiency are also achieved in these systems. For example, while a cobalt derivative of face to-face porphyrin catalyse the cathodic reduction of dioxygen by a four-electron process to yield H<sub>2</sub>O, the same monomeric porphyrin catalyse this reduction via a two-electron process to yield a different product, H<sub>2</sub>O<sub>2</sub><sup>16,17</sup>. Also  $\mu$ -oxo dimer of FeTPP (FeTPP-O-FeTPP) has been found to inhibit the catalytic oxygenation reactions<sup>18</sup>. While some of the factors contributing to the specific properties of porphyrin dimers are known in homogeneous conditions, no studies have been reported with regard to either synthesis or reaction properties of polymer bound/ dispersed, dimeric/associated porphyrin systems.

In this chapter we describe the strategy and report the synthesis of a series of new binary porphyrin systems appended on some selected polymer surfaces. Both mono-as well as tetra-cationic MPs covalently bonded to DVB cross linked polystyrene are initially developed for the purpose. While these immobilised monomeric cationic porphyrins are interesting systems on their own, they are also used as precursor species to generate novel 'dimeric'/binary porphyrins held together through ionic interactions. Attempts were made to synthesise a large number of homo-as well as hetero-binary metalloporphyrins and to characterise these systems by spectral analysis. The precursor metalloporphyrins employed for grafting on the functionalised polymer support are meso tetrapyrridylporphyrin, H<sub>2</sub>TPyP or MTPyP (M = Mn<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Ag<sup>2+</sup>). These are further subjected to interact with tetrasulphonated tetraphenylporphyrins H<sub>2</sub>TPPS/MTPPS (M = Mn<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Ag<sup>2+</sup>) to yield the expected binary porphyrin (either homo or hetero type). Divinylbenzene (DVB) cross-linked chloromethylated polystyrene beads and polyvinylchloride (PVC) granule were used as polymer support. For convenience the general term TPyP/TPP is used occasionally in this chapter, to denote both free base and metalloderivatives of porphyrins in common. Also, the cross-linked chloromethylated polystyrene beads without any cationic centre are denoted as PS throughout this chapter.

## 6.2 Experimental

### 6.2.1 Preparative details

The porphyrins employed for developing the binary systems are H<sub>2</sub>T4PyP and H<sub>2</sub>TPPS and their metallo derivatives. The preparative details of these compounds are already discussed in Chapter 3. H<sub>2</sub>T3PyP was prepared from 3-pyridine carboxaldehyde and pyrrole by the same procedure employed for H<sub>2</sub>T4PyP. The synthetic details of the polymer support (chloromethylated polystyrene) are also presented in the same chapter.

### 6.2.2 Generation of polymer supported H<sub>2</sub>TPyP<sup>+</sup>/MTPyP<sup>+</sup>

Chloromethylated polystyrene beads, PS(4g) were stirred with metallo/free-base tetrapyrrolylporphyrin MT4PyP/H<sub>2</sub>T4PyP(4 x 10<sup>-4</sup> mole) in DMF (25 ml) at 70–80°C for 72h. At the end of the reaction the resulting porphyrin anchored polymer beads (PS-H<sub>2</sub>TPyP<sup>+</sup>/PS-MT4PyP<sup>+</sup>) were collected by filtration and washed 5 times with DMF, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH to remove any unreacted porphyrins. Attempts were also made to prepare these supported pyridyl porphyrins under different conditions, namely, in DMF, CHCl<sub>3</sub> and in toluene/water under refluxing conditions to see any effect due to solvent/temperature. Polyvinylchloride, PVC (2g) were also employed in place of polystyrene beads for polymer grafting under similar reaction conditions in these solvents.

Analogous procedure was employed for immobilisation of H<sub>2</sub>T3PyP/MT3PyP on the polystyrene support (PS-H<sub>2</sub>T3PyP<sup>+</sup>/PS-MT3PyP<sup>+</sup>).

### 6.2.3 Generation of polymer grafted H<sub>2</sub>TMPy<sup>4+</sup>/MTMPy<sup>4+</sup> species

The methylation of free pyridine units on porphyrin macrocycle was carried out to generate polymer supported tetracationic porphyrins. This was done by quaternisation reaction with CH<sub>3</sub>I. Polystyrene anchored pyridyl porphyrin (metallated or free base), PS-T4PyP<sup>+</sup> (2g) in CHCl<sub>3</sub>/CH<sub>3</sub>I mixture (5/15 ml) was

refluxed at 40°C in a 100 ml round bottomed flask fitted with a water condenser. Some more quantity of CH<sub>3</sub>I(10 ml) was added during the reaction process after 6h and 8h successively. After 12h the remaining CH<sub>3</sub>I and CHCl<sub>3</sub> were removed by filtration and the polymer beads (PS-H<sub>2</sub>TM4PyP<sup>4+</sup>/PS- MTM4PyP<sup>4+</sup>) were washed carefully with CHCl<sub>3</sub> and acetone and dried in an oven at 60°C.

#### 6.2.4 Generation of binary porphyrins on polymer supports

Para-sulphonated tetraphenylporphyrin H<sub>2</sub>TPPS/MTPPS (1 × 10<sup>-4</sup> mole) was dissolved in 25ml water in a flask and heated on a boiling water bath. PS-H<sub>2</sub>TM4PyP<sup>4+</sup> beads (500mg) were added to this solution and stirred slowly for 72h. The colour intensity of the TPPS solution was seen to decrease by this time indicating the uptake of the anionic porphyrin from the solution by the polymer beads. After the specified time, the free anionic porphyrin in solution was removed by filtration. The PS-H<sub>2</sub>TM4PyP<sup>4+</sup>: MTPPS<sup>4-</sup>/H<sub>2</sub>TPPS<sup>4-</sup> systems so generated was washed thoroughly with water until the washings became colourless. The beads were then washed with methanol and acetone before drying. The PS-MTM4PyP<sup>4+</sup>: H<sub>2</sub>TPPS<sup>4-</sup>/MTPPS<sup>4-</sup> systems were also developed by the same technique.

Analogous procedure was employed for generating PS-T4PyP<sup>+</sup>:TPPS<sup>4-</sup> systems also.

#### 6.2.5 Physical measurements

The electronic spectra (in solution) of the porphyrins were measured either in CHCl<sub>3</sub>, DMF, CH<sub>3</sub>OH or in H<sub>2</sub>O as the case may be. As mentioned in Chapter 3 electronic spectra of the supported porphyrins were measured in solid state with Nujol and IR spectra were recorded in the solid state in the form of KBr pellets. ESR measurements of both the polymer grafted monomeric and dimeric MPs (bearing Cu<sup>2+</sup> and Ag<sup>2+</sup> centers) were carried out in solid state. The g marker employed was DPPH.

## 6.3 Results and Discussion

### 6.3.1 Synthesis of polymer grafted $H_2TPyP^+/MTPyP^+$ systems

The strategy employed to generate polymer bound pyridyl porphyrins is based on the well known quaternisation reaction between a pyridine moiety and C-Cl function of an another molecular species with the formation of a stable covalent bond as represented in Scheme 10.

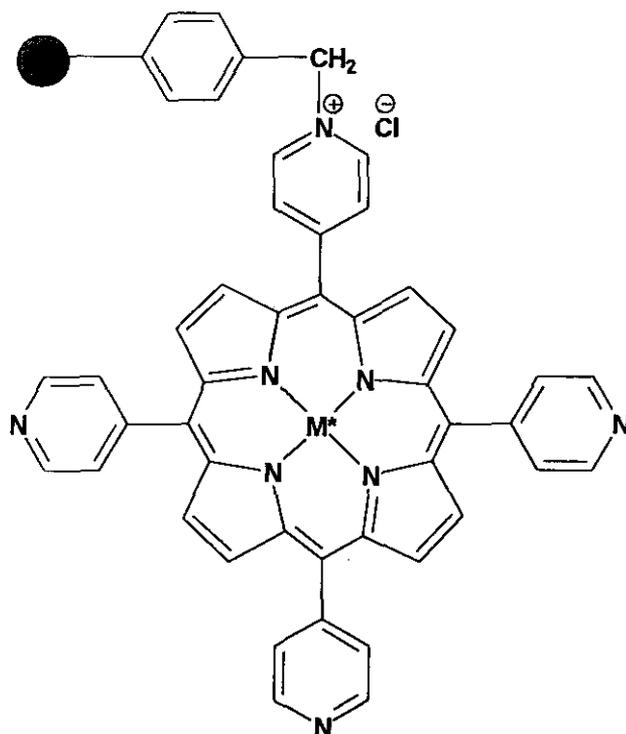


29

Scheme 10

Porphyrins of the type, tetrapyrrolylporphyrin ( $H_2TPyP/MTPyP$ ) has four pyridine sites at their meso positions. Therefore, the N-atom in such pyridyl porphyrins could undergo quaternisation reaction with  $CH_2\text{-Cl}$  function of the chloromethylated polystyrene resulting in porphyrin grafted polymer beads.

A trail experiment was carried out by adding chloromethylated polystyrene beads (PS) to the refluxing  $CHCl_3$  containing Mn(III) meso tetra-4-pyridyl porphyrin(MnT4PyP) for 24h. During this time the uptake of MnT4PyP by polymer support was indicated as evidenced by the distinct pale green colour formation on the pale yellow polymer beads. A decrease in the intensity of absorption peaks of porphyrin solution was also found to occur confirming the uptake of the MP by the solid polymer. The repeated washing with any solvent even in hot condition did not change the porphyrin colour of the beads indicating a strong chemical bonding between the polymer and porphyrin. As indicated the type of species generated could be given by 30. The amount of MnT4PyP bonded to the polymer surface was estimated spectrophotometrically by measuring the absorbance decrement of Soret band of MnT4PyP in solution before and after the reaction procedure. However, the estimated value was



30

observed to be very low (less than  $0.1 \times 10^{-4}$  M MnT4PyP per g of the polymer resin). So the reaction was continued further for 72h, but no improvement in porphyrin uptake was observed. Then the same reaction was carried out in refluxing DMF for 72h. DMF was used because polar solvents are known to facilitate the quaternisation reaction rate<sup>19</sup>. But at refluxing condition ( $\sim 150^{\circ}\text{C}$ ) the demetallation of the porphyrins was observed. This was confirmed by the solid state electronic spectra of the resulting polymer beads, which showed a well separated peak at 423nm and the indication of the characteristic 4- line peaks in the Q-region, typical of free-base porphyrins. Electronic absorption spectra of aliquots of the remaining DMF solution after the porphyrinisation reaction also showed the existence of demetallated  $\text{H}_2\text{T4PyP}$  (420nm band) as a major component. So the reaction was carried out at mild temperature ( $70\text{--}80^{\circ}\text{C}$ ) in DMF for 72h. At this reaction condition no demetallation was observed (verified by electronic spectra) from MT4PyP and the amount of porphyrin anchored on polystyrene was estimated to be about  $0.6 \times 10^{-4}$  mole of porphyrin per g of polymer, which is quite higher than that observed for porphyrinisation reaction under refluxing  $\text{CHCl}_3$ . As discussed in Chapter 3, the amount of

anionic MTPPS moieties bonded to the polymer surface is about  $1 \times 10^{-4}$  mole/g of resin. So an amount of  $0.6 \times 10^{-4}$  M of porphyrin/g of polymer is a fairly good uptake considering the bulky nature of the porphyrin macrocycle and the steric factors at the polymer surface for the quaternisation reaction. From these data it can also be assumed that 2 or even more of pyridyl moieties of a single porphyrin unit are capable of interacting with  $\text{-CH}_2\text{Cl}$  functions from polystyrene surface. The solid state electronic spectra of PS-MnT4PyP<sup>1+</sup> system is given in Fig.6.1. along with that of unsupported MnT4PyP dispersed in nujol. The slight changes observed in the band positions of PS-MnT4PyP<sup>1+</sup> spectra as compared to that of free MnT4PyP is in agreement with the results discussed in Chapter 3.

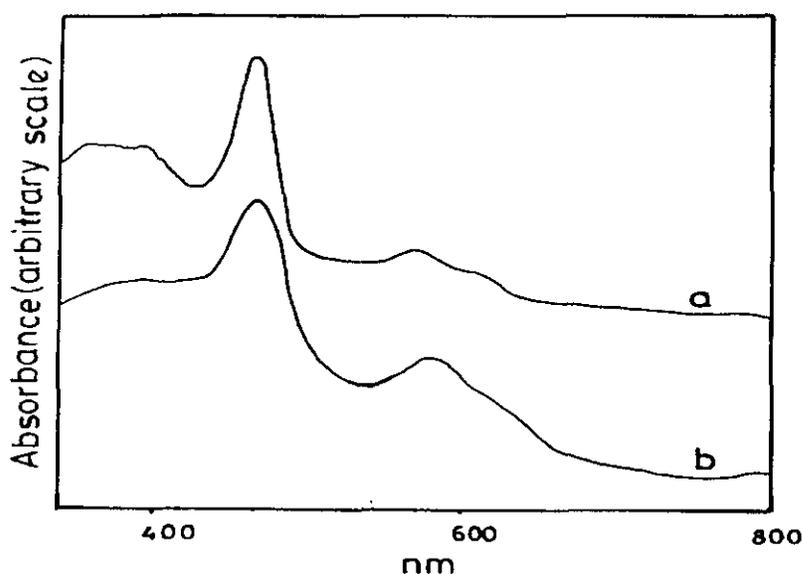


Fig.6.1 Solid state electronic spectra of (a) MnT4PyP (b) PS-MnT4PyP<sup>+</sup>.

Metal-free tetraphenylporphyrin ( $\text{H}_2\text{T4PyP}$ ) was also anchored on polystyrene just similar to MnT4PyP. The reaction was carried out both in refluxing DMF ( $150^\circ\text{C}$ ) and in DMF at  $70\text{-}80^\circ\text{C}$ . No perceptible changes in porphyrin uptake was observed in these two different reaction conditions ( $0.50 \times 10^{-4}$  and  $0.45 \times 10^{-4}$  mole of  $\text{H}_2\text{T4PyP}$  uptake per g of resin at  $150^\circ\text{C}$  and  $80^\circ\text{C}$  respectively for a reaction time of 72h). CuT4PyP, AgT4PyP and ZnT4PyP were also immobilised on polystyrene by the same procedure employed for MnT4PyP. In the case of AgT4PyP some demetallation was observed (as evident from the appearance of

peaks characteristic of free bases in the beads after the reaction) even when the reaction was carried out at 70°C in DMF. Some demetallation was also suspected for this porphyrin when the reaction was carried out even in CHCl<sub>3</sub>. The solid state electronic absorptions of these various appended porphyrins along with that of unsupported porphyrins are given in **Table 6.1**.

**Table 6.1** Solid state electronic spectral values of some T4PyP and PS-T4PyP<sup>+</sup> systems in nujol.

Porphyrin System	Absorption maxima (nm)	
	Soret	Q bands
H <sub>2</sub> T4PyP	423	517, 526, 591, 646
PS- H <sub>2</sub> T4PyP <sup>+</sup>	432	523, 546, 596, 645
MnT4PyP	474	541, 576, 619, 770
PS- MnT4PyP <sup>+</sup>	477	581 626 774
ZnT4PyP	417	547 577
PS- ZnT4PyP <sup>+</sup>	444	568 626
CuT4PyP	418	544 577
PS- CuT4PyP <sup>+</sup>	436	547
AgT4PyP	428	540 582
PS- AgT4PyP <sup>+</sup>	438 (broad)	526, 564, 598

The variations in the demetallation process found in these MTPyPs on polymer appending can be attributed to the ionic size variation of the central metal ions. The Ag<sup>2+</sup> ionic radius, being higher than that of the other ions, has lesser fit with the cavity size of the porphyrins which would enable it to get dislodged even in slight distorted within the porphyrin-frame work. The Cu<sup>2+</sup>, Mn<sup>3+</sup> and Zn<sup>2+</sup> are known to have compatible size with the cavity and ability to accommodate itself even in moderately distortion geometry. It is interesting to note the pronounced red shift in the case of Zn-and Cu- pyridyl porphyrins on polymer appending

which could be explained in terms of the decrease in  $d\pi$ - $eg(\pi^*)$  overlap, as discussed in detail in Chapter 3.

The EPR spectra of  $\text{PS-CuT4PyP}^+$  and  $\text{PS-AgT4PyP}^+$  were recorded in solid state. Both the spectra exhibited porphyrin-like parallel and perpendicular lines with N-superhyperfine structures, indicating that the porphyrin identity is maintained upon polymer grafting. Fig. 6.2 shows the EPR spectra of  $\text{PS-AgTPyP}^+$  recorded in solid state.

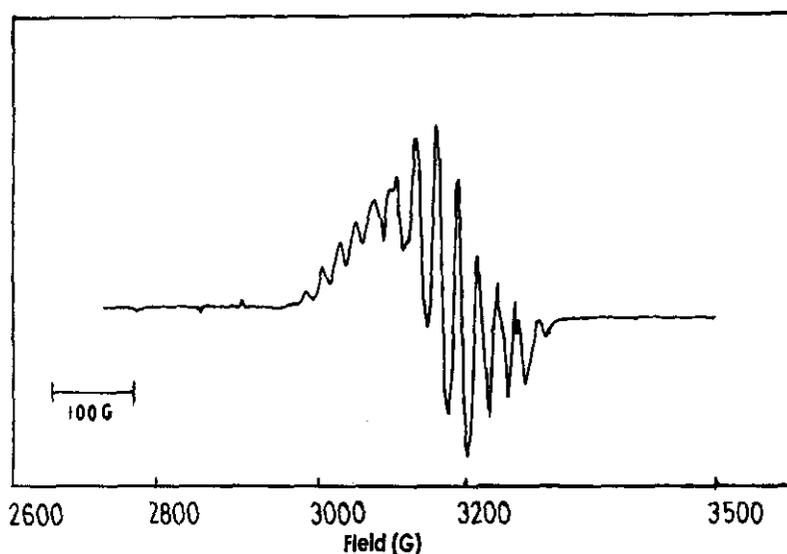


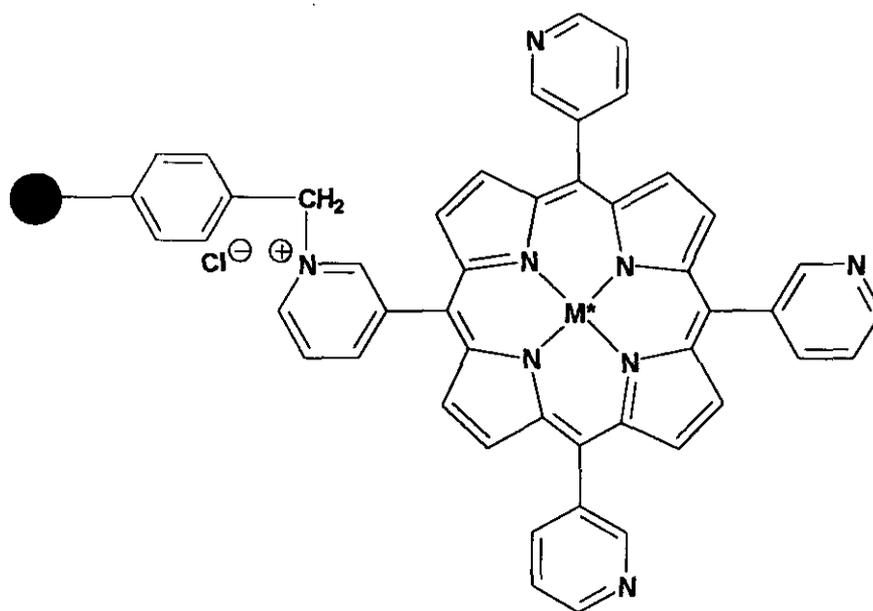
Fig.6.2 EPR spectra of  $\text{PS-AgT4PyP}^+$  (solid state, room temperature).

The coloured polystyrene beads obtained after interacting with  $\text{H}_2\text{TPyP/MnTPyP}$  was analysed further to verify whether the porphyrin is bonded to the support by a covalent chemical bond (through quaternisation). This was done by  $\text{AgNO}_3$  test<sup>20</sup> which indicated the presence of free  $\text{Cl}^-$  ions and hence a C-N (pyridyl) bond.

When the partially demetallated  $\text{PS-MnT4PyP}^+$  system was refluxed with aqueous solution of  $\text{Mn}(\text{CH}_3\text{COO})_2$  for 12h, the entire porphyrin units were found to be fully metallated again with Mn-ions resulting in Mn(III) porphyrins. This was evidenced by the absence of any free-base peaks in the solid state electronic spectra in the polymer sample. But a similar process to metallate the  $\text{PS-H}_2\text{T4PyP}$  with Co(II) or Fe(II) ion was not fully successful. Metallation with these ions were carried out in other reaction conditions also (in refluxing DMF,  $\text{CHCl}_3/\text{CH}_3\text{OH}$

and other solvent mixtures) but the result was not quite satisfactory, except that some indication of a metal-incorporated species could be seen from the electronic spectra.

As evident from **30** the appending of pyridylporphyrins  $H_2T4PyP/MT4PyP$  on to the polymer support is such that there is least possible steric disturbance possible on the porphyrin frame-work from the support because of the 'para connectivity' of the pyridyl moiety. But if the meso pyridyl groups are either 3 or 2-derivatised ( $T3PyP$  or  $T2PyP$ ), upon polymer grafting moderate to severe  $\pi$ -framework distortion is expected to occur. The quaternisation reaction between chloromethylated polystyrene (PS) with tetra 3-pyridyl porphyrins ( $H_2T3PyP/MT3PyP$ ) was, therefore, carried out. The conditions employed for this reaction is same as that carried out for 4-pyridyl analogues. Both  $H_2T3PyP$  and  $MnT3PyP$  could be anchored on polystyrene surface by quaternisation. But the amount of porphyrin uptake on polymer support in this case was found to be smaller than that observed for  $T4PyP$  species. This can be attributed to the unfavourable meta position of the pyridyl N site. The nature of the PS- $T3PyP^+$  systems generated is given in **31**.



**31**

The spectral (electronic) details of PS-  $H_2T3PyP^+$  and PS- $MnT3PyP^+$  are given in Table 6.2.

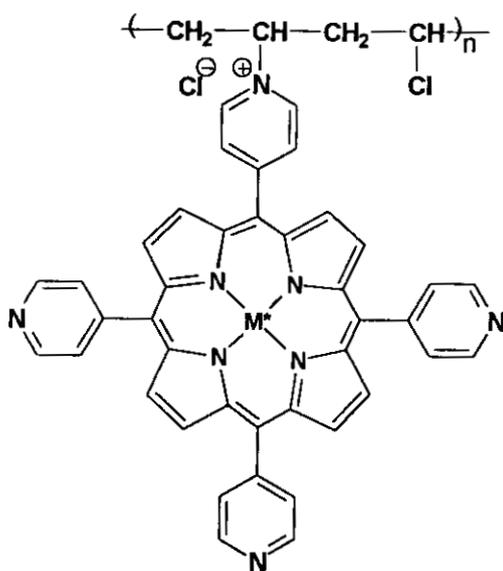
**Table 6.2** Spectral details of some T3PyP and PS-T3PyP<sup>+</sup> systems recorded in nujol.

<b>Porphyrin System</b>	<b>Spectral data (nm)</b>
H2T3PyP	423, 525, 562, 597, 655
PS-H <sub>2</sub> T3PyP <sup>1+</sup>	431, 519, 547, 591, 661
MnT3PyP	480, 534, 579, 615, 719
PS- MnT3PyP <sup>1+</sup>	481, - , 583, 619,

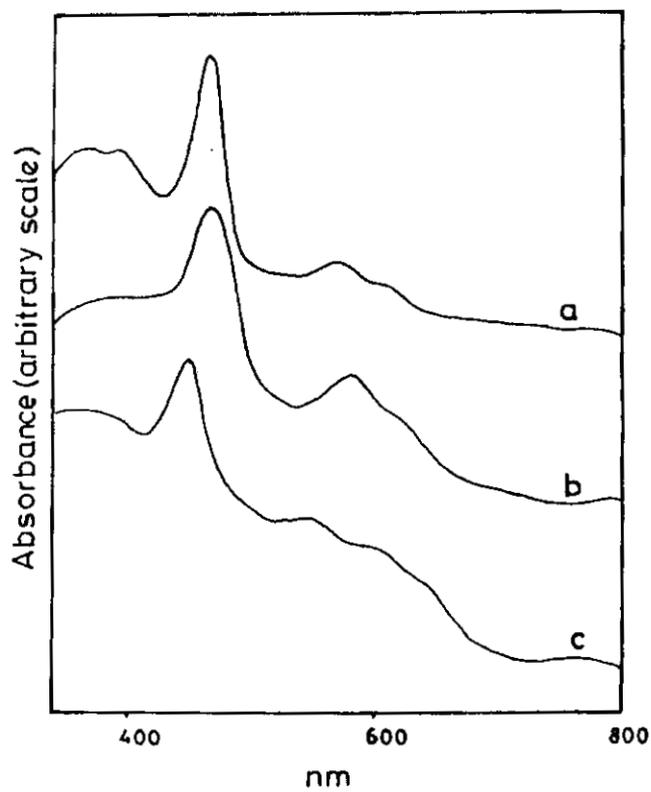
Shift in absorption values of these polymer supported 3-porphyrins from their unsupported species is seen to be not much deviated as compared to their 4-pyridyl analogues. This is rather surprising. We expect that to offset the effect of the enhanced  $\pi$ -framework distortion there would be some electronic effect (due to the 3-position of the pyridinium function) operating within the polymer supported porphyrin systems.

An interesting polymer support occurred to us is polyvinylchloride (PVC) and anchoring of porphyrins on this is possible because of the periodically spread –CH-Cl units in it. The method of grafting is similar to the one described earlier and the nature of the PVC-T4PyP<sup>+</sup> system is presented in 32.

We found that the attachment of pyridine N-atom to the C-Cl function of PVC surface through quaternisation was rather difficult under normal reaction conditions (DMF would dissolve the PVC granule and hence could not be employed as the medium for this quaternisation reaction). However, heating PVC granule and pyridyl porphyrin in CH<sub>3</sub>OH/H<sub>2</sub>O mixture for 4-5 days resulted in sufficient immobilisation of the porphyrin on the surface of PVC as evident from the distinct colour formation. The solid state electronic spectra of PVC-MnT4PyP<sup>+</sup> showed some distinct change as compared to that of the unsupported porphyrin and also PS-MnT4PyP<sup>+</sup> (Fig.6.3).



32



**Fig.6.3** Solid state electronic spectra of MnT4PyP, (b) PS-MnT4PyP<sup>+</sup> and (c) PVC-MnT4PyP<sup>+</sup> in nujol.

It is interesting to note that while the Soret band of PS-MnT4PyP<sup>+</sup> is red shifted as compared to the unsupported MnT4PyP, the PVC-MnT4PyP<sup>+</sup> Soret is blue shifted. Since both the supports (PS and PVC) are -CH-Cl functionalised and supporting of MnT4PyP is through quaternisation the strikingly different absorption characteristics in these two systems appear intriguing at first glance. However a closer look at these two systems provide a reasonable answer. In PS-MnT4PyP<sup>+</sup>, the quaternisation is possible only at one or two pyridyl centers. The red shift in these systems have been already explained in terms of distortion of  $\pi$ -framework and corresponding decrease in metal  $d\pi$ -eg( $\pi^*$ )overlap (lower HOMO-LUMO gap). In PVC- MnT4PyP<sup>+</sup> because of the better homogeneity there would be extensive quaternisation (of 3 or even 4 of the pyridine moieties) with more effective encapsulation by the flexible PVC network. While the encapsulating network would bring about distortion within the porphyrin framework (including tilt of the mesopyridyl moieties) there would be concerted electron depleting effect from the pyridinium cations on the porphyrin  $\pi$ -frame work. This would considerably lower the energies of the HOMO, resulting in greater HOMO-LUMO gap. This explains the blue shift observed in the PVC-bonded systems.

Hence the differences in band shifts imposed by different polymeric environments on porphyrins moiety conclusively confirmed that in addition to providing a heterogeneous character, the polymer background is also giving some tuning effects to porphyrin catalysts. So the polymer-porphyrin system will have a greater role in catalysis since, even slight variations in porphyrin electronic states would drastically change its overall specificity and selectivity as catalysts.

The quaternisation reaction between PVC and MnT4PyP was also carried out in DMF at 70-80<sup>0</sup>C. Since PVC is soluble in DMF, the anchored porphyrin would be well dispersed in PVC matrix. The PVC-MnT4PyP<sup>+</sup> system from the solution can be recovered by repeated precipitation using methanol. Dissolving the PVC-MnT4PyP<sup>+</sup> in THF and slow evaporation of the entire THF resulted in a translucent polymer film with distinct yellow colour, which was seen highly resistant towards stretching load (higher tensile strength). This could be attributed to the cross-linking possible in PVC-MnT4PyP<sup>+</sup> through quaternisation at

different ends of the porphyrin periphery. The film cast by interacting H<sub>2</sub>T4PyP and MnT4PyP with PVC in DMF medium gave good absorption spectra and their spectral maximum are tabulated in **Table 6.3**. along with that of polymer free porphyrin analogues obtained as a film in glass plate.

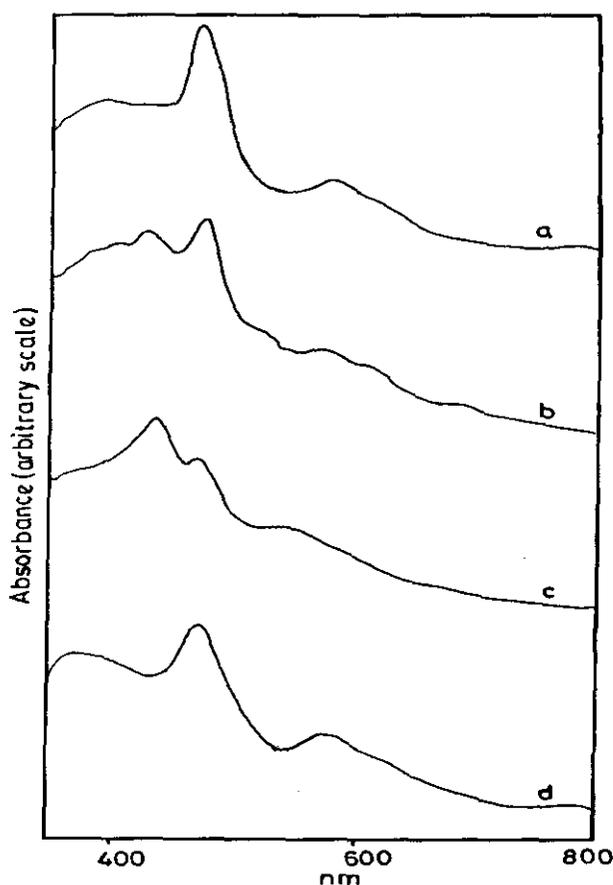
**Table 6.3** The spectral data of some TPyP and PVC-TPyP<sup>+</sup> systems recorded as a film on glass plate.

Polymer System	Spectral Values (nm)
H <sub>2</sub> T4PyP	428, 522, 554, 594, 657
PVC- H <sub>2</sub> T4PyP <sup>+</sup>	422, 519, 557, 594, 654
MnT4PyP	470, 570 621 770
PVC- MnT4PyP <sup>+</sup>	466 568 620 770

### 6.3.2 Incorporation of additional anionic porphyrins on PS-TPyP<sup>+</sup> systems (possible porphyrin “dimer” formation)

The quaternised attachment of pyridyl porphyrins (H<sub>2</sub>TPyP/MT4PyP) on chloromethylated polystyrene support (PS) provided at least one cationic centre per porphyrin moiety. The possible dimer formation was attempted based on the anticipation that these immobilised mono-cationic porphyrins would coulombically bind the anionic H<sub>2</sub>TPPS/MTPPS. Interaction of solid PS-TPyP<sup>+</sup> with a solution of the anionic porphyrins resulted in gradual uptake of H<sub>2</sub>TPPS/MTPPS as evident from the colour fading of the anionic porphyrin solution. The uptake of the second porphyrin from the solution was seen to be irreversible as evident from the unleachable nature of the system. Evidently the binding between the porphyrins must be electrostatic in nature. The immobilisation of TPPS by PS-TPyP<sup>+</sup> was further confirmed by recording the electronic spectra of the above system.

The spectra of PS-MnT4PyP<sup>1+</sup>:H<sub>2</sub>TPPS, PS-MnT4PyP<sup>1+</sup>:CoTPPS and PS-MnT4PyP<sup>1+</sup>:MnTPPS along with that of PS-MnT4PyP<sup>1+</sup> are reproduced in **Fig.6.4** While the parent PS-MnT4PyP<sup>1+</sup> gave peaks at 477, 581, 626 and 774nm, the PS-MnT4PyP<sup>1+</sup>: H<sub>2</sub>TPPS showed clearly the free base peaks at 421, 525 and 685nm in addition to the MnT4PyP<sup>1+</sup> absorptions. Some bands at Q band region are found broadened due to the overlap of MnT4PyP bands with H<sub>2</sub>TPPS absorptions. However, the Soret corresponding to MnT4PyP and H<sub>2</sub>TPPS are seen clearly well separated at 473 and 421nm respectively. Similarly the PS-MnT4PyP<sup>1+</sup>: CoTPPS gave characteristic peaks of both the porphyrins (437, 470, 540 and 578nm). The spectra obtained for PS-MnT4PyP<sup>1+</sup>: MnTPPS appeared to be that of either PS-MnT4PyP<sup>1+</sup> or MnTPPS as both the cationic 'Mn' and anionic 'Mn' have almost similar absorption maxima. No attempt was made to evaluate the extent of spectral band shifts in these systems, as it was difficult to identify the individual peak maxima.



**Fig.6.4** Solid state electronic spectra of (a) PS-MnT4PyP<sup>1+</sup>, (b) PS-MnT4PyP<sup>1+</sup>:H<sub>2</sub>TPPS, (c) PS-MnT4PyP<sup>1+</sup>:CoTPPS and (d) PS-MnT4PyP<sup>1+</sup>:MnTPPS

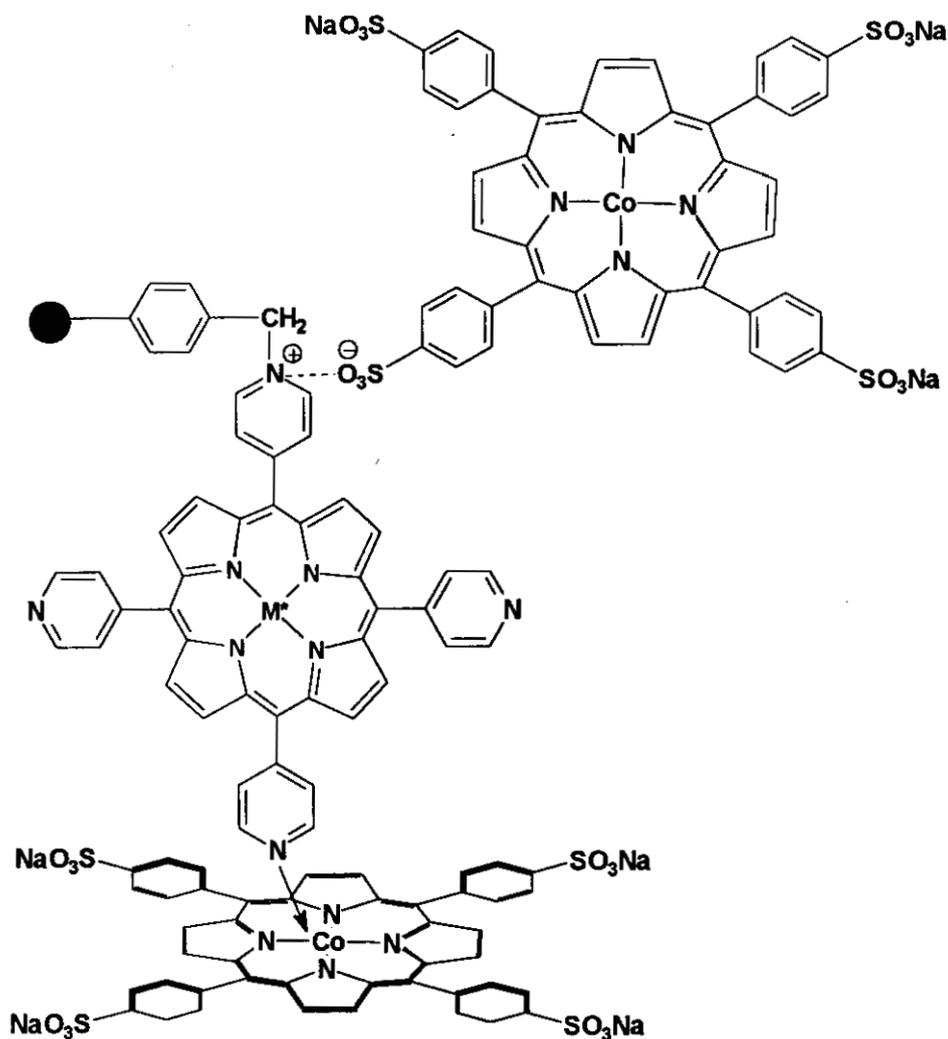
The possibility of formation of several such “dimers” (homo-and hetero-type) were tried and the spectral absorptions obtained for them (only identifiable) are presented in **Table 6.4**.

**Table 6.4** Spectral details of some PS-T4PyP<sup>+</sup>-TPPS systems recorded in nujol (\* indicates broad peaks).

<b>Porphyrin System</b>	<b>Absorption Peaks (nm)</b>
PS-H <sub>2</sub> T4PyP <sup>+</sup> : H <sub>2</sub> TPPS	425* 527, 591, 661
PS-H <sub>2</sub> T4PyP <sup>+</sup> : MnTPPS	470, 535, 574, 687
PS-H <sub>2</sub> T4PyP <sup>+</sup> : FeTPPS	428*, 572, 659
PS-H <sub>2</sub> T4PyP <sup>+</sup> : CoTPPS	430* , 525, 592, 664
PS-MnT4PyP <sup>+</sup> : H <sub>2</sub> TPPS	421, 473, 525, 573, 611, 685
PS-MnT4PyP <sup>+</sup> : MnTPPS	476, 581, 643
PS-MnT4PyP <sup>+</sup> : FeTPPS	426, 472, 581
PS-MnT4PyP <sup>+</sup> : CoTPPS	437, 470, 540, 578
PS-CuT4PyP <sup>+</sup> : H <sub>2</sub> TPPS	432*, 519, 560, 597, 639
PS-CuT4PyP <sup>+</sup> : MnTPPS	428, 472, 556, 613.
PS-CuT4PyP <sup>+</sup> : FeTPPS	425*, 560*
PS-CuT4PyP <sup>+</sup> : CoTPPS	437* 557*

The stoichiometry of the pyridyl and sulphonated phenyl-porphyrins in PS-T4PyP<sup>+</sup>-TPPS systems was also evaluated by estimating the amount of TPPS which get anchored on PS-TPyP<sup>+</sup> whose porphyrin content (MT4PyP/H<sub>2</sub>T4PyP) was already known. This was easily achieved by measuring the absorbance decrement of Soret band of TPPS solution before and after the immobilisation (on PS-TPyP<sup>+</sup>) process. For PS-H<sub>2</sub>T4PyP<sup>+</sup>: MnTPPS system the ratio of H<sub>2</sub>T4PyP: MnTPPS was seen to be nearly 1:1 but for PS-H<sub>2</sub>T4PyP<sup>+</sup>: CoTPPS system the amount of CoTPPS getting anchored was found to be nearly twice than that of H<sub>2</sub>T4PyP. The excess CoTPPS uptake seen in PS-H<sub>2</sub>T4PyP<sup>+</sup>: CoTPPS is quite reasonable because the free pyridine moieties on PS-H<sub>2</sub>T4PyP<sup>+</sup> could

coordinatively bind to the Co-atom of CoTPPS at the 5th and/or 6th coordination site (as in **33**) resulting in additional uptake to CoTPPS.

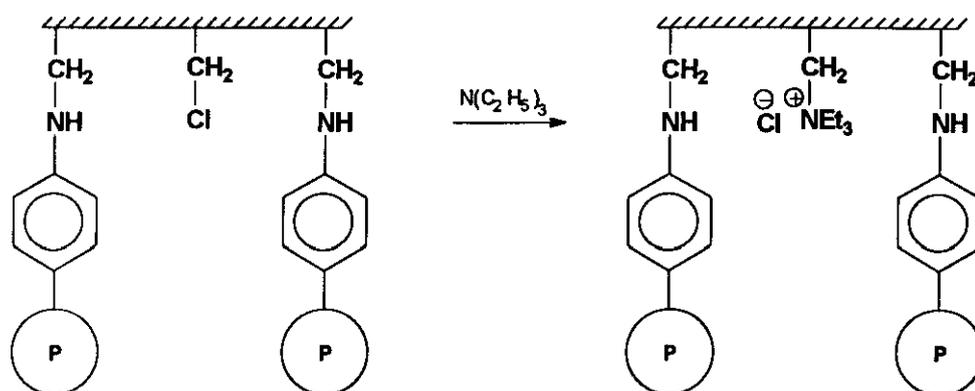


33

Similar situation is also expected for ZnTPPS and CdTPPS incorporated systems. In addition to these complications other such “dimeric” systems developed in the present study (Table 6.4) cannot guarantee a 1:1 stoichiometry because of the charge-imbalance between these bulky porphyrins.

### 6.3.3 Generation of polymer grafted tetracationic porphyrin systems

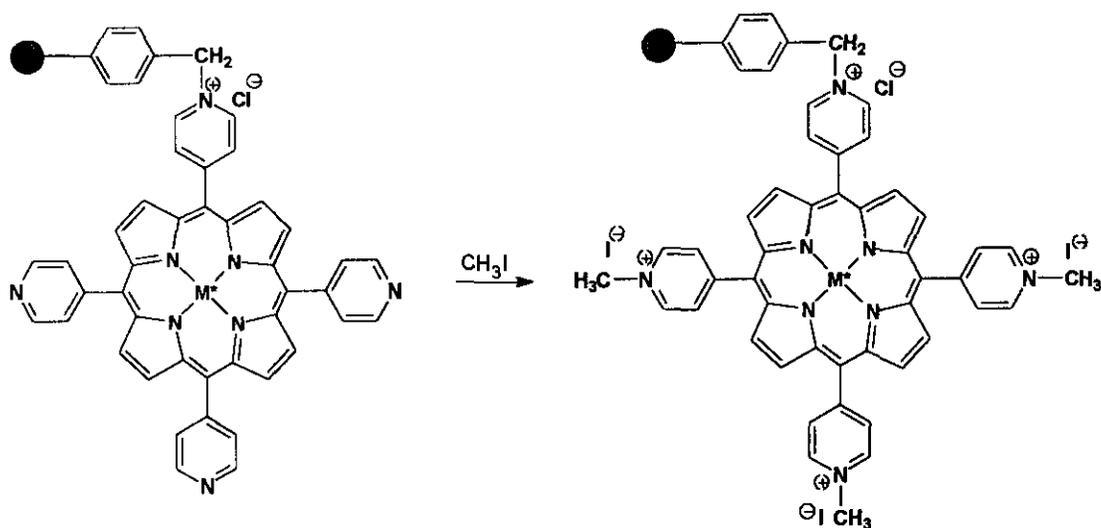
Since all life processes involving metalloporphyrins occur in aqueous medium, the biomimetic reaction using synthetic MPs should ideally be carried out in water. So an ideal model system would be polymer supported porphyrins which have enough ionic centers to make it appreciably water compatible. Although polystyrene or polyvinylchloride are hydrophobic in nature, the introduction of charged centers on polymeric surface would make them somewhat hydrophilic. A large number of ionic centers are highly suitable for such systems in this context. Achieving this on polystyrene-based support would provide desirable hydrophobic-hydrophilic environment necessary for biomimetic studies. As indicated earlier the quaternised appending of MTPyP on polystyrene result only in one or two cationic sites on polymer per porphyrin. Also the uptake of porphyrins on polymer surface is limited due to the bulky nature of the porphyrin macrocycle. One of the techniques to introduce more ionic centers on the polymer support (as in **34**) is interaction of polymer-supported systems with appropriate reagents as typified in **Scheme 11**.



Scheme 11

34

In the case of our PS-TpyP<sup>+</sup> systems there are often three (or some times two) free pyridine sites per unit of the appended porphyrin moiety. Since, pyridine can easily undergo quaternisation reaction with alkyl halides (especially CH<sub>3</sub>-I), the treatment of PS-TpyP<sup>+</sup> systems with CH<sub>3</sub>I would alkylate the free pyridine sites of PS-TpyP as in **Scheme 12** and species generated is illustrated in **35**.



Scheme 12

35

Thus by using this strategy it is possible to generate 4 cationic sites per porphyrin unit on polymer surface. The exhaustive alkylation of the free pyridine site was very easily performed by refluxing PS-TpyP<sup>+</sup> beads in CH<sub>3</sub>I just similar to the procedure employed for monomeric pyridylporphyrins (H<sub>2</sub>T4PyP/MT4PyP). For free monomeric pyridylporphyrins a stoichiometric amount of CH<sub>3</sub>I is only needed for the exhaustive methylation (6h reaction time). But for PS-TpyP<sup>+</sup> systems a large excess of CH<sub>3</sub>I was used and the reaction was continued to 12h in order to overcome any matrix(polymer) effects possible. The quaternisation of free pyridine sites on PS-TpyP<sup>+</sup> was confirmed by AgNO<sub>3</sub> test, which showed the presence of free I<sup>-</sup> in the polymer surface. We observed that the electronic modifications of the polymer system brought about by the exhaustive quaternisation (PS-H<sub>2</sub>TMPyP<sup>4+</sup>/ PS-MTMPyP<sup>4+</sup>) is significant as evident from the spectral absorptions. The absorption peaks of some PS-TMPyP<sup>4+</sup> systems

developed are given in **Table 6.5**. The spectral details of corresponding PS-TPyP<sup>1+</sup> systems are also given for comparison.

**Table 6.5** Spectral details of some PS-TMPyP<sup>4+</sup> and PS-PyP<sup>1+</sup> systems developed in the present study \*.sign indicated for broad peaks.

Porphyrin System	Spectral Maxima (nm)
PS-H <sub>2</sub> T4PyP <sup>1+</sup>	432 523 564 634
PS-H <sub>2</sub> TM4PyP <sup>4+</sup>	434* 536 578 654
PS-H <sub>2</sub> T3PyP <sup>1+</sup>	431 519 547 591 661
PS-H <sub>2</sub> TM4PyP <sup>4+</sup>	435* 520 544 591 662
PS-MnT4PyP <sup>1+</sup>	477 581 626 691 770
PS-MnTM4PyP <sup>4+</sup>	477 584 - 671 770
PS-CuT4PyP <sup>1+</sup>	437 548 -
PS-CuTM4PyP <sup>4+</sup>	440 556 600
PS-AgT4PyP <sup>1+</sup>	439* 526 564 598 651
PS-AgTM4PyP <sup>4+</sup>	445* 528 567 598 653

The EPR spectra of Cu<sup>2+</sup> and Ag<sup>2+</sup> derivatives of the present systems (PS-MTM4PyP<sup>4+</sup>) are measured in solid state. As shown in **Fig.6.5** the spectra of PS-CuTM4PyP<sup>4+</sup> appears almost identical to that of the monocationic PS-MT4PyP<sup>1+</sup> systems. The EPR parameters of these Cu systems were also evaluated based on the axial symmetry (**Table 6.7 Section 6.3.4**). The value of  $\alpha^2$  is found to be greater in the case of tetracationic PS-CuTM4PyP<sup>4+</sup> than that of monocationic PS-CuT4PyP<sup>1+</sup> system (0.80 and 0.78 respectively). This difference could be accounted as follows. When the free pyridine sites in the PS-CuT4PyP<sup>1+</sup> is exhaustively methylated, more distortion in the porphyrin  $\pi$  frame-work is possible due to the addition of bulky-CH<sub>3</sub> moieties on the porphyrin periphery. This structural distortion in turn would reduce the porphyrin-metal interaction (both  $\pi$  and  $\sigma$  type). As a result the delocalisation of the unpaired electron from Cu to the porphyrin-N is expected to decrease. This restricted delocalisation of

the unpaired electron density as discussed in Chapter 3 would correspondingly increase the value of  $\alpha^2$  (decrease in  $\sigma$  covalency). This is also evident from the slight increase in the value of  $A_{II}$  in PS-CuTM4PyP<sup>4+</sup> system.

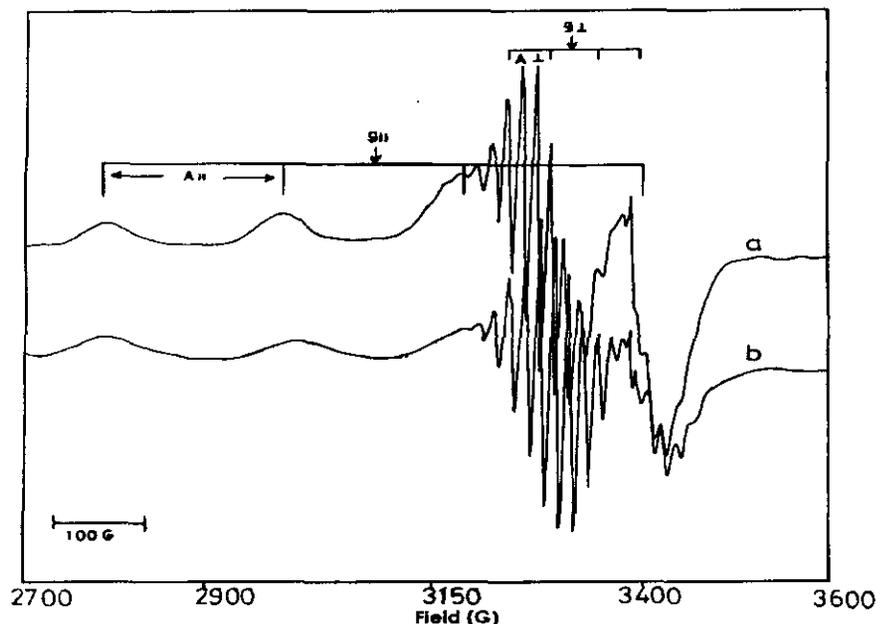


Fig. 6.5 EPR spectra of (a) PS-CuT4PyP<sup>1+</sup> and (b) PS-CuTMPyP<sup>4+</sup> (solid state, room temperature).

There were attempts to immobilise various cationic MTMPyPs on cation exchange resins (Chapter 2.) In such cases the porphyrins are held firmly to the polymer surface by electrostatic interaction which can be expected to result in non-flexible static arrangement. In catalytic applications this arrangement would allow the substrate molecule to approach the metal active site of the porphyrin only through one side because the supporting polymeric network would block the other side almost completely. This situation might inhibit the catalytic activity in cases when both 5th and 6th coordination sites of the metal ion is needed for catalytic process. An example is the proximal effects exhibited by Mn-porphyrins in enzyme model studies<sup>21</sup>. In this case a N-coordinating pyridine or imidazole derivative coordinated to the 5th position of Mn ion enhances the O-transfer oxygenation reactions and hence non-availability of one coordinating site of Mn ion, as in the above case, would retard the catalytic efficiency. But in our PS-MTMPyP<sup>4+</sup> system this problem gets circumvent since, the porphyrins are

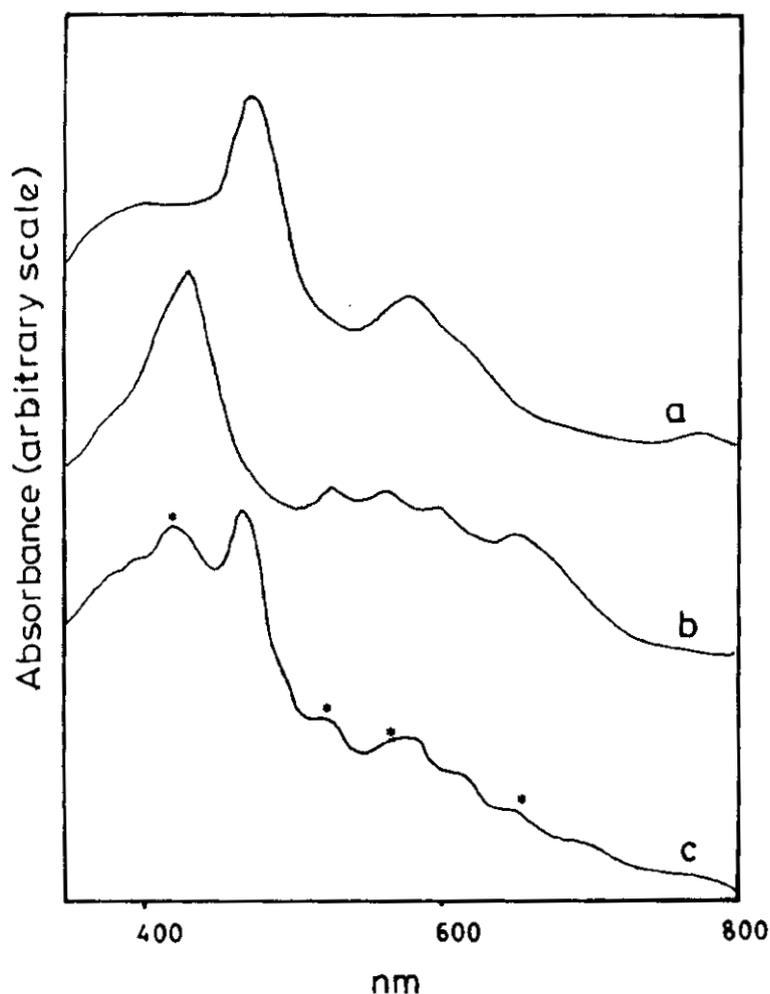
attached to the polymer support only through one covalent bond via peripheral pyridine moiety and thereby allowing it to hang freely from the polymer surface. This arrangement would make the central metal available for 5th and 6th coordination. The presence of the covalent bond between the porphyrin and polymer would make this system extremely stable towards drastic reaction conditions and resistant towards leaching.

#### **6.3.4 Ionically held binary metalloporphyrins grafted on polystyrene surface**

As discussed above the exhaustive methylation technique provides 4 equispaced cationic centres in the porphyrin moiety of PS-TPyP<sup>1+</sup> yielding PS-TMPyP<sup>4+</sup>. The tetrakis-para-sulphonated teraphenylporphyrins (H<sub>2</sub>TPPS/MTPPS) developed in this study have 4 equispaced anionic sites at their periphery. Hence it is possible for these anionic porphyrins to combine strongly with the cationic PS-TMPyP<sup>4+</sup> systems through coulombic interaction. Since MTMPyP and MTPPS have almost identical size and ionic site compatibility each anionic site on MTPPS is expected to bond with the corresponding cationic site on PS-MTMPyP<sup>4+</sup> in expectedly face to-face manner.

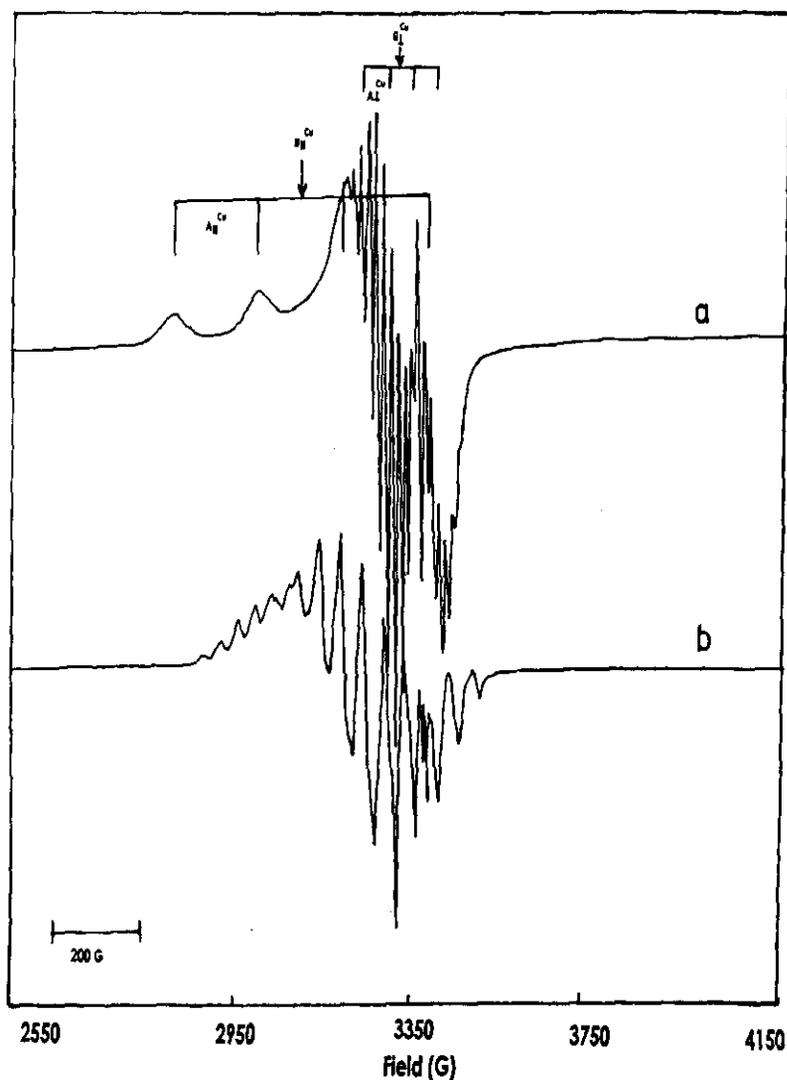
Attempts made to develop such binary systems were found to be highly successful in our hands. The PS-MnTM4PyP<sup>4+</sup> beads were added to the aqueous solution of H<sub>2</sub>TPPS and heated for 2-3 h. The solid polymer was then recovered and washed several times with water, methanol and acetone to remove any physically adsorbed or free state H<sub>2</sub>TPPS. The original greenish colour of the beads were found to change into light brown indicating the incorporation of H<sub>2</sub>TPPS on the original PS-MnTMPyP<sup>4+</sup> beads.

The solid state electronic spectra of the resulting beads were taken, which contained additional peaks. Careful analysis showed characteristic peaks of H<sub>2</sub>TPPS along with the peaks due to the original MnTM4PyP. The spectra is reproduced in Fig. 6.6 along with that of PS-MnTM4PyP<sup>4+</sup> and H<sub>2</sub>TPPS (in solid state).



**Fig 6.7** Solid state electronic spectra of (a) PS-MnTM4PyP<sup>4+</sup>, (b) H<sub>2</sub>TPPS and (c) PS-MnTM4PyP<sup>4+</sup>: H<sub>2</sub>TPPS<sup>4+</sup>. The peaks corresponding to H<sub>2</sub>TPPS taken up by the polymer system are marked with asterisk.

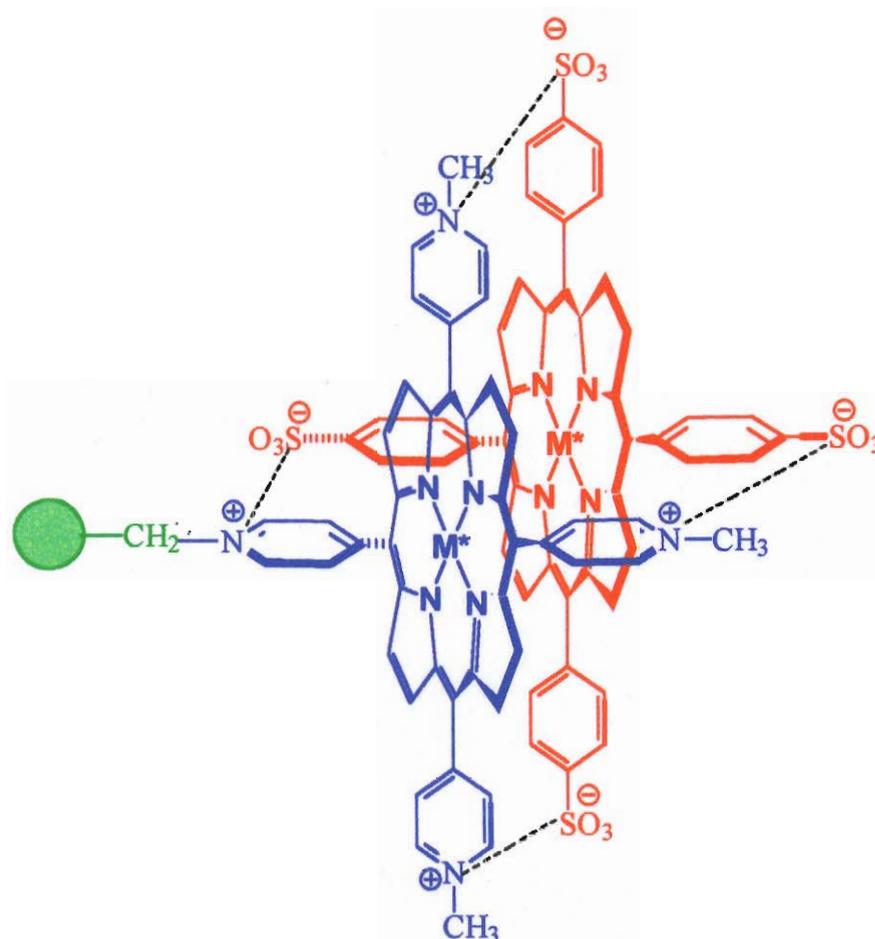
Similarly the EPR spectra of PS-H<sub>2</sub>TM4PyP<sup>4+</sup> beads after reacting with aqueous solution of either CuTPPS or AgTPPS for 4h gave well resolved spectral pattern corresponding to Cu/Ag porphyrins (**Fig 6.7**). The appearance of EPR lines for this initially EPR inactive PS-H<sub>2</sub>TM4PyP<sup>4+</sup> system clearly indicated the uptake of CuTPPS/AgTPPS species by the polymer beads.



**Fig 6.7.** EPR spectra of (a) PS-H<sub>2</sub>TM<sub>4</sub>PyP<sup>4+</sup>:CuTPPS<sup>4+</sup> and (b) PS-H<sub>2</sub>TM<sub>4</sub>PyP<sup>4+</sup>:AgTPPS<sup>4+</sup> (solid state, room temperature).

The amount of H<sub>2</sub>TPPS taken up by the PS-MnTMPyP<sup>4+</sup> was also estimated to determine the stoichiometry of the combination. This was done by interacting a known amount of PS-MnTM<sub>4</sub>PyP<sup>4+</sup> with H<sub>2</sub>TPPS solution of known concentration. The number of moles of H<sub>2</sub>TPPS incorporated into PS-MnTM<sub>4</sub>PyP<sup>4+</sup> (whose porphyrin content is known) was easily estimated spectrophotometrically by noting the absorbance decrement of Soret band of H<sub>2</sub>TPPS before and after the polymer appending. The stoichiometry of the combined species was evaluated and it was seen to be exactly 1:1 between MnTM<sub>4</sub>PyP and H<sub>2</sub>TPPS. The 1:1 agreement was seen to be better in this case

when compared to PS-MTPyP<sup>1+</sup>; MTPPS systems discussed earlier (Section 6.3.2). Repeated experiments with varying amount of samples in different solvents also showed strong preference for this 1:1 stoichiometry between the cationic and anionic porphyrins. This is expected when we consider the location of the 4-cationic centres in the grafted MnTM4PyP<sup>4+</sup> and the corresponding anionic centres in H<sub>2</sub>TPPS. The maximum coulombic interaction between these two species would favour a face-to-face disposition. A possible arrangement of such a binary system is shown in Fig 6.8.



**Fig 6.8** Schematic representation of the possible arrangement of porphyrins in PS-MnTM4PyP<sup>4+</sup>: MTPPS<sup>4-</sup>. (M\* may be metal or free-base).

Instead of this “[Mn]<sup>4+</sup>: [H<sub>2</sub>]<sup>4-</sup>” combination the reverse “[H<sub>2</sub>]<sup>4+</sup>: [Mn]<sup>4-</sup>” combination was also developed by interacting PS-H<sub>2</sub>TM4PyP<sup>4+</sup> with a solution of MnTPPS. The exact 1:1 stoichiometry of the combining species was seen to be maintained in this case also. In addition to MnTPPS other anionic porphyrins

like FeTPPS, CoTPPS, CuTPPS and AgTPPS were also found to get incorporated into PS-H<sub>2</sub>TM<sub>4</sub>PyP<sup>4+</sup> system maintaining a 1:1 stoichiometry. Table 6.6 present the electronic characteristics of PS-H<sub>2</sub>TM<sub>4</sub>PyP<sup>4+</sup>-MTPPS<sup>4-</sup> systems developed in the present study.

**Table 6.6** Spectral data of some PS-H<sub>2</sub>TM<sub>4</sub>PyP<sup>4+</sup>: MTPPS<sup>4-</sup> systems.

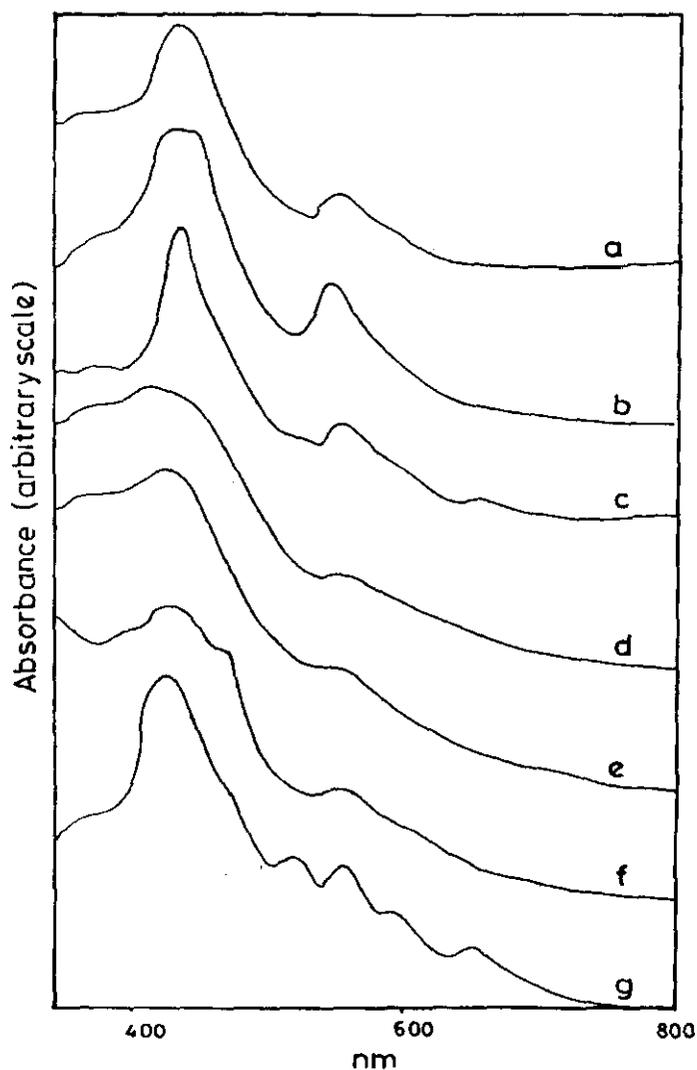
Systems	Absorption-maxima(nm)	Colour of the beads	Amount of MTPPS/g resin (mole)
PS-H <sub>2</sub> TM <sub>4</sub> PyP <sup>4+</sup> :MnTPPS <sup>4-</sup>	426,474,540,571,610	green	0.43x10 <sup>-4</sup>
PS-H <sub>2</sub> TM <sub>4</sub> PyP <sup>4+</sup> :FeTPPS <sup>4-</sup>	429,572,651	greenish yellow	0.44x10 <sup>-4</sup>
PS-H <sub>2</sub> TM <sub>4</sub> PyP <sup>4+</sup> :CoTPPS <sup>4-</sup>	431,550,572	greenish brown	0.45x10 <sup>-4</sup>
PS-H <sub>2</sub> TM <sub>4</sub> PyP <sup>4+</sup> :CuTPPS <sup>4-</sup>	426, 519, 556, 580	yellow brown	0.45x10 <sup>-4</sup>
PS-H <sub>2</sub> TM <sub>4</sub> PyP <sup>4+</sup> :AgTPPS <sup>4-</sup>	431, 544, 579	light brown	0.44x10 <sup>-4</sup>

(The uptake of original H<sub>2</sub>TM<sub>4</sub>PyP per g of PS is 0.44x10<sup>-4</sup> mole).

Some of the absorption peaks could not be identified because of the poor resolution. Except for MnTPPS, the Soret peak of various MTPPS was found to get overlapped with that of grafted H<sub>2</sub>TM<sub>4</sub>PyP resulting in broad peak.

With a view to develop various 'bimetallic' (both homo and hetero type) porphyrin systems, some PS-MTMPyP<sup>4+</sup> (where M = Mn(III),Cu(II)and Ag(II)) were developed and made to interact with anionic MTPPS (M = Mn(III), Fe(III), Co(III), Zn(II), Cu(II) and Ag(II)). All the PS-MnTM<sub>4</sub>PyP<sup>4+</sup> systems were found to incorporate MTPPS moiety adhering to 1:1 stoichiometry. The resulting beads exhibited a wide range of colours due to the co-existence of differently coloured

porphyrins. The electronic absorption spectra of some of these PS-CuTM4PyP<sup>4+</sup>:MTPPS<sup>4+</sup> systems are given in Fig 6.9.



**Fig. 6.9** Solid state electronic spectra of various PS-CuTM4PyP<sup>4+</sup>:MTPPS<sup>4+</sup> systems, where M=Cu(b), Ag(c), Fe(d), Co(e), Mn(f) and H<sub>2</sub>(g) and also PS-CuTM4PyP<sup>4+</sup>(a).

The solid state electronic spectra of these dimeric systems are seen complicated by the overlap of the spectral absorptions of the constituent porphyrins. Except for Mn-systems, the MPs employed in this work have spectral bands at almost same positions (in the range 415-445 for Soret band 520-560 for Q bands). Hence the already broadened solid state spectra of the polymer grafted metalloporphyrins were further broadened by the overlap of two such absorptions in this 'dimer' systems. Therefore it is not possible to specify the exact position of the spectral maxima exhibited by individual porphyrins and this made it

difficult to estimate any possible electronic modulations brought about on each porphyrin moiety upon the expected 'dimer' formation.

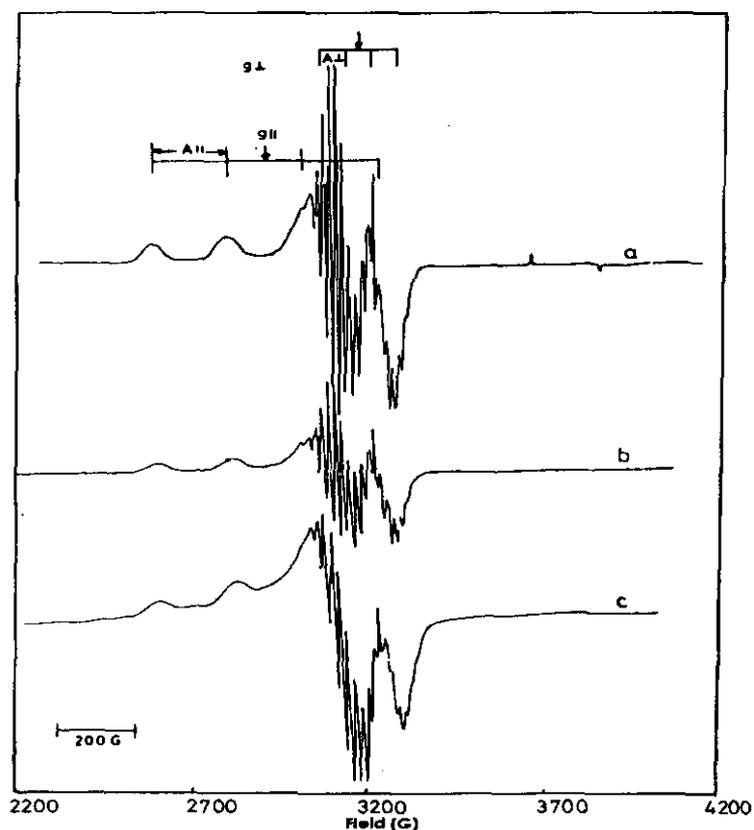
The EPR spectra of Cu- and Ag-bearing porphyrin systems were recorded in solid state. The binary porphyrin-system used for EPR studies include PS-H<sub>2</sub>TM4PyP<sup>4+</sup>:CuTPPS<sup>4-</sup>, PS-CuTM4PyP<sup>4+</sup>:H<sub>2</sub>TPPS<sup>4-</sup>, PS-CuTM4PyP<sup>4+</sup>:CuTPPS<sup>4-</sup>, PS-CuTM4PyP<sup>4+</sup>:AgTPPS<sup>4-</sup>, PS-AgTM4PyP<sup>4+</sup>:CuTPPS<sup>4-</sup>, PS-AgTM4PyP<sup>4+</sup>:AgTPPS<sup>4-</sup>, PS-AgTM4PyP<sup>4+</sup>:H<sub>2</sub>TPPS<sup>4-</sup> and PS-H<sub>2</sub>TM4PyP<sup>4+</sup>:AgTPPS<sup>4-</sup>. All the spectra especially those of Cu are well resolved both in parallel and perpendicular regions (**Fig. 6.10, 6.11 and 6.12**). MTM4PyP and MTPPS (M = Cu and Ag) systems exhibited almost identical EPR spectra and hence in the case of homo dimers no broadening was observed due to the overlap of both type of metalloporphyrin lines. But in the case of Cu : Ag and Ag : Cu hetero dimers, overlap of some Cu and Ag lines were found to occur. The following observations could be made from the nature of EPR spectra of the 'porphyrin dimers' studied in the present work:

- (a) In the case of CuTM4PyP and CuTPPS and also for AgTM4PyP and AgTPPS the EPR splitting pattern appears similar.
- (b) The EPR parameters of both type of porphyrins (either cationic or anionic) are not altered much upon the 'dimer' formation. But in the case of CuTM4PyP, the covalency parameter,  $\alpha^2$ , is seen decreased slightly when it is bonded to anionic porphyrins, either free base or metalloderivatives (**Table 6.7**). The calculated value of  $\alpha^2$  of the anionic CuTPPS is also found to decrease in its 'dimeric' system.
- (c) For PS-CuTM4PyP<sup>4+</sup> : CuTPPS<sup>4-</sup> systems slight broadening and baseline drift are observed indicating the possibility of interaction between two Cu centers (compared to that of PS-CuTM4PyP<sup>4+</sup> : H<sub>2</sub>TPPS<sup>4-</sup> system (**Fig 6.10**).
- (d) In the case of PS-Ag<sup>4+</sup> : Ag<sup>4+</sup> system Ag-Ag interaction appears to be nearly absent(**Fig. 6.11**).

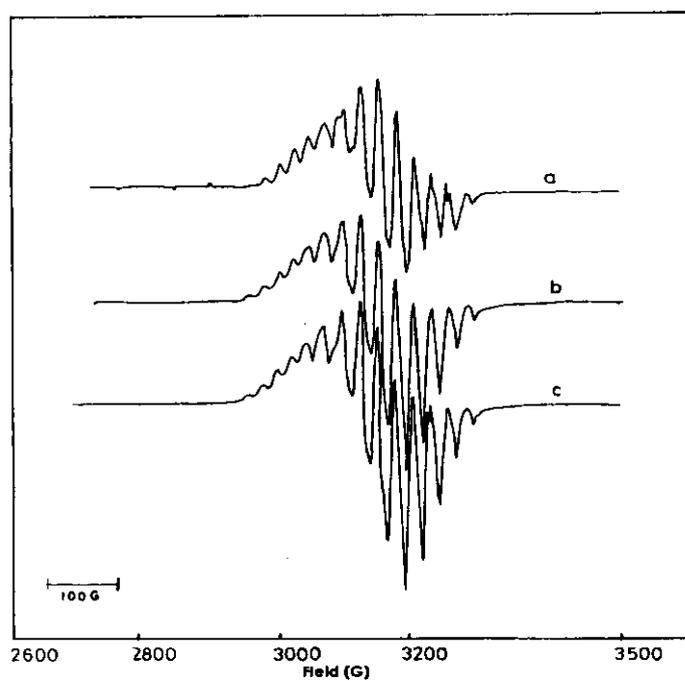
**Table 6.7** The EPR parameters for Cu bearing dimeric porphyrins (in solid state, RT).

Dimer System	$A_{\parallel}$ (G)	$A_{\perp}$ (G)	$g_{\parallel}$	$g_{\perp}$	$\alpha^2$
PS-Cu <sup>+</sup>	196.5	56.4	2.1946	2.029	0.7897
PS-Cu <sup>4+</sup>	204.7	53.6	2.187	2.0325	0.8063
PS-Cu <sup>4+</sup> *	203.2	54.0	2.179	2.018	0.7889
PS-H <sub>2</sub> <sup>4+</sup> -Cu <sup>4+</sup>	192.8	57.0	2.176	2.026	0.7593
PS-Cu <sup>4+</sup> H <sub>2</sub> <sup>4+</sup>	196.5	58.2	2.1833	2.241	0.7763
PS-Cu <sup>4+</sup> -Cu <sup>4+</sup>	204.7	60.0	2.1837	2.023	0.7989
PS-Cu <sup>4+</sup> -Ag <sup>4+</sup>	192.5	52.2	2.1974	2.025	0.7799
PS-Ag <sup>4+</sup> -Cu <sup>4+</sup>	195.25	47.6	2.195	2.033	0.7881

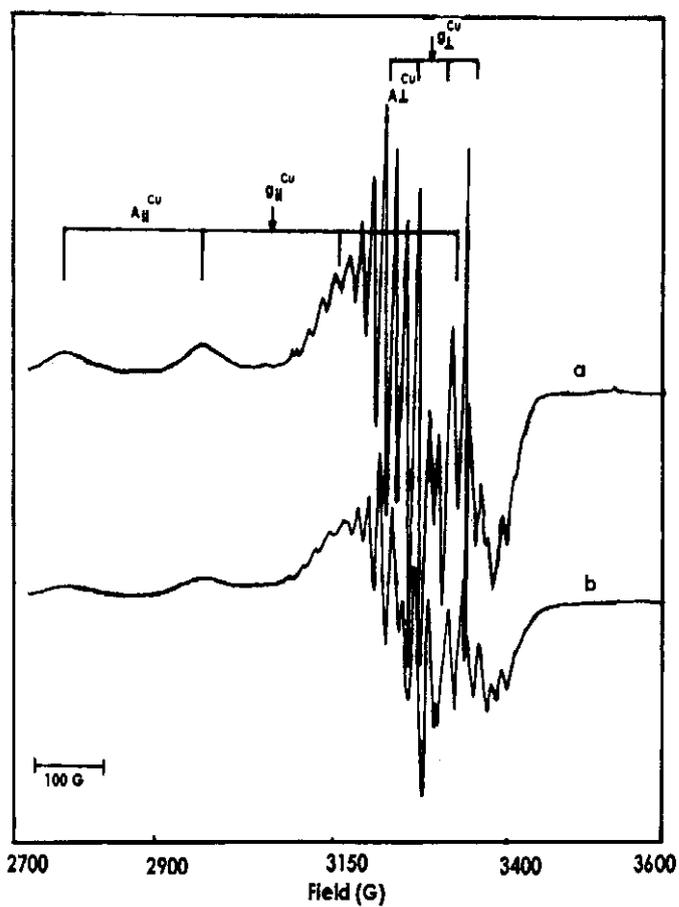
\* PS-Cu<sup>4+</sup> denotes PS-CuTPPS, discussed in Chapter 3.



**Fig 6.10.** EPR spectra of (a)PS-CuTM4PyP<sup>4+</sup>, (b)PS-CuTM4PyP<sup>4+</sup>:H<sub>2</sub>TPPS<sup>4+</sup> and (c) PS-CuTM4PyP<sup>4+</sup>:CuTPPS<sup>4+</sup> (solid state, LNT).



**Fig. 6.11.** EPR spectra of (a) PS-AgTM4PyP<sup>4+</sup>, (b) PS-AgTM4PyP<sup>4+</sup>:H<sub>2</sub>TPPS<sup>4-</sup> and (c) PS-AgTM4PyP<sup>4+</sup>:AgTPPS<sup>4-</sup> (solid state, LNT)



**Fig. 6.12.** EPR spectra of (a) PS-CuTM4PyP<sup>4+</sup>:AgTPPS<sup>4-</sup> and (b) PS-AgTM4PyP<sup>4+</sup>:CuTPPS<sup>4-</sup> (solid state, RT).

- (e) For PS-Cu<sup>4+</sup>:Ag<sup>4-</sup> and PS-Ag<sup>4+</sup>:Cu<sup>4-</sup> hetero systems porphyrin interactions appear to be slightly different as evident from the values of EPR parameters given in **Table 6.7**.

The results of the EPR spectral analysis indicate that there is possibility of some weak interaction between the cationic and anionic porphyrins in our 'dimeric' system. However this effect is seen to be not as much as expected to influence the basic features of the individual porphyrin systems. Hence it can be assumed that the porphyrins are capable of maintaining their individual identity to a great extent upon these 'dimer' formation. In the case of PS-Cu<sup>4+</sup>-Cu<sup>4-</sup> system, though some Cu-Cu interaction is suspected, the two Cu centers are not very close to each other. A rough simulation study of its EPR spectra indicated that the Cu-Cu distance in the system is around 10Å<sup>0</sup>. Hence in these binary systems both the porphyrins need not be oriented exactly in face-to-face manner, but slipped considerably to each other. This appears reasonable when we consider the possible steric constraints from the polymeric network and the bulky substituents in the meso positions of the porphyrin macrocycle.

Though the present binary systems is quite different from the several diporphyrin systems reported, the compounds developed in this study appears to be unique because of their 1:1 (cationic/anionic) stoichiometry. The system has cationic and anionic porphyrins periodically spaced but without any significant metal-to-metal influence. This along with the proximal placing of anionic and cationic porphyrins on polymer surface is expected to make the various binary systems developed in our study promising candidates for probing special biological functions. Investigations in this line are envisaged.

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