Chapter 4

Linear and Dendritic Macromolecules Modified with Porphyrin and Metalloporphyrin: Synthesis and Characterisation

4.1 Introduction

The word porphyrin is derived from the Greek word porphura meaning purple, and all porphyrins are intensely coloured. The porphyrins lie at the focal point formed from divergent fields of research, including solar energy conversion, catalysis, spectroscopy, and the development of organic materials\(^1\). A constant theme among the diverse areas is the creation of structured assemblies containing porphyrins located in well-defined chemical environments. The precise sculpturing of the porphyrin environment requires the synthesis of porphyrin derivatives carrying functional groups attached at the periphery of the macrocycle. The meso tetraphenylporphyrins offer attractive features of this context and have been used in a wide variety of model studies. The structure of tetra phenyl porphyrin is fairly rigid and has extensive electron delocalisation in the molecule. The
presence of highly delocalised $\pi$ electron system in a molecule such as porphyrin makes them unique for a variety of applications\(^2\). Indeed, one of the ways to enhance the use of porphyrins in optoelectronic devices is to further expand the existing $\pi$ electron system\(^3\). The porphyrins lie in the focus of several different fields of research like the photosynthetic reaction center and many artificial assemblies incorporate porphyrin derivatives as light receptors in energy conversion and in the design of molecular scale electronic devices\(^4,5\). The synthesis of well-defined asymmetric porphyrin derivatives is of great interest for the development of new molecular structures\(^6\). The chemical transformation of natural and synthetic porphyrin macrocycle and their peripheral substituents have been an important area of research\(^7\). Nature produces a wide variety of biologically important molecules. Thus, many of the synthetically modified porphyrin compounds have been used as models for natural porphyrin systems\(^8\). In the present work we have prepared porphyrin bound with various linear and hyperbranched polymeric systems where the polymeric units are covalently fused as meso aryl substituent. When porphyrin is coupled with polymer, both the absorption and emission spectra were significantly changed\(^9\). Herein we describe the synthesis and photo physical characterization of porphyrin - polymer system and the changes in spectral characteristics observed in different polar environments. The met-alloporphyrin ring is found in a variety of important biological system where it is the active component of the system or in some ways intimately connected with the activity of the system\(^10\). Many of these porphyrins synthesized are the basic structure of biological porphyrins, which are the active sites of numerous proteins, whose functions range from oxygen transfer and storage (hemoglobin and myoglobin) to electron transfer (cytochrome C, cytochrome oxidase) to energy conversion (chlorophyll). They also have been proven to be efficient sensitizers and catalyst in a number of chemical and photochemical processes, especially in photodynamic therapy (PDT)\(^10\). The diversity of their functions is due in part to the variety of metals that bind in the pocket of the porphyrin ring system.

Hyperbranched polymers represent an interesting class of branched soluble macromolecules, which has witnessed growing attention during the past decade. Synthesis of three-dimensional dendritic polymers by constructing branches upon branches, either in the stepwise fashion to get polymers or in one step process to get hyperbranched poly-
mers has received much attention\textsuperscript{11}. These highly branched non-entangled and globular structures have been explored because of their unusual properties. Although dendrimers have been studied extensively for their size, shape and surface functional group related properties, their large scale synthesis has been limited to only a few structures because of the inherent difficulties in the step wise growth process. However, the one step process for the synthesis of hyperbranched polymers has potential for large-scale preparation, as it lacks in well defined and monodisperse structure of dendrimers\textsuperscript{12}.

The various polymeric systems employed for the study are polymers like PVA, PEG, and linear polyglycerol adipate and hyperbranched polyglycerol systems. All the above polymers have a feature of free hydroxyl groups for coupling with the chlorosulphonated porphyrin systems. The metals employed to incorporate in the porphyrin system are Zn, Cu and Fe. To make the porphyrin system suitable for coupling, we made chlorosulphonated porphyrin systems. The polymer systems could strongly interact with the TPP as well as MTPPs as sulphonyl esters. The linear systems differ from the hyperbranched system in their electronic spectra. The hydrophobic porphyrin system achieves some hydrophilicity on binding with these linear as well as hyperbranched polymeric systems. The spectroscopic properties of porphyrin complexes have attracted considerable experimental and theoretical interest because of their vital role in biological processes such as photosynthesis and respiration and their potential technological applications.

\section{4.2 The Porphyrin System}

\subsection{4.2.1 Synthesis of tetraphenyl porphyrin}

The macrocyclic porphyrin was synthesized by the reaction between pyrrole and benzaldehyde in presence of propionic acid under reflux conditions\textsuperscript{13}. The reaction involved in the synthesis of TPP is given in scheme 4.1. The synthesized TPP was purple colored crystalline solid and was freely soluble in common organic solvents but insoluble in water and other polar solvents. The product was purified by column chromatography by basic alumina as the adsorbent and chloroform as the eluent.
4.2.2 Characterisation of tetraphenyl porphyrin

The tetraphenyl porphyrin was characterized by UV-visible, FTIR and $^1$H NMR spectroscopic studies.

(i) UV-visible spectral analysis

UV-visible spectrum was recorded on a Shimadzu UV/vis spectrophotometer, operating in the region 190-1100 nm. The UV-visible absorption spectrum of porphyrin macrocycle exhibits an intense signal at 416nm (the soret band or B band), followed by several weaker absorptions at higher wavelengths called the Q bands. These are $Q_1$, $Q_2$, $Q_3$, and $Q_4$ bands at 514 nm, 550 nm, 591 nm, and 648 nm respectively (figure 4.1).

Figure 4.1. The UV-vis spectrum of TPP
(ii) IR spectral analysis

The IR spectrum of TPP was recorded in the solid state as KBr discs in the scanning range of 4000-400 cm\(^{-1}\) and the spectrum is given in figure 4.2. The prominent IR signals and the peak assignments are given in table 4.1.

![Figure 4.2. The IR spectrum of TPP](image)

**Table 4.1.** IR signals of TPP

<table>
<thead>
<tr>
<th>Bands cm(^{-1})</th>
<th>Peak assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3315</td>
<td>N-H stretch in porphyrin</td>
</tr>
<tr>
<td>3045</td>
<td>C-H stretch in phenyl group</td>
</tr>
<tr>
<td>3016</td>
<td>CH, CH2 stretch</td>
</tr>
<tr>
<td>1670</td>
<td>C=C stretch in phorphyrin, C=N stretch</td>
</tr>
<tr>
<td>1580</td>
<td>C=C stretch in phenyl group</td>
</tr>
<tr>
<td>1320</td>
<td>C-N stretch</td>
</tr>
<tr>
<td>1240</td>
<td>C-C stretch in porphyrin</td>
</tr>
</tbody>
</table>
(iii) $^1$H NMR spectra

The $^1$H NMR spectrum of TPP was recorded in CDCl$_3$ at 298 K and shown in figure 4.3. There are three prominent peaks. The peak at $\delta$ 8.1 (20H) represents the porphyrin meso aryl protons and the peak at $\delta$ 7.8 (8H) represents the $\beta$-H protons. The N-H protons show a signal at $\delta$ 2.5 (2H).

![Figure 4.3. The NMR spectrum of TPP](image)

4.3 Chlorosulphonation of TPP

4.3.1 Syntheses of chlorosulphonated TPP

The tetra chlorosulfonated TPP was prepared by adding chlorosulfonic acid to the TPP solution in CHCl$_3$. The reaction was carried at 5$^\circ$C for a period of 8 hrs (scheme 4.2).
The chlorosulphonated product having intense green colour was highly soluble in polar solvents and insoluble in chloroform. The drastic change in solubility showed the chlorosulphonation of the phenyl rings of TPP. The product was purified by column chromatography using 2:8 mixtures of chloroform and methanol.

4.3.2 Characterisation of chlorosulphonated TPP

The chlorosulphonated TPP was characterized by UV-visible, FTIR and $^1$H NMR spectroscopic methods.

(i) UV-visible spectra

The UV-visible spectrum of chlorosulphonated TPP is given in figure 4.4. The soret band of TPP got red shifted to 439 nm from 416 nm after chlorosulphonation. The $Q_1$, $Q_2$, $Q_3$, and $Q_4$ bands were also red shifted from 514 nm to 525 nm, 550 nm to 559 nm, 591 nm to 601 nm and 648 nm to 656 nm respectively. The lone pairs on the sulphur atom causes increased electron delocalisation with the porphyrin macrocycle $\pi$-electron framework. The SO$_2$Cl group enhances the $\pi$ conjugation and the HOMO-LUMO energy gap is reduced. This effect is reflected in the red shift shown by these systems.
(ii) IR spectral analysis

The IR spectrum shows typical absorption at 1230 cm\(^{-1}\) and 1060 cm\(^{-1}\) corresponding to S-O asymmetric and S-O symmetric stretching vibrations respectively in addition to the normal absorptions by TPP. The signals corresponding to S-O stretching vibrations (both symmetric and asymmetric) clearly showed the successful chlorosulphonation of the phenyl rings (figure 4.5). The other signals are: 3250 cm\(^{-1}\) (N-H str), 1600 cm\(^{-1}\) (C=C str), 1500 cm\(^{-1}\) (C=C str of aromatic group), 1300 cm\(^{-1}\) (C-N str), and 600 cm\(^{-1}\) (C-S str).

Figure 4.4. The UV-vis spectrum of chlorosulphonated TPP

Figure 4.5. The IR spectrum of chlorosulphonated TPP
(iii) NMR spectral analysis

The NMR spectrum of the chlorosulphonated TPP is given in figure 4.6. There are three prominent peaks. The peak at $\delta$ 7.8 (8H) represents the porphyrin $\beta$-H peaks and the peak at $\delta$ 8.5 (16H) represents the meso aryl protons. The N-H protons give a signal at $\delta$ 2.6 (2H).

![NMR spectrum of chlorosulphonated TPP](image)

**Figure 4.6.** The NMR spectrum of chlorosulphonated TPP

### 4.4 Functionalization of Linear Polymers with Tetr phenyl porphyrin

The linear polymers selected were polyvinyl alcohol (PVA), polyethylene glycol (PEG) and polyglycerol polyol (PG). PVA contains a large number of hydroxyl groups and they can be easily modified by the esterification with compounds containing COOH group or SO$_3$H group. Similar is the case with PEG and PG. Both possess primary alcoholic terminal groups and are accessible to common reactions such as esterification or etherification.
4.4.1 Functional modification of polyvinyl alcohol with tetraphenyl porphyrin

(a) Synthesis of PVA-TPP ester

A porphyrin ring having phenyl groups at the periphery can act as a guest of groups such as sulphonic acid, carboxylic acid etc. PVA contains hydroxyl groups and they can be easily modified by the esterification with compounds containing COOH or SO$_3$H group. Polyvinyl alcohol is a water-soluble synthetic polymer with excellent film forming, emulsifying, and adhesive properties. Polyvinyl alcohol was functionally modified by coupling with chlorosulphonated TPP. The reaction was carried at 80$^0$C for a period of 8 hrs (scheme 4.3).

![Scheme 4.3. Synthesis of PVA-TPP sulphonate ester](image)

(b) Characterisation of PVA-TPP ester

The PVA-TPP was characterized by UV-visible, FTIR and $^1$H NMR spectroscopic methods.

(i) UV-visible spectral analysis

The UV-visible spectrum of TPP bound PVA was recorded in DMF and given in figure 4.7. The PVA-bound TPP showed the signals corresponding to soret band at 414nm and Q$_1$ band at 513nm. Q$_2$, Q$_3$, and Q$_4$ bands were of very low intensity.

The soret as well as the Q bands of TPP-SO$_2$Cl were blue shifted on coupling with polyvinyl alcohol. The soret band was shifted from 439 nm to 414 nm and the Q$_1$, Q$_2$, Q$_3$, and Q$_4$ bands were also blue shifted from 525 nm to 513 nm, 559 nm to 547 nm, 601
nm to 590 nm and 656 nm to 644 nm respectively. The extent of shifting for the soret band was 25 nm. The extent of blue shifting for Q₁ band was 12 nm, for Q₂ band 12 nm, for Q₃ band 11 nm and for Q₄ band the shifting was 12 nm. On binding the TPP macrocycle on to the polymeric framework, the planarity of the macrocycle becomes perturbed by the entangled polymeric structure, and this causes an increase in the HOMO-LUMO gap of the porphyrin macrocycle. This is quite evident from the blue shifting observed in the UV-visible spectrum.

![Graph](image)

**Figure 4.7.** UV-vis spectrum of TPP bound PVA

(ii) IR spectral analysis

When chlorosulphonated porphyrin was bound to PVA, a prominent peak was obtained at 3420 cm⁻¹ which was due to the unreacted -OH groups of PVA. The absorption peak corresponding to N-H stretching was merged with it and it appeared as a broad band (figure 4.8). The other signals are: 2967 cm⁻¹ (C-H stretch), 1689 cm⁻¹ (C=N str.), 1603 cm⁻¹ (C==C str), 1565 cm⁻¹ (C=C str of aromatic group), 1340 cm⁻¹ (S-O asym str), 1248 cm⁻¹ (C-N str), 1190 cm⁻¹ (S-O sym str) and 600 cm⁻¹ (C-S str).
(iii) $^1$H NMR spectral analysis

The proton NMR spectrum of PVA is shown in figure 4.9. It has three well-defined peaks. The peak at 3.8ppm due to OH protons and a multiplet at 3.3 ppm due to CH protons attached to OH group and a doublet at 2.6 ppm due to CH$_2$ protons attached to CHOH.

The porphyrin bound PVA was subjected to proton NMR analysis. The results give conclusive evidence for the binding of porphyrin on the PVA skeleton. In the NMR spectrum of PVA-TPP system, the peak at $\delta$ 8.2 (16H) is due to aromatic protons (meso aryl group) from TPP. The position of the peaks due to aryl protons is shifted on binding from $\delta$ 8.5 of TPPSO$_2$Cl to $\delta$ 8.2. The peaks due to $\beta$ -H protons appears at $\delta$ 8.0 ppm and N-H protons is at $\delta$ 2.5 ppm. The PVA protons give signals at $\delta$ 3.8 ppm due to the hydroxyl proton, $\delta$ 3.1 ppm due to the CH- proton, $\delta$ 2.5 ppm due to the CH$_2$ protons (figure 4.10).
Figure 4.9. $^1$H NMR spectrum of PVA

Figure 4.10. $^1$H NMR spectrum of TPP bound PVA
4.4.2 Porphyrin bound polyethylene glycol

(a) Synthesis of PEG-TPP ester

Poly ethylene glycol (MW. 6000) was covalently bonded to porphyrin macrocycle by sulphonyl linkages and was characterized by IR, UV-visible and proton NMR analysis. The successful binding of porphyrin macrocycle to PEG skeleton is clearly evident from the spectral results. The study provides some useful information about the nature and extent of electronic modifications that can be brought by covalently binding PEG to the porphyrin macrocycle.

The porphyrin bound PEG was prepared in two steps. The tetra chlorosulfonated TPP was prepared by adding chlorosulfonic acid to the TPP solution in CHCl₃ (scheme 4.2). The chlorosulphonated TPP was treated with PEG for functional modification. The reaction was performed at 80°C with constant stirring. The pink coloured pasty solid obtained was washed with toluene to make it free from pyridine. The purification was done by column chromatography using alumina and 1:2 mixture of chloroform and DMF. The yield was noted as 80% (scheme 4.4).

\[
\text{HO} \left[ \text{CH}_2\text{CH}_2\text{O} \right]_n \text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{N} = \text{N} + \text{SO}_2\text{Cl} \rightarrow \text{PEG} \cdot \text{SO}_2\text{Cl} \rightarrow \text{PEG} \cdot \text{SO}_2\text{PEG}
\]

Scheme 4.4. Synthesis of PEG-TPP sulphonate ester

(b) Characterisation of teraphenyl porphyrin bound polyethylene glycol

(i) UV-visible spectral analysis

The UV-visible spectrum of PEG-TPP system was recorded in DMF. The spectrum shows signals at 411 nm and at 509 nm corresponding to the soret and Q₁ bands (figure 4.11). On binding with the polymer, the soret band showed shifting of 28 nm to shorter
wavelength region from 439 nm compared to the soret band of TPP-SO$_2$Cl. The Q bands also showed decrease in their $\lambda_{max}$ values. The Q$_2$, Q$_3$, and Q$_4$ bands were obtained at 541nm, 583 nm and 639 nm respectively. The Q$_1$ band get blue shifted by 16 nm from 525 nm to 509 nm, Q$_2$ band by 18 nm from 559 nm to 541 nm, Q$_3$ band by 18 nm from 601 nm to 583 nm and Q$_4$ band by 17 nm from 656nm to 639 nm of the corresponding bands of TPP-SO$_2$Cl.

The result can be explained by considering the steric strain imparted on the highly sensitive porphyrin $\pi$-electron framework by the polymeric backbone. The steric hindrance causes both blue shift and a decrease in intensity of absorption (figure 4.11).

![UV-visible spectrum of PEG-TPP](image)

**Figure 4.11.** UV-visible spectrum of PEG-TPP

(ii) IR spectral studies

The IR spectrum was recorded in the solid state as KBr discs and the spectrum shows typical absorption at 1350 and 1197 cm$^{-1}$ corresponding to S-O asymmetric and S-O symmetric stretching vibrations respectively. The absorption at 3506 cm$^{-1}$ is due to the OH stretching vibration corresponding to the unreacted -OH groups of PEG (figure 4.12). The other signals are at 3225 cm$^{-1}$ (N-H), 3008 cm$^{-1}$ (C-H str. aromatic), 2870 cm$^{-1}$ (C-H str. aliphatic), 1674 cm$^{-1}$ (C=N), 1648 cm$^{-1}$ (C==C str), 1350 cm$^{-1}$ (S-O asy str), 1249 cm$^{-1}$ (C-N str), 1197 cm$^{-1}$ (S-O sym str), 1107 cm$^{-1}$ (C-O str).
(iii) NMR spectra

The free PEG and the porphyrin bound PEG were subjected to proton NMR spectral analysis. The results give conclusive evidence for the binding of porphyrin on to the PEG skeleton.

In the \(^1\text{H}\) NMR spectrum of PEG (figure 4.13) there are two well-defined peaks, one at 4.6 ppm due to the PEG -OH protons and the other at 3.4 ppm due to -CH\(_2\) protons. In the PEG- porphyrin system there are peaks at 8.2 ppm due to aryl protons (16H) and an 8H signal at 7.2 ppm. The multiplet observed at 3.6 ppm due to -CH\(_2\) protons and the new peak at 2.8 ppm due to N-H protons of porphyrin. The peak at \(\delta\) 4.2 is assigned to unreacted OH protons (figure 4.14).
Figure 4.13. The NMR spectrum of PEG

Figure 4.14. The $^1$H NMR spectrum of PEG- TPP system
4.4.3 Modification of linear poly glycerol adipate with porphyrin

(a) Synthesis of PG-TPP ester

Polyglycerol adipate can be modified by coupling with sulphonated TPP as sulphonyl esters. The presence of a large number of end hydroxyl groups facilitates the reaction and condensation takes place to give sulphonate ester with appreciable loading. The reaction is shown in scheme 4.5.

(b) Characterisation of linear polyglycerol adipate modified with tetraphenyl porphyrin

(i) UV-visible spectra

When TPP is bound to linear PG we observed blue shift in both soret and Q bands but to a very low extent for Q bands when compared to PVA and PEG bound TPP. The soret and Q1 bands were blue shifted from 439 nm and 525 nm of TPP-SO₂Cl to 414 nm and 512 nm respectively. The Q₂, Q₃, and Q₄ bands were blue shifted from 559 nm to 546 nm, 601 nm to 590 nm and 656 nm to 647 nm respectively (figure 4.15). The extent of blue shifting from the corresponding bands of TPP-SO₂Cl were soret band = 25 nm, Q₁ = 13 nm, Q₂ = 13 nm, Q₃ = 11 nm and Q₄ = 9 nm respectively.
(ii) IR spectral studies

The IR spectrum of PG was recorded in the transmission mode as KBr pellets in the scanning range 4000 cm\(^{-1}\) - 400 cm\(^{-1}\). The signals present in the spectra are: 3488 cm\(^{-1}\) (OH stretching), 2947 cm\(^{-1}\) (aliphatic C-H stretching), 1731 cm\(^{-1}\) (C=O stretching), 1130 cm\(^{-1}\) (C-O-C stretching). The IR spectrum of polyglycerol polyol is given below in figure 4.16.
The IR spectrum of PG-TPP system was recorded in the solid state as KBr discs and the spectrum shows typical absorption at 1344 and 1161 cm\(^{-1}\) corresponding to S-O asymmetric and S-O symmetric stretching vibrations of the porphyrin sulphonate group respectively. In addition, it shows a prominent peak at 3515 cm\(^{-1}\) due to unreacted -OH stretching vibrations of polyglycerol polyol (figure 4.17). We observed other peaks at 2939 cm\(^{-1}\) (C-H str. aromatic), 2871 cm\(^{-1}\) (C-H str. aliphatic), 1732 cm\(^{-1}\) (C==O str.), 1671 cm\(^{-1}\) (C=N str.), 1661 cm\(^{-1}\) (C=C str.), 1536 cm\(^{-1}\) (aromatic C=C str.), 1449 cm\(^{-1}\) (C-H def.), 1257 cm\(^{-1}\) (C-N str.), and 1134 cm\(^{-1}\) (C-O str.).

![IR spectrum of TPP bound PG](image)

**Figure 4.17.** IR spectrum of TPP bound PG

(iii) NMR spectral analysis

The \(^1\)H NMR spectra of pure polyglycerol polyol and TPP bound PG are given in figures 4.18 and 4.19 respectively. The three distinct peaks at 4.2 ppm, 3.6 ppm and 2.9 ppm in the spectrum of polyglycerol polyol indicate OH, CH\(_2\) and CH protons. In the NMR spectrum of porphyrin bound polyglycerol, in addition to these peaks of polyglycerol polyol, peaks characteristic of the porphyrin macrocycle were also obtained. The peak at 8.1 (8H) represents the porphyrin -H peaks and the peak at 8.2 (16H) represents the meso aryl protons. The N-H protons are at 2.3 (2H).
Figure 4.18. $^1$H NMR spectrum of polyglycerol adipate

Figure 4.19. $^1$H NMR spectrum of TPP bound polyglycerol polyol adipate
4.5 Hyperbranched Polyglycerol Functionalised with Porphyrins and Metalloporphyrins

Hyperbranched polyglycerol (HPG) represents the first hyperbranched polymer that can be prepared in a controlled synthesis. HPG possesses an inert polyether scaffold. Each branch ends in a hydroxyl function, which renders hyperbranched polyglycerol a highly functional material, e.g., a molecule with a molecular weight of 5000g/mol possesses 68 hydroxyl end groups. The high functionality in combination with the versatile and well-investigated reactivity of hydroxyl functions is the basis for a variety of derivatives obtained from HPG. A synthetic route enabling the preparation of hyperbranched polyglycerol was the ring opening multibranching polymerization (ROMP) of glycidol. Scheme 4.6. describes the synthesis of hyperbranched polyglycerol.

Scheme 4.6. Synthesis of hyperbranched polyglycerol

4.5.1 Hyperbranched polyglycerol functionalised with chlorosulphonated porphyrin

A porphyrin ring having phenyl groups at the periphery can act as a guest of groups such as sulphonic acid, carboxylic etc. In the present study the chlorosulphonated TPP molecules were coupled with the free hydroxyl groups of HPG. We synthesized hyperbranched polyglycerol functionalised with TPP as a sulphonate ester (scheme 4.7). The synthesis of HPG-TPP system was performed using essentially the same synthetic method
described for linear PVA, PEG and PG. With DMF as solvent and pyridine as catalyst the sulphonyl chloride of porphyrin groups are directly attached to the HPG by an esterification reaction resulting in HPG- TPP system (scheme 4.7).

Scheme 4.7. Synthesis of porphyrin bound hyperbranched polyglycerol

4.5.2 Characterisation of HPG- TPP system

(i) Electronic spectral studies

In the UV-visible absorption spectrum, the highly conjugated porphyrin macrocycle on chlorosulphonation shows intense absorption at 439 nm (the soret band) followed by several weaker absorptions (Q bands) at higher wavelengths 500 to 700 nm ($Q_1 = 525$ nm, $Q_2 = 559$ nm, $Q_3 = 601$ nm and $Q_4 = 656$ nm). The HPG-TPP system shows signals at 472 nm, 563 nm, 600 nm, 640 nm and 694 nm in the UV-visible spectrum (figure 4.20). The soret band showed a red shift of 33 nm and the Q bands showed red shift of 38 nm,
41 nm, 39 nm and 38 nm corresponding to $Q_1$, $Q_2$, $Q_3$ and $Q_4$ bands respectively.

**Figure 4.20.** UV-visible spectrum of TPP bound HPG

When the UV spectra of equimolar solutions of pure TPP and TPP bound HPG were compared, a prominent increase in the intensity was observed for the Q bands of the UV-visible spectrum of HPG-TPP system.

(ii) **IR spectral analysis**

The IR spectrum of TPP-bound HPG was recorded and compared with that of pure HPG. The spectrum of pure HPG showed signals that are characteristic of the groups present in hyperbranched polyglycerol. The important signals and the corresponding groups are: $3359\text{cm}^{-1}$ (OH stretching), $2923\text{cm}^{-1}$ (C-H stretching), $1249\text{cm}^{-1}$ (C-C stretching) and $1114\text{cm}^{-1}$ (C-O-C stretching). The IR spectrum is given in figure 4.21.
The spectrum of HPG-TPP showed additional signals at: 1331 cm\(^{-1}\) and 1120 cm\(^{-1}\) corresponding to the S-O asymmetric and S-O symmetric stretching vibrations. The other prominent signals are: 3571 cm\(^{-1}\) (OH stretching vibrations of hyperbranched polyglycerol), 3133 cm\(^{-1}\) (N-H str.), 3076 cm\(^{-1}\) (C-H str. aromatic), 2974 cm\(^{-1}\) (C-H str. aliphatic), 1667 cm\(^{-1}\) (C=N str.), 1602 cm\(^{-1}\) (C=C str.), 1546 cm\(^{-1}\) (aromatic C=C str.), 1415 cm\(^{-1}\) (C-H def.), 1284 cm\(^{-1}\) (C-N str.), and 1210 cm\(^{-1}\) (C-O str.) (figure 4.22).

**Figure 4.21.** The IR spectrum of HPG

**Figure 4.22.** IR Spectrum of TPP bound HPG
(iii) NMR spectra

The free HPG and the porphyrin bound HPG were subjected to proton NMR analysis. The NMR spectrum of hyperbranched polyglycerol was recorded using dimethylsulphoxide (DMSO) as solvent. The prominent signals observed are: $\delta$ 4.902 (s, OH protons), $\delta$ 3.796 - $\delta$ 3.320 (m, CH$_2$ and CH protons). The NMR spectrum is given in figure 4.23.

![Figure 4.23. $^1$H NMR spectrum of HPG](image)

In the TPP bound HPG system there are three new peaks in addition to the peaks of polyglycerol, that is a signal at 8.2 ppm due to meso aryl protons of the porphyrin macrocycle and a signal at 7.9 ppm due to porpyrin beta protons and a peak corresponding to N-H protons at 2.5 ppm. The successful binding of porphyrin macrocycle to hyperbranched polyglycerol skeleton is clearly evident from the NMR spectrum (figure 4.24).
4.6 Synthesis of Metalloporphyrins

It is known that porphyrins incorporate almost all the metal ions in the central cavity to generate metalloporphyrins with varying degree of oxidation state for the metal ion. Many such metalloporphyrins have been reported to be versatile catalysts both in chemical conversions and also in the photochemical reactions. Besides, many metallo porphyrins also have been employed as model compounds.

It is seen that porphyrins undergo metallation with Zn$^{2+}$, Cu$^{2+}$, and Fe$^{2+}$, with varying degree of efficiency. Even though the nature of metal carriers has an important effect on the rate of formation of the metalloporphyrin, we have employed metal in its acetate form. A polar and non-polar mixture of solvents was necessary, as the porphyrin is soluble only in non-polar solvents while metal carrier needs a polar solvent. Upon metallation the porphyrin ring system deprotonates, forming a dianionic ligand. The metal ions behave as Lewis acids, accepting lone pairs of electrons.

In agreement with the reported data we can assign the metallation reaction proceeding based on scheme 4.8.
4.7 Modification of Polymeric Cores with Metallo-porphyrins

The metallo porphyrin ring is found in a variety of important biological systems where it is the active component of the system or in some ways intimately connected with the activity of the system\(^1\). Many of these porphyrins synthesized as the basic structure of biological porphyrins which are the active sites of numerous proteins, whose functions range from oxygen transfer and storage (hemoglobin and myoglobin) to electron transfer to energy conversion (chlorophyll). They also have been proven to be efficient sensitizers and catalyst in a number of chemical and photochemical processes especially photodynamic therapy. The diversity of their functions is due in part to the variety of metals that bind the pocket of the porphyrin ring system. In the present work we have made an attempt to account for the electronic changes observed in metallo porphyrins due to the polymer-porphyrin interactions.

4.7.1 Modification of PVA with MTPP

Polyvinylalcohol was anchored with metalloporphyrins by the free-OH groups of PVA. Chlorosulphonated metalloporphyrin was bound to PVA by esterification reaction (scheme 4.9).
4.7.2 Characterisation of PVA- MTPP system

(a) PVA-ZnTPP system

(i) Electronic spectra

The electronic spectra of PVA-ZnTPP has three prominent peaks, one at 415 nm and two weaker Q bands at 514 nm and 549 nm (figure 4.25). The disappearance the two Q bands of porphyrin on metallation was explained by M. Goutermann\textsuperscript{15,16}. The spectral absorptions arise from $\pi - \pi^*$ transitions of the aromatic porphyrin ligand. The allowed transitions $a_{1u} - eg^*$ and $a_{2u} - eg^*$ are assumed to be degenerate in energy. As a consequence, the states undergo configuration interaction and give rise to new states. The resulting spectrum shows a high-energy band B in which the transition dipoles add (high intensity) and a low energy Q band in which the transition dipoles nearly cancel (low intensity). The two Q bands are vibronic components of the same transition.
(ii) IR analysis

The IR spectrum of PVA-ZnTPP is shown in figure 4.26. The signal at 3198 cm$^{-1}$ (N-H str) is not seen in the spectrum and this indicates the insertion of the metal in the porphyrin core. The other signals are: 3460 cm$^{-1}$ (O-H str), 3014 cm$^{-1}$ (C-H str. aromatic), 2927 cm$^{-1}$ (C-H str. aliphatic), 1637 cm$^{-1}$ (C=N str.), 1598 cm$^{-1}$ (aliphatic C==C str), 1560 cm$^{-1}$ (C=C str of aromatic group), 1439 cm$^{-1}$ (C-H def.), 1320 cm$^{-1}$ (S-O asym str), 1261 cm$^{-1}$ (C-N str), 1175 cm$^{-1}$ (S-O sym str) and 1114 cm$^{-1}$ (C-O str).
(iii) $^1$H NMR spectral analysis

The PVA-ZnTPP was subjected to proton NMR analysis. In the NMR spectrum of PVA-ZnTPP system, the peak at $\delta 8.3(16H)$ is due to aromatic protons (meso aryl group) from TPP. The position of the peaks due to $\beta$-H protons is at 7.2. The PVA protons give signals at 4.8ppm due to the hydroxyl group, 4.0 ppm due to the CH- proton (figure 4.27).

Figure 4.27. $^1$H NMR spectrum of PVA-ZnTPP

(b) PVA- FeTPP system

(i) Electronic spectra

The electronic spectra of PVA-FeTPP system showed a high-energy band B at 419 nm in which the transition dipoles add (high intensity) and two low energy Q bands at 517 nm and 554 nm in which the transition dipoles nearly cancel (low intensity). The two Q bands are vibronic components of the same transition (figure 4.28). When compared with the metal free PVA-TPP system we have observed red shifting in both soret and Q bands. The soret band get shifted from 414 nm to 419 nm, $Q_1$ band from 513 nm to 517 nm and $Q_1$ band from 547 nm to 554 nm.
(ii) IR analysis

The IR spectrum of PVA-FeTPP is shown in figure 4.29. The intensity of the signal corresponding to N-H stretching was diminished in the spectrum and this indicates the insertion of the metal in the porphyrin core. The other prominent signals are: 3456 cm\(^{-1}\) (O-H str), 3234 cm\(^{-1}\) (N-H str), 3090 cm\(^{-1}\) (C-H str. aromatic), 2877 cm\(^{-1}\) (C-H str. aliphatic), 1664 cm\(^{-1}\) (C=N str.), 1655 cm\(^{-1}\) (aliphatic C==C str), 1597 cm\(^{-1}\) (C=C str of aromatic group), 1462 cm\(^{-1}\) (C-H def.), 1338 cm\(^{-1}\) (S-O asym str), 1279 cm\(^{-1}\) (C-N str), 1134 cm\(^{-1}\) (S-O sym str) and 1106 cm\(^{-1}\) (C-O str).

![Figure 4.29. The IR spectrum of PVA bound FeTPP](image-url)
(iii) **$^1$H NMR spectral analysis**

The PVA-FeTPP was subjected to proton NMR analysis. In the NMR spectrum of PVA-FeTPP system, the peak at $d$ 8.2 (16H) is due to aromatic protons (meso aryl group) from TPP. The position of the peaks due to $\beta$-H protons of porphyrin is at 8.0 ppm. The PVA protons give signals at 3.8 ppm due to the hydroxyl proton and at 3.3 ppm due to the CH-proton (figure 4.30).

![NMR Spectrum](image)

**Figure 4.30.** $^1$H NMR spectrum of PVA-FeTPP

(c) **PVA- CuTPP system**

(i) **Electronic spectra**

The electronic spectra of PVA-CuTPP has three prominent peaks, one at 419 nm and two weaker Q bands at 519 nm and 553 nm (figure 4.31). The soret band get red shifted by 5nm from the corresponding band of the metal free PVA-TPP system. The extend of shifting of $Q_1$ and $Q_2$ bands are by 6nm from the corresponding bands of the metal free system. The disappearance of the two Q bands is due to metallation.
(ii) IR analysis

The IR spectrum of PVA-CuTPP is shown in figure 4.32. The spectrum showed successful insertion of the metal in the porphyrin core. The prominent signals are: 3452 cm\(^{-1}\) (O-H str), 2935 cm\(^{-1}\) (C-H str. aromatic), 2887 cm\(^{-1}\) (C-H str. aliphatic), 1645 cm\(^{-1}\) (C=N str.), 1597 cm\(^{-1}\) (aliphatic C==C str), 1539 cm\(^{-1}\) (C=C str of aromatic group), 1336 cm\(^{-1}\) (S-O asym str), 1260 cm\(^{-1}\) (C-N str), 1125 cm\(^{-1}\) (S-O sym str) and 1039 cm\(^{-1}\) (C-O str).

Figure 4.31. UV-vis spectrum of PVA-CuTPP

Figure 4.32. The IR spectrum of PVA bound CuTPP
(iii) 1H NMR spectral analysis

The PVA-CuTPP was subjected to proton NMR analysis. In the NMR spectrum of PVA-CuTPP system, the peak at \( \delta 8.1 \) (16H) is due to aromatic protons (meso aryl group) from TPP. The position of the peaks due to \( \beta \)-H protons is at \( \delta 7.6 \). The PVA protons give signals at 4.6 ppm due to the unreacted hydroxyl proton and at 4.5 ppm due to the CH- proton (figure 4.33).

![1H NMR spectrum of PVA-CuTPP](image)

Figure 4.33. 1H NMR spectrum of PVA-CuTPP

4.7.3 Modification of PEG with MTPP

The polyethylene glycol core system was functionalised with metallo porphyrin by the esterification of the free hydroxyl groups of PEG with chlorosulphonated MTPP (scheme 4.10).
4.7.4 Characterisation of PEG- MTPP system

(a) PEG-ZnTPP system

(i) Electronic spectra

The electronic absorption bands of Zn (II)TPP bound to PEG was found to be almost same as that of PEG bound metal free TPP (figure 4.11). This can be accounted by the fact that metal ions with d^{10} or d^{0} configuration have very little interaction with the π-π* electronic energy. The absorptions obtained were at 412 nm, 512 nm and 545 nm of soret, Q_1 and Q_2 bands respectively. Two of the Q band signals were disappeared on metallation. This gives additional proof for metallation (figure 4.34).
(ii) IR analysis

The IR spectrum of PEG-ZnTPP was recorded as KBr pellets (figure 4.35). The prominent signals are: 3503 cm$^{-1}$ (O-H str), 2931 cm$^{-1}$ (C-H str. aromatic), 2859 cm$^{-1}$ (C-H str. aliphatic), 1512 cm$^{-1}$ (C=C str of aromatic group), 1435 cm$^{-1}$ (C-H def.), 1389 cm$^{-1}$ (S-O asym str), 1252 cm$^{-1}$ (C-N str), 1098 cm$^{-1}$ (S-O sym str) and 1050 cm$^{-1}$ (C-O str). The signals corresponding to C=N stretching and aliphatic C=C stretching were merged and appeared as a broad band centered at 1675 cm$^{-1}$.

![IR spectrum of ZnTPP bound PEG](image)

**Figure 4.35.** IR spectrum of ZnTPP bound PEG

(iii) NMR spectral analysis

In the PEG-ZnTPP system there are peaks at 8.4 ppm due to aryl protons (16H) and an 8H signal at 7.5 ppm due to the $\beta$-H protons of the porphyrin macrocycle. The multiplet observed at 3.6 ppm due to -CH$_2$ protons. The spectrum is shown in figure 4.36.
When FeTPP was bound to PEG, we observed a red shift in the soret (2nm) as well as the Q bands of porphyrin due to the interaction of the unfilled d orbital of the metal with the electronic absorption of the porphyrin (figure 4.37). In the PEG-metal free TPP system all the Q bands of the TPP were of low intensity but in PEG-FeTPP system the absorption at the Q₁ and Q₂ bands became prominent and Q₁ band was red shifted to 515 nm from 509 nm and Q₂ band was red shifted to 554 nm from 541 nm.

(b) PEG-FeTPP system

Figure 4.36. The $^1$H NMR spectrum of PEG-ZnTPP

Figure 4.37. UV-vis spectrum of PEG-FeTPP
(ii) IR analysis

The IR spectrum of PEG Fe TPP was recorded and analysed. The absorption at 3457 cm\(^{-1}\) is due to the OH stretching vibration corresponding to the unreacted OH groups of PEG (figure 4.38). The other signals are: 2931 cm\(^{-1}\) (aromatic C-H str), 2860 cm\(^{-1}\) (aliphatic C-H str.), 1438 cm\(^{-1}\) (C-H def.), 1409 cm\(^{-1}\) (S-O asy str), 1254 cm\(^{-1}\) (C-N str), 1182 cm\(^{-1}\) (S-O sym str), and 1092 cm\(^{-1}\) (C-O str). The signals corresponding to the stretching vibrations of C=N, aliphatic C=C and aromatic C=C were merged together and gave a signal centered at 1653 cm\(^{-1}\).

![IR spectrum of FeTPP bound PEG](image)

**Figure 4.38.** IR spectrum of FeTPP bound PEG

(iii) NMR spectral analysis

In the PEG-FeTPP system there are peaks at 8.6 ppm due to aryl protons (16H) and an 8H signal due to \(\beta\)-H protons at \(\delta\) 7.2 ppm. The multiplet observed at \(\delta\) 3.4 ppm is due to -CH\(_2\) protons and \(\delta\) 4.2 ppm is due to unreacted OH protons (figure 4.39).
Due to the interaction of the unfilled d orbital of the metal with the electronic absorption of the porphyrin, we observed a red shift in the soret as well as the $Q_1$ and $Q_2$ bands of UV-visible spectrum (figure 4.40). In the PEG-metal free TPP system all the $Q$ bands of the TPP were of low intensity but in PEG-CuTPP system the absorption showed red shift of 5 nm from 411 nm to 416 nm, 9 nm from 509 nm to 518 nm and 14 nm from 541 nm to 555 nm in the soret, $Q_1$ and $Q_2$ bands respectively.

(c) PEG-CuTPP system

(i) Electronic spectra

Due to the interaction of the unfilled d orbital of the metal with the electronic absorption of the porphyrin, we observed a red shift in the soret as well as the $Q_1$ and $Q_2$ bands of UV-visible spectrum (figure 4.40). In the PEG-metal free TPP system all the $Q$ bands of the TPP were of low intensity but in PEG-CuTPP system the absorption showed red shift of 5 nm from 411 nm to 416 nm, 9 nm from 509 nm to 518 nm and 14 nm from 541 nm to 555 nm in the soret, $Q_1$ and $Q_2$ bands respectively.
(ii) IR analysis

The IR spectrum of PEG- Cu TPP showed important signals at: 3484 cm$^{-1}$ (O-H str), 2935cm$^{-1}$ (C-H str. aromatic), 2881cm$^{-1}$ (C-H str. aliphatic), 1470cm$^{-1}$ (C-H def.), 1366 cm$^{-1}$ (S-O asym str), 1270cm$^{-1}$ (C-N str), 1106 cm$^{-1}$ (S-O sym str) and 1068cm$^{-1}$ (C-O str). The signals corresponding to C=N stretching, aliphatic C=C stretching and aromatic C=C stretching were merged and appeared as a band centered at 1670cm$^{-1}$.
(iii) NMR spectra

In the PEG- CuTPP system there are peaks at δ 8.3 ppm due to aryl protons (16H) and an 8H signal at δ 7.9 ppm due to the β -H protons of the porphyrin macrocycle. The multiplet observed at δ 3.6 ppm due to -CH₂ protons. The peak corresponding to OH protons are observed at δ 4.2 ppm. (figure 4.42).

Figure 4.42. The NMR spectrum of PEG-CuTPP

4.7.5 Modification of PG with MTPP

Linear polyglycerol polyol (PG) was functionalised with metalloporphyrin by the esterification of the free OH groups of PG with chlorosulphonated MTPP (scheme 4.11)

Scheme 4.11. Synthetic route to PG-MTPP
4.7.6 Characterization of PG-MTPP

(a) PG-ZnTPP system

(i) UV visible spectra

When linear polyglycerol poly adipate was bound with metalloporphyrins, we have observed the same trend as that was in the case of polyethylene glycol-metalloporphyrin system. No characteristic spectral shifting was observed for system having Zn$^{2+}$ since this metal ion having filled d level and has very little interaction with electronic absorption by the TPP system. The soret band was observed at 416 nm and the Q$_1$ band Q$_2$ bands were at 512 nm and 544 nm respectively.

![UV-vis spectrum of PG-ZnTPP](image)

**Figure 4.43.** UV-vis spectrum of PG-ZnTPP

(ii) IR spectral studies

The IR spectrum of PG-ZnTPP system recorded in the solid state as KBr discs showed typical absorption at 1387 cm$^{-1}$ and 1101cm$^{-1}$ corresponding to S-O asymmetric and S-O symmetric stretching vibrations of the porphyrin sulphonate group. In addition, it shows a prominent peak at 3591cm$^{-1}$ due to OH stretching vibrations of polyglycerol polyol (figure 4.44). The absorption peaks corresponding to aromatic and aliphatic C-H stretching vibrations are merged and gave a band at 2926 cm$^{-1}$. the other signals were: 1533 cm$^{-1}$ (aromatic C=C str.), 1261 cm$^{-1}$ (C-N str.), and 1050 cm$^{-1}$(C-O str.). The
signals corresponding to the stretching vibrations of C=O, C=C, and C=N are merged together and gave a band at 1658 cm$^{-1}$.

![IR spectrum of PG-ZnTPP](image)

**Figure 4.44.** IR spectrum of PG-ZnTPP

(iii) NMR spectra

The peak at $\delta$ 7.9 (8H) represents the porphyrin -H peaks and the peak at 8.2 (16H) represents the meso aryl protons (figure 4.45). The signal at $\beta$ 3.6 ppm is due to the aliphatic protons of polyglycerol. The hydroxyl protons gave a signal at 4.8 ppm.

![NMR spectrum of ZnTPP bound poly glycerol polyol adipate](image)

**Figure 4.45.** NMR spectrum of ZnTPP bound poly glycerol polyol adipate
(b) PG-FeTPP system

(i) UV visible spectra

When linear polyglycerol poly adipate was bound with FeTPP, we have observed red shift in both soret (4nm) and Q₁ (4nm) and Q₂ band (5nm) compared to PG-TPP due to interaction of the d level with electronic absorption by the TPP system. The signal due to soret band was shifted from 414 nm to 418 nm, Q₁ band from 512 nm to 516 nm and the Q₂ band from 546 nm to 551 nm (figure 4.46).

![Figure 4.46. UV-vis spectrum of PG-FeTPP](image)

(ii) IR spectral studies

The IR spectrum of PG FeTPP was recorded as KBr pellets. In the IR spectrum the signals corresponding to OH stretching and aromatic and aliphatic C-H stretchings were merged and gave a band between 3400 cm⁻¹ and 2800 cm⁻¹. The other prominent signals are: 1751 (C=O str.),1645 cm⁻¹ (C=N str.),1606 cm⁻¹ (aliphatic C==C str), 1560 cm⁻¹ (C=C str of aromatic group), 1472 cm⁻¹ (C-H def.), 1376 cm⁻¹ (S-O asym str), 1231 cm⁻¹ (C-N str), 1183 cm⁻¹ (S-O sym str) and 1058 cm⁻¹ (C-O str).
(iii) NMR spectra

The peak at 8.0 (8H) represents the porphyrin β-H peaks and the peak at 8.2 (16H) represents the meso aryl protons (figure 4.48). The polyglycerol poly adipate core protons gives its characteristic signals at 3.4 ppm and 4.5 ppm. The unreacted hydroxyl protons gave a signal at 4.7 ppm.
(c) PG-CuTPP system

(i) UV visible spectra

When linear polyglycerol poly adipate was bound with CuTPP, soret band of metal free PG-TPP system get shifted from 414nm to 416nm, the $Q_1$ band from 512 nm to 518 nm and the $Q_2$ band from 546 nm to 550 nm. We have observed red shift in both soret (4nm), $Q_1$ band (6nm) and $Q_2$ band (4nm) due to interaction of the d level with electronic absorption by the TPP system (figure 4.49).

![UV-vis spectrum of PG-CuTPP](image)

**Figure 4.49.** UV-vis spectrum of PG-CuTPP

(ii) IR spectral studies

The IR spectrum of PG-CuTPP system showed typical absorption at 1318 cm$^{-1}$ and 1145cm$^{-1}$ corresponding to S-O asymmetric and S-O symmetric stretching vibrations of the porphyrin sulphonate group respectively. In addition, it shows a prominent peak at 3327 cm$^{-1}$ due to OH stretching vibrations of polyglycerol polyol (figure 4.50). We observed other peaks at 2927cm$^{-1}$ (aromatic C-H str), 2820cm$^{-1}$ (aliphatic C-H str), 1723 cm$^{-1}$ (C==O str.), 1658 cm$^{-1}$ (C=N str.), 1628 cm$^{-1}$(aliphatic C=C str.), 1434 cm$^{-1}$(C-H def.), 1244 cm$^{-1}$ (C-N str.), and 1077 cm$^{-1}$(C-O str.).
(iii) NMR spectra

The peak at 7.3 (8H) represents the porphyrin $\beta$-H protons and the peak at 8.5 (16H) represents the meso aryl protons (figure 4.51). The signals in the aliphatic region are due to the protons of the polyglycerol polyadipate, which is the core material.
4.7.7 Modification of HPG with MTPP

Metalloporphyrin was attached on to the hyperbranched polyglycerol core material by the esterification of the free hydroxyl groups of the hyperbranched polyglycerol with chlorosulphonated metalloporphyrins (scheme 4.12).

![Scheme 4.12. Synthetic route to HPG-MTPP](image)

**Characterisation of HPG-MTPP**

(a) HPG-ZnTPP system

(i) UV-visible analysis

The UV-visible spectra obtained for HPG-MTPP system exhibited appreciable red shifts in all the porphyrin bands (soret and Q) except in the case of zinc, for which the shift is not appreciable. But when the metal ion Zn$^{2+}$ is inserted in the porphyrin core, there is no considerable shift (figure 4.52). This is due to the fact that the metal ions with
vacant or fully filled d level have very little interaction with the $\pi - \pi^*$ electronic energy. The most favorable geometry for an effective MTPP $\pi$ overlap is when the porphyrin ring system is completely planar and central metal ion is in the molecular plane. Consequently any deviation from the planarity for the porphyrins would reduce this $\pi$ overlap with d orbitals and hence lower the energy of LUMOs of the MTPPs. The UV-visible spectrum of HPG-ZnTPP shows signals at 458 nm (soret band) and at 557 nm and 587 nm ($Q_1$ and $Q_2$ bands). When compared to metal free HPG-TPP system, the soret as well as the $Q$ bands were blue shifted in HPG-ZnTPP system. The soret band get shifted from 472 nm to 458 nm, $Q_1$ band from 563 nm to 557 nm and $Q_2$ band from 600 nm to 587 nm.

![Figure 4.52. UV-Vis spectrum of HPG-ZnTPP](image)

(ii) IR spectral analysis

The IR spectrum of ZnTPP-bound HPG was recorded as KBr pellets and showed signals at: 3358 cm$^{-1}$ (O-H str.), 2945 cm$^{-1}$ (aromatic C-H str), 2878 cm$^{-1}$ (aliphatic C-H str), 1463 cm$^{-1}$ (C-H def.), 1328 cm$^{-1}$ (S-O asym str.), 1250 cm$^{-1}$ (C-N str.), 1145 cm$^{-1}$ (S-O sym str.), and 1049 cm$^{-1}$ (C-O str.). The signals corresponding to C=N and aliphatic and aromatic C=C are merged and gave signal at 1645 cm$^{-1}$.
(iii) NMR spectra

The ZnTPP bound HPG was subjected to proton NMR analysis. The $^1$H NMR spectrum of HPG shows the methylene and methine protons of HPG as one broad resonance around 3.4 ppm where as the hydroxyl protons give signal at 4.8 ppm. The signal at 8.2 ppm due to aryl protons and a signal at 7.9 ppm due to $\beta$ -H protons of the porphyrin macrocycle (figure 4.54).

(b) HPG-FeTPP system

(i) UV-visible analysis

The UV-visible spectra obtained for HPG-FeTPP system exhibited red shifts in all the porphyrin bands. The extent of shifting of these signals are due to the most favorable geometry for an effective MTPP $\pi$ overlap when the porphyrin ring system is completely planar and central metal ion is in the molecular plane. The soret band was shifted from 472 nm to 475 nm by 3nm, $Q_1$ band from 563 nm to 574 nm by11nm and $Q_2$ band from 600nm to 609 nm by 9nm.
(ii) IR spectral analysis

The IR spectrum of FeTPP-bound HPG was recorded as KBr pellets, showed signals at: 3558 cm\(^{-1}\) (O-H str.), 2918 cm\(^{-1}\) (aromatic C-H str.), 2887 cm\(^{-1}\) (aliphatic C-H str.), 1654 cm\(^{-1}\) (C=N), 1626 cm\(^{-1}\) (aliphatic C=C), 1520 cm\(^{-1}\) (aromatic C=C), 1462 cm\(^{-1}\) (C-H def.), 1347 cm\(^{-1}\) (S-O asy), 1260 cm\(^{-1}\) (C-N str), 1135 cm\(^{-1}\) (S-O sy) and 1047 cm\(^{-1}\) (C-O str.) (figure 4.56).
(iii) NMR spectra

The FeTPP bound HPG was subjected to proton NMR analysis. The $^1$H NMR spectrum of HPG shows the methylene and methine protons of HPG as one broad resonance around 3.5 ppm where as the hydroxyl protons give signal at 4.3 ppm. The signal at 8.2 ppm due to aryl protons and a signal at 7.5 ppm due to $\beta$-H protons of the porphyrin macrocycle. The successful insertion of metal ion in to the porphyrin macrocycle is clearly evident from the NMR spectral results (figure 4.57).

(c) HPG-CuTPP system

(i) UV-visible analysis

When compared to metal free system, the HPG-CuTPP system exhibited red shifts in both soret and Q bands. The soret band get shifted from 472 nm to 476 nm, $Q_1$ band from 563 nm to 566 nm and $Q_2$ band from 600 nm to 603 nm.
(ii) IR spectral analysis

The IR spectrum of CuTPP bound HPG was recorded and it showed signals at: 3530 cm\(^{-1}\) (O-H str.), 2931 cm\(^{-1}\) (aromatic C-H str.), 2854 cm\(^{-1}\) (aliphatic C-H str.), 1640 cm\(^{-1}\)
(C=N), 1614 cm$^{-1}$ (aliphatic C=C), 1568 cm$^{-1}$ (aromatic C=C), 1441 cm$^{-1}$ (C-H def.), 1338 cm$^{-1}$ (S-O asy), 1235 cm$^{-1}$ (C-N str), 1135 cm$^{-1}$ (S-O sy) and 1063 cm$^{-1}$ (C-O str.) (figure 4.59).

![IR spectrum of HPG-CuTPP](image)

**Figure 4.59.** IR spectrum of HPG-CuTPP

(iii) NMR spectra

The CuTPP bound HPG was subjected to proton NMR analysis. The $^1$H NMR spectrum of HPG-CuTPP shows the methylene and methine protons of HPG as one broad resonance around 3.8 ppm where as the hydroxyl protons give signal at 4.6 ppm (figure 4.60). The signal at 8.4ppm due to meso aryl protons of the porphyrin macrocycle and a signal at 7.7 ppm due to porpyrin $\beta$ protons.
Figure 4.60. NMR spectrum of HPG-CuTPP

Functionally modified porphyrin macrocycle and their metallo derivatives (where metal= Zn, Fe and Cu) were attached on to polyvinyl alcohol, polyethylene glycol and linear polyglycerol poly adipate by suitable functional transformation reactions. The products were purified and characterized by IR, UV-visible and NMR spectral studies. Spectra showed conclusive evidence for the functional modification of tetr phenyl porphyrins, and their metalloderivatives and binding of TPPs and their metallo derivatives on to the polymeric core systems. Studies on electronic spectra of these systems gave results justifying the perturbation of the planar porphyrin macrocycle and the $\pi$ -electron framework by the entangled linear polymer cores.

Hyperbranched polyglycerols are excellent specialty polymer with a dendritic structure containing an inert polyether scaffold. The peripheral core positions are rich in hydroxyl functions and these active groups were modified with tetraphenyl porphyrins and their metalloderivatives through chlorosulphonation. The products were purified by column chromatography or membrane dialysis using cellulose semi permeable membrane and chloroform as the solvent. The hyperbranched polyglycerol modified with TPP and metalloporphyrins were characterized by IR, UV-visible, and NMR studies. The spectral results gave evidences for functional changes and the electronic properties of porphyrin macrocycle assisted by the dendritic structure of HPG were studied in detail.
4.8 References


