CHAPTER 2
Review of literature

In recent past, the attention has been focused on the use of porphyrin materials as model structures for explaining the general behaviour of the organic solid state, and more particularly on their technological possibilities in various types of devices, electrodes and solid catalysts for dealing with pollution problems or energy generating processes\textsuperscript{36,37,38}. The structures, reactivity, and biological functions of metalloporphyrins continue to be the subjects of considerable investigations. Knowledge of interactions between the metal, the porphyrin ring, and associated molecules is of vital importance in an understanding of biological function of metalloporphyrins. Recent crystallographic studies on the structures of metalloporphyrins in the solid phase have shown that there can be considerable geometric flexibility in the conformation of the porphyrin ring and location of the metal atom\textsuperscript{39,40,41,42}. This type of information promises to be of great value in disclosing the mechanisms of porphyrin catalysis.

2.1 Synthetic Porphyrins

In synthetic porphyrins, in general, three types of porphyrins are used by inorganic chemists as models for various reactions. viz. octaethyl porphyrin (OEP), meso-tetraphenyl porphyrin (TPP) and meso-tetra(p-tolyl) porphyrin(TTP). Tetraphenyl porphyrin (TPP) is most widely used by porphyrin chemists because of its easy synthesis than OEP. The phenyl groups in the structure favour crystallization of the TPP. In the case of p-substituted phenyl
groups, the shapes of the o- and m-phenyl $^1$Hnmr signals assist in the assignment of the coordination type$^{43,44}$. Furthermore, the tetraphenyl moiety has a greater π-acceptor capacity than the octaethyl porphyrin. In the present work, we have focused our attention towards TPP, TPPS$_4$ and their corresponding metalloporphyrins with di-, tri-, and tetravalent metal ions as photocatalysts. Therefore, it is necessary to know their salient features with respect to synthesis, structural features, properties and applications.

2.2 Synthesis of porphyrins

The synthesis of water insoluble free-base TPP is carried out by many research workers. Paul Rothemund$^{45}$ generalized the synthesis by condensing more than twenty five aliphatic, aromatic and heterocyclic aldehydes with pyrrole in the sealed tubes at 140 °C to 150 °C. The above synthesis was further modified to condensation of benzaldehyde and pyrrole in pyridine solution, in a sealed tube at 220 °C for forty eight hours$^{46}$. Further, Ball et. al.$^{47}$ modified the procedure of synthesis by addition of metal salt and the yield of TPP was increased from 4-5% to 10-11%. But the use of a sealed tube and length of time of 22-48 hours for synthesis, made it inconvenient to synthesize TPP easily. This method was then modified by Adler$^{31}$, where a propionic acid was chosen as solvent and refluxing time was reduced to half an hour and the yield of the TPP was found around 20%. Thus, this method proved to be beneficial in all ways with respect to time for synthesis, yield of the product and nature of crystals followed by purity.
When metals are inserted in porphyrin hole by the replacement of two protons in TPP, the resulting compounds are called metalloporphyrins. When metals are divalent, four bonds are formed with four equivalent nitrogen atoms as shown in Fig. 2.2. For tri and tetravalent metals, five and six bonds are formed with central metals as shown in Fig. 2.3 and Fig. 2.4 respectively. The metalloporphyrins were synthesized by Rothemund and Menotti\textsuperscript{48} by using TPP as precursor and different solvents with different duration of refluxing time. Further, Dorough et. al.\textsuperscript{49} synthesized metalloporphyrins using glacial acetic acid as a solvent. Their synthesis involved porphyrins of divalent metal ions like Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Ag\textsuperscript{2+} etc. Variety of metal porphyrins was also synthesized by Thomas and Martell\textsuperscript{50} but it suffered from optimization of refluxing time in general. In all the above methods, it was seen that poor solubility of metal carrier and TPP in the same selected solvent for synthesis. When metal salt was soluble in a solvent, TPP exhibited poor solubility in the same solvent and vice versa. This fact was taken into account by Adler et. al.\textsuperscript{32} and they investigated number of suitable solvents which showed maximum solubility of TPP and corresponding metal salts. The solvents used for synthesis were methanol, ethanol, propanol, butanol, phenol, tetrahydro furan, dimethyl sulfoxide and N, N' dimethyl formamide. Among these solvents dimethyl formamide showed higher solubility of TPP i.e. 1g /100mL with high dielectric constant. The refluxing reactions were completed within 10 minutes with the exception for SnTPPCl\textsubscript{2}. For Sn(IV) and Mg(II) porphyrins, the synthesis took more than two and half hours. This method was equally applicable for the synthesis of trivalent and tetravalent metals Fe\textsuperscript{3+}, Cr\textsuperscript{3+},
Mn^{3+}, Sn^{4+}, alkali metal porphyrins like Ba^{2+}, Ca^{2+} meso-tetraphenyl porphyrin, proto, hemato, deuteron, meso, phyllo, rhodo and meso-tetra(p-methyl)phenyl porphyrins. This reaction medium has also proven very convenient for the kinetic study of these reactions. With regards to the synthesis of non-aqueous dimers, it was observed by Fleisher et. al.\(^3\) that in alkaline medium monomers MnTPPCl and FeTPPCl undergo dimerization to form [O-(MnTPP)]\(_2\) and [O-(FeTPP)]\(_2\) respectively. These dimers were further isolated in the form of solids.

Water soluble porphyrins were synthesized to improve upon the limitations produced by non-aqueous porphyrins of TPP. Due to insolubility of TPP and its metalloporphyrins in water, the study of physicochemical properties and oxidation-reduction reactions was hampered\(^{51,52}\). Therefore, attempts were made to synthesize aqueous porphyrins by substituting ionized groups to the porphyrin molecule. Fleischer\(^53\) synthesized meso-tetra (4-pyridyl)porphyrin and some metal complexes with nickel, copper and zinc. The efforts were further carried on by various research workers\(^{54,55}\) where carboxylic, sulphonic and N-methylpyridyl groups were substituted to convert TPP into water-soluble porphyrins. This theme of synthesis made Fleischer\(^3\) to report tetraammonium tetra(p-sulphonyl)porphyrin followed by TPPS\(_4\), FeTPPS\(_4\)Cl and [O-(FeTPPS\(_4\))]\(_2\)]. The synthesis of TPPS\(_4\) by this method proved that it was a tetra sulphonated but tri sodium derivative and was a cumbersome method. Contemporarily, Pasternack et al reported synthesis which was devised by Menotti and further developed by Winkleman et. al.\(^{56}\) of tri sulphonated derivative (TPPS\(_3\)), tetrphenyltetracarboxyporphyrin (TCPP)\(^57\), and tetra(N-methyltetrapyridyl)porphyrin(TMPyP). It was also observed that TPPS\(_3\) and TCPP
contain negatively charged groups on their periphery while TMPyP contains positive groups at these positions. It was also shown that the nature of charge of the peripheral groups had a very large effect on the acidity and basicity of the porphyrin and more particularly, of the pyrrole nitrogens. Further, it was concluded that cationic porphyrins (TMPyP and TPyP) were considerably less basic than the anionic porphyrins (TPPS$_3$ and TCPP). Similarly, for meso- substituted porphyrins, the anionic porphyrins aggregate in water while the cationic porphyrins do not$^{58}$. The more simplified version of synthesis of tetrasydium meso-tetra (p-sulphophenyl)porphyrin (TPPS$_4$) was devised and reported by T. S. Srivastava and M. Tsutsui$^{34}$. This was confirmed by UV-vis spectroscopy, infrared spectroscopy and $^1$Hnmr spectroscopy. This method involves long duration for synthesis but confirms the product accurately. Similarly by virtue of the method, it involves water of crystallization i.e. a hydrated free-base porphyrin. Recently, the newly synthesized water soluble free base porphyrins are reported$^{59}$, where substitution of Br, OH, is observed. It is also observed that porphyrins are synthesized by substitution of Br and SO$_3$H or OCH$_3$ and SO$_3$H on the same phenyl ring. In addition to above mentioned methods of synthesis of metalloporphyrins$^{33,53}$ the attempts were done by other research workers. Cheung et. al.$^{60}$ synthesized CuTPPS$_4$ and ZnTPPS$_4$ to study the rates of incorporation of Zn$^{2+}$, demetallation of Zn$^{2+}$ and displacement of Zn$^{2+}$ in ZnTPPS$_4$ by Cu$^{2+}$ ions. Further, Corsini et. al.$^{61}$ studied the reactivity of TPPS$_4$ with variety of metals in the periodic table. They had the conclusion that TPPS$_4$ reacts slowly with metal ions and prolonged heating is required for metalloporphyrin formation. The extension of this study made Krishnamurthy et. al.$^{62}$ to examine
monomer-dimer equilibrium of water soluble porphyrins as a function of the coordinated metal ion. They further found that TPPS₄ and its Cu²⁺, Pd²⁺ and Ag²⁺ complexes undergo dimerization whereas TPPS₄ complexes of Zn²⁺, V⁴⁺, Cr³⁺, Mn³⁺ and Co³⁺ remain monomeric in nature. Horrocks et al.⁶³ reported water soluble complexes of lanthanides where TPPS₄ ligand formed complexes with Ho, Er, Tm, Yb and Lu respectively. The method of synthesis required an inert atmosphere of dry nitrogen and metal acetylacetonates of corresponding metals.

2.3 Purification of porphyrins

Metalloporphyrins after isolation from the reactions are purified by three possible methods viz. i) adsorption chromatography or column chromatography ii) crystallization, and iii) sublimation⁶⁴.

i) Adsorption chromatography or column chromatography

In most of the cases alumina or silica are used as stationary phase and mobile phases may be chloroform, dichloromethane or benzene. If the complex is strongly adsorbed, due to the presence of axial ligands, methanol or solvents of similar polarity have to be added to the eluents. Chromatography generally separates unreacted porphyrin acid, chlorin, metallochlorin etc. The distinction among different components is done on the basis of their UV-vis spectra. In case of difficult separations, silica plates (20 × 100 cm) with an adsorbent layer of 0.5 - 1.0 mm. thickness are very effective⁶⁵. These plates can be loaded with approximately 50 - 200 mg, according to the problems encountered. They are especially useful in separating complexes of very different polarity. Further, dry
column chromatography method was recommended for superior separations of components in a given mixture but it had the disadvantage of separation of isomers in pure state.

ii) Crystallization

It was frequently observed that many porphyrins were not stable in the presence of sunlight or diffused light. In this situation, there was every possibility of decomposition of porphyrins on the column itself. Therefore, in such cases a method of recrystallization was used.

iii) Sublimation

This is another reliable method for the purification of porphyrins. This was tried by Adler et. al where crude TPP was sublimed using purified nitrogen gas as the carrier. In this method, large, single-crystal needles of TPP of high purity were obtained. Alternatively, TPP was also purified by vacuum sublimation, which gave octahedral or rhombohedral crystals, rather than needles.
2.4 Structural features of porphyrins

The unique nature of chemistry in metalloporphyrins has developed growing interest among chemists. The progress in synthetic porphyrins has shown that the porphyrin moiety is tetradentate but also can act as bi-, tri-, or hexadentate ligand\(^{67-70}\). In addition, metal ion has been observed to possess 4-, 5-, 6-, or 8-coordination. These things are of interest because of their obvious relevance as biological models. Metalloporphyrins are studied for other reasons such as the search for new semiconductors, conductors\(^{71}\), catalysts\(^{72}\) and chemical shift reagent\(^{73}\).

Porphyrins like other \(\pi\)-macrocycles have a central 'hole' or 'core' (Fig. 2.1 – 2.6) of fixed size which can be altered by the puckering of the porphyrin macrocycle. The range of the variation of the 'core' has been observed to lie between 2.098 \(\text{Å}\) and 1.929 \(\text{Å}\). In certain complexes the metal ion is unable to fit into this 'hole' and therefore lies out of the porphinato nitrogen plane\(^{74}\). It was also observed that the ionic radius of a metal, which is a best-fit for the 'hole' in the moiety of the porphinato ligand was 0.64\(\text{Å}\). This selection is based on the metal ion of ionic radius between 0.69 \(\text{Å}\) [Sn(IV)] and 0.60 \(\text{Å}\) [Ni(II)] may produce a coplanar MN\(_4\)- moiety in a metalloporphyrin and the smaller ions will produce considerable radial strain\(^{75}\).
Fig. 2.1 Structure of free-base TPP

(1)
Fig. 2.2 Structure of MTPP, $M = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+},$ and $\text{Ag}^{2+}$

(II)
Fig. 2.3 Structure of MTPPCl, $M = \text{Mn}^{3+}$ and $\text{Fe}^{3+}$
Fig. 2.4 Structure of SnTPPCh

(IV)
Fig. 2.5 Structure of free-base $\text{TPPS}_4\text{Cl}$. 

(V)
Fig. 2.6 Structure of O-(FeTPPS₄)₂ dimer, the sulphonated phenyl groups are left out of clarity

( VI )
The basic unit of a free-base TPP [Fig. 2.1] is porphyrin ring which contains four pyrrole rings joined with four methine bridges and forms the conjugated system, which contains 18 delocalized $\pi$ electrons ($4n + 2$, where $n = 4$). The pyrrole rings build up closed aromatic plane, playing the role of a nucleus of the compound. The four phenyl rings are perpendicular to the plane of porphyrin ring. The flat porphyrin ring can be deformed in the process of metalation, where a metal ion replaces the hydrogen atoms in imide groups of pyrrole. The porphyrin ring possesses rectangular geometry with $D_{2h}$ symmetry. When acid is added to TPP it forms dication $[\text{H}_4\text{TPP}]^{2+}$ and porphyrin possesses square geometry with four fold symmetry.

The process of metalation involves formation of $P^{2-}$ moiety by replacement of two imide hydrogens and substitution of respective metal in the porphyrin core. When divalent metal ions like $\text{Co}^{2+}$, $\text{Ni}^{2+}$, $\text{Cu}^{2+}$, $\text{Zn}^{2+}$ and $\text{Ag}^{2+}$ are present (Fig. 2.2) then coordination number of metal is four with square planar geometry and $D_{4h}$ symmetry. Thus in this case coordination sphere is completed by balancing the charge on the $P^{2-}$ moiety by divalent metals. In this series of complexes, $\text{CoTPP}$, $\text{NiTPP}$ and $\text{CuTPP}$ are possessing ruffled cores whereas $\text{ZnTPP}$ and $\text{AgTPP}$ possess planar cores. The complexes of this type are called four coordinate complexes.

For trivalent metals like $\text{Mn}^{3+}$ and $\text{Fe}^{3+}$, central metal forms four bonds with four nitrogens and one bond with Cl to complete coordination sphere. This additional ligand Cl is called an axial ligand. Therefore, $\text{MnTPPCl}$ and $\text{FeTPPCCl}$
(Fig. 2.3) form five coordinate complexes with square pyramidal geometry. In these complexes, as per X-ray studies the metals are slightly shifted from the center of porphyrin core and are present out of plane of the porphyrin ring.

In case of SnTPPCl₂, in addition to tetradentate porphyrin ligand, two Cl ions are present one above and one below the plane of the porphyrin ring. This makes a complex six coordinate with octahedral geometry. Since, two axial ligands are identical; therefore, the complex possesses D₄h symmetry. The metal Sn is present in the plane of porphyrin ring (Fig. 2.4).

In the context of water soluble porphyrins, sodium salt of sulphonic acid is substituted at the para- position (4-position) of four phenyl rings in TPP and is abbreviated as TPPS₄. Due to its well defined structure (Fig. 2.5) and properties, TPPS₄ is widely used in clinical experiments as a potential sensitizer for the photodynamic therapy. The structural features of TPPS₄ and other corresponding metalloporphyrins with Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag²⁺, Mn³⁺, Fe³⁺, and Sn⁴⁺ are identical as mentioned for TPP and its metalloporphyrins.

Further, it was also investigated that dimers of MnTPPCl and FeTPPCl existed in basic medium and the structures have been determined by X-ray diffraction. As discussed earlier the Fe³⁺ ions of two porphyrin rings are shifted slightly out of plane and they are bonded through a bridge of oxygen. Therefore, these compounds are named as µ-Oxo- bis[tetraphenylporphinatoiron(III)]. O-(FeTPP)₂ and O-(MnTPP)₂ µ-Oxo-bis[tetraphenylporphinatomanganese(III)]. These are five coordinate complexes where each porphyrin ring is centrosymmetrically bonded to Fe³⁺. Similarly, it was also found that FeTPPS₄ exist as monomer in
acids and undergoes dimerization in basic medium at pH greater than 9 to give a dimer, O-(FeTPPS₄)₂. This was a six coordinate complex, especially when it contained presence of water of hydration (Fig. 2.6). Further, Krishnamurthy et al., reported that TPPS₄ and its complexes with Cu²⁺, Pd²⁺, and Ag²⁺ showed dimerization whereas with Zn²⁺, V⁴⁺, Cr³⁺ Mn³⁺ and Co³⁺ were found in monomeric forms.

2.5 Properties of porphyrins

The porphyrins and their metal complexes are found to possess many interesting properties, which can be investigated by various analytical techniques. The characteristic properties of these molecules include spectroscopic, thermal stability, photoconduction, photoemission and surface activity.

2.5.1 UV-visible spectroscopy

The porphyrins exhibit high molar absorbance coefficients in the order of 10⁴-10⁶, which becomes their most specific property. This is the reason to make them to be identified by UV-visible spectroscopy. On account of strong chromophore in porphyrins, in no way it allows the interference of absorbance bands due to metals. The free-base porphyrins and metalloporphyrins show characteristic spectra.

1) Q bands: There are two visible bands between 500 and 600 nm, which are separated by ≈ 1250 cm⁻¹. The lower energy band (sometimes called α) is the electronic origin Q (0,0) of lowest excited singlet state. The higher energy band
(sometimes called \( \beta \)) includes one mode of vibrational excitation\(^9\) and is denoted \( Q(1,0) \).

2) B bands: An exceedingly intense band (sometimes called the Soret band) appears between 380 and 420 nm. It is the origin \( B(0,0) \) of the second excited singlet state. In this region one more band may be possible and is denoted by \( B(1,0) \).

3) N, L, M bands: To the blue of Soret band, metalloporphyrins generally show a weaker \( N \) band\(^9\) at \( \approx 325 \) nm and an \( M \) band at \( \approx 215 \) nm. Between these bands often \( L \) band is present.

The spectra of metalloporphyrins can be classified as "regular" or "irregular depending on whether the metal inside the porphyrin ring has an open or closed valance electron shell\(^2\). The regular porphyrins show fluorescence e.g. TPP, TPPS\(_4\), ZnTPP, SnTPPCL\(_2\). The solid state samples are purple in colour and in solution form free-base porphyrins exhibit purple colour whereas metalloporphyrins show wine red colour. In normal type absorption spectra of regular porphyrins there are no or little interactions between the atomic orbitals of metal and \( \pi \)-molecular orbitals of porphyrin ring.

In case of "irregular" metalloporphyrins there are two types of spectra viz. hypso-, and hyper--type. The hypso-spectra show as usual in regular porphyrins but it is only blue shifted. Therefore, it is not recognized as a special case. The porphyrins of metal ions \( \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+} \) and \( \text{Ag}^{2+} \) (i.e. \( d^6 - d^9 \) configurations) show hypso-type spectra.
The hyper-type spectra is a consequence of charge transfer and metal ligand interactions. There are two types in this category: p-type and d-type hyper spectra. The p-type hyper spectra are the consequence of charge transfer from the metal p-orbitals to the empty porphyrin π*-orbitals. The metal ions like Sn²⁺, Pb²⁺, and Sb³⁺ show this type of spectra. The d-type hyper spectra are seen due to the transfer of charge from filled porphyrin π-orbital to the empty d-orbitals of the transition metals. This process is called ring-to metal charge transfer. The examples of this type of spectra are porphyrins of Mn³⁺ and Fe³⁺ ions (d¹ - d⁵ configurations). These types of porphyrins are brown or green coloured in solid state as well as in the solution form³.

2.5.2 Infrared spectroscopy

The nature of the coordinate linkage in metal porphyrins was investigated by infrared spectroscopy. The weak N-H stretching vibrations above 3300 cm⁻¹ for all ligands disappear in the chelates, since acidic hydrogens are replaced by respective metal ion. Replacement of these imino hydrogen atoms results in shifts of many absorption bands of the ligand to both higher and lower frequencies. The main absorption bands of the metal chelates of tetraphenyl porphyrin appear near 1600 cm⁻¹ and at lower frequencies. The strong absorption band near 1000 cm⁻¹ appears to be a vibration of the porphyrin ring or the pyrrole units, which is sensitive to the nature of metal ion and which is directly related to the strength of the metal-nitrogen bonds in the tetraphenyl porphyrin chelates⁴,⁵,⁶. It is also seen that the porphyrin ring and phenyl rings are not coplanar; therefore,
interactions of the substituents at meso- positions with metal-ligand bonds are inductive rather than resonance effect.

When metalloporphyrins are containing axial ligands, the metal-to-ligand vibrations are very characteristic but metal-to-nitrogen vibrations are difficult to recognize. Moreover, many axial ligands have their own characteristic inner vibrations that can be identified besides the porphyrin bands. For example, the metal-ligand moieties involved have the following typical bands: MO-H, 3580 – 3640 cm\(^{-1}\); M = O, 820 – 1100 cm\(^{-1}\); M-O-M, 630 – 900 cm\(^{-1}\); M-O, 450 - 650; M-Cl, 260 - 360 cm\(^{-1}\).

The axial ligands containing triply bonded atoms are, of course, very easily detected: N\(_3\) (2055 cm\(^{-1}\)), NCS (2042 cm\(^{-1}\)), CN (2100 cm\(^{-1}\)), CO (1891 - 2100 cm\(^{-1}\)) etc.

### 2.5.3 Proton magnetic resonance spectroscopy (\(^{1}\)Hnmr)

In the early applications of NMR to porphyrins, \(^{1}\)Hnmr was the most widely used as an analytical tool, and the new structural insights that are resulted were a major reason for the revival of interest in porphyrin chemistry. The first \(^{1}\)Hnmr spectra of porphyrins were reported by Becker and Bradley [96] and by Ellis et. al.\(^{97}\). The early survey of a variety of porphyrin structures was carried out by Caughey and Koski\(^{98}\). Based on the extensive synthetic work, a series of researches were carried out by Abraham on a number of special aspects of porphyrin behaviour, especially the effects of substitution, the self aggregation in solution, isomerism of porphyrins, and interactions of nucleophiles with the central metal
atom of metalloporphyrins. The effects of meso substitution on the $^1$Hnmr of porphyrins differ significantly from the effects of $\beta$ substitution. In addition to being qualitatively different, the changes in chemical shift from meso substituents are quantitatively much larger. The presence of methyl or phenyl group at a meso position, results in a general upfield shift for all outer peripheral protons and down-field shift for the inner N-H protons. This behaviour is consistent with a diminished ring current in the macrocycle. The $^1$Hnmr studies of porphyrins are classified into two classes, namely, diamagnetic and paramagnetic porphyrins. Free-base porphyrins and metalloporphyrins of Ni$^{2+}$, Zn$^{2+}$ and Sn$^{4+}$ are found to be diamagnetic whereas porphyrins of Co$^{2+}$, Cu$^{2+}$, Ag$^{+}$, Mn$^{3+}$, Fe$^{3+}$ are paramagnetic in nature. It was also reported that the range of paramagnetic shifts is many orders of magnitude larger than the range of diamagnetic shifts for a given functional group.

2.5.4 Mass spectroscopy

The porphyrins and metalloporphyrins undergo fragmentations in the mass spectrometer which are easily rationalized in terms of normal organic mass spectrometry. In the absence of labile or certain functionalized side-chains, the base (100%) peak is usually molecular ion. The predictable intensity of the molecular ion is particularly useful for molecular weight determination. Mass spectra of porphyrins and their derivatives are best recorded at the lowest possible temperature (usually approx. 200-250 °C). If higher temperatures are used, more opportunity for pyrolysis and fragmentation of the molecular ion is
possible. At very high temperatures (400-800 °C), thermal degradation of the
nucleus into monopyrroles is known to occur\textsuperscript{102,103}. The intensity of molecular
ions in mass spectra of porphyrins has also been used\textsuperscript{104,105} in the studies of
deuteration (as a general example of electrophilic substitution) of porphyrins,
metalloporphyrins and some reduced derivatives.

As is seen in usual mass spectrometry the physical appearance of the
molecular ion enables one to ascertain the presence of halogens, metals etc. in
compounds. This is useful in the identification of unknown metalloporphyrins
because of the general tendency for metal ions not to be lost in fragmentation
process. Many metalloporphyrins sublime in high vacuum without
decomposition\textsuperscript{106}. Many others containing neutral axial ligands dissociate on
heating. First the axial ligand L, and then, on further heating, the species M(P) or
M(P)X appears in the mass spectrum. In these cases, it cannot be decided whether
L is really present as an axial ligand or only a crystal solvate molecule.
Occasionally, the solid or the vapour of a metalloporphyrin suffers thermolysis,
hydrolysis, condensation, or both of the latter alterations. Therefore, it is
recommended to rely on the mass spectra only in the straight forward situation. In
spite of this fact, mass spectra, serve very well to identify the central metal
because the $M(P)^+$ fragment ion is normally the one occurring with the highest
intensity in the mass spectrum\textsuperscript{106}. 

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2.5.5 Fluorescence spectroscopy

It is generally accepted that the prominent electronic transition of porphyrins and their metal complexes are $\pi - \pi^*$ transitions associated with the porphyrin ring. Most of the luminescence and photochemistry observed from these compounds is associated with the $\pi - \pi^*$ states of the porphyrin ring, even though, the lifetimes and reactivities of these states depend strongly on the metal ion incorporated\textsuperscript{107}. In general most of the free base porphyrins, chlorins, and related compounds show strong fluorescence at room temperature and in rigid glasses they show fluorescence and phosphorescence. Metalloporphyrins luminescence falls into several categories, which is dependent upon the electronic structure of metal. For free-base TPP, fluorescence $\lambda_{\text{max}}$ and singlet energies are 660 nm and 45 kcal/mol. When metals are containing either empty or full d-shells and form complexes with tetraphenyl porphyrin or octaethyl porphyrin then they show fluorescence at room temperature\textsuperscript{108,109} and both fluorescence and phosphorescence at liquid nitrogen temperature. The fluorescence yield tends to decrease with increasing atomic number of the metal as does the phosphorescence. The emission spectra are usually shifted to longer wavelengths as the square-planar metalloporphyrin accepts axial ligands in the fifth and sixth coordination positions\textsuperscript{110}.

The porphyrins besides fluorescence show three types of emissions.

i) Phosphorescence: Phosphorescent metalloporphyrins show weak fluorescence, that is, $\Phi_f < 10^{-3}$, and in many cases no fluorescence at all is observed.
Phosphorescence yields are variable over the entire range from $1 > \Phi_p > 10^{-4}$.

Phosphorescence lifetimes are short, with $\tau_p < 3$ msec.

ii) Luminescence: Luminescent porphyrins contain paramagnetic metals. These emissions cannot be characterized as fluorescence or phosphorescence because the molecular states are not singlet and triplets. The emission yields are above $10^{-4}$, and emission parameters often show strong temperature dependence.

iii) Radiationless emissions: Radiationless porphyrins show at most very weak emission, that is, total emission yields are under $10^{-4}$. In many cases no emission at all has been documented.

2.5.6 X-ray diffraction studies

It was observed fact that within the accuracy of the experimental data, there exist small differences between naturally occurring porphyrins and the synthetic derivatives. For structural analysis, derivatives of symmetric porphyrins like TPP, OEP, TPyP (tetra pyridyl porphyrin) and Etio (Etioporphyrin) were used. When porphyrin acts as a tetradentate ligand, the symmetry and relative rigidity of the porphinato core are the properties of interest for a wide range of metal ions. The X-ray diffraction technique has been extensively used to determine the bond lengths and bond angles among the different atoms in a given structure. The parent compound TPP has four phenyl rings which are perpendicular to the plane of the porphyrin ring and establishes its non-coplanarity. It is also observed that depending upon the nature of the metal present in porphinato core the coordination number of metal changes and variety of structures are coming into
existence\textsuperscript{112,113}. Thus the stereochemistry of the porphyrins is best studied by X-ray diffraction method. Therefore, it is quite rational to consider the stereochemistry as a function of d electron configuration in porphyrin chemistry\textsuperscript{114}.

i) The d\textsuperscript{0} complexes include Mg, Ti, Hf and Zr derivatives. Magnesium porphyrins are of interest because of the importance of chlorophyll in photosynthesis. The large size of the Magnesium ion leads to five coordinate square-pyramidal geometry. In H\textsubscript{2}OMgTPP\textsuperscript{115} the magnesium ion is displaced 0.27 Å from the mean plane. Similarly, the large size of the Hf\textsuperscript{4+} and Zr\textsuperscript{4+} in (OAC)\textsubscript{2}HfOEP and (OAC)\textsubscript{2}ZrOEP the metal is displaced 1.0 Å from the plane of the nitrogen atoms.

ii) The d\textsuperscript{1} complexes has only example of vanadyldeoxophylloerythroetioporphyrin, which is an asymmetrically modified porphyrin\textsuperscript{116} closely related to ‘chlorophyll a’. The V\textsuperscript{4+} ion is displaced from the mean plane of four nitrogen atoms by 0.48 Å.

iii) The d\textsuperscript{4} complexes are including the derivatives of Mn\textsuperscript{3+}, which are high spin derivatives with four unpaired electrons. Five coordinate Mn(III) structures include MnTPPCl. The reasons for the displacement of Mn(III) ion out of plane by 0.27 Å are not clear.

iv) The d\textsuperscript{5} complexes include the stereochemistry of high spin Fe(III), which are the most thoroughly studied porphyrins. In FeTPPCl, a square-pyramidal complex, the Fe atom is displaced from the plane of four nitrogen atoms by 0.38 Å. The dimer of iron(III) i.e. [O-(FeTPP)\textsubscript{2}] where Fe atom is displaced\textsuperscript{117} from the plane is by 0.50 Å.
v) The $d^6$ complexes are containing Co(III), Fe(II), Ru(II), Os(II), Rh(III) in their respective porphyrins. In 2-MeImFeTPP complex, Fe is displaced out of plane by 0.42 Å whereas in ONFeTPP and (acetonyl)CoTPP, the respective Fe and Co are displaced by 0.21 Å and 0.11 Å from the porphyrinato plane.

vi) All cobalt porphyrins i.e. Co(II), are $d^7$ low spin complexes. The stereochemistry of cobalt porphyrins displays considerable diversity according to the oxidation state and the number of axial ligands. It was observed that in NMeImCoTPP$^{118}$ and DiMeImCoTPP$^{119}$ the Co(II) ion is displaced out of the porphyrinato plane by 0.14 Å and 0.18 Å.

vii) The $d^8$ metalloporphyrins have been studied intensively as Ni(II) derivatives. The square-planar coordination is especially stable for this electronic configuration and many low-spin four-coordinate complexes of Ni(II) have been characterized. The examples are NiTPP, NiOEP and NiEtio etc. these complexes are found to be planar or nearly planar with respect to four nitrogen atoms of porphyrin ring.

viii) The $d^9$ complexes prefer planar geometry. These complexes have little tendency to add axial ligands, and all characterized metalloporphyrins of this group are four coordinate. The examples of this type are, CuTPP, AgTPP etc. The crystals of CuTPP are isomorphous with the PdTPP derivative and accordingly have $S_4$ symmetry. The Cu-N bond distance is 1.981 Å. The porphinato core is slightly more ruffled than in PdTPP derivative with the methane carbon atoms displaced, $+0.42$ Å and $-0.42$ Å from the mean plane of the porphyrin nucleus. The crystals of meso-tetra-n-propylporphyrin (CuTPrP) have required $C_3$ symmetry and the porphinato core is essentially planar. As a result, longer Cu-N bonds could be expected in this complex.
compared to CuTPP. The crystal structure of AgTPP provides an example of a metalloporphyrin structure in which unequal M-N distances are observed.

ix) The $d^{10}$ complexes of this group are closed shell ions of the main groups of periodic table. The size of the most metal ions of this group tends to be larger than the normal centre to nitrogen distance of the plane of porphyrin ring. The examples of this type are ZnTPP, PyZnTPyP, H$_2$OZnTPP, ClO$_4$ZnTPP, SnTPPCl$_2$ and SnOEPCl$_2$ etc. In PyZnTPyP, the Zn (II) ion is displaced 0.33 Å and in ZnTPP there is no displacement of Zn(II) ion from the plane of the porphyrin ring. In SnTPPCl$_2$ due to presence of two axial ligands the expanded porphinato core is seen and Sn(IV) is present at its centre. In SnOEPCl$_2$, the porphinato core expansion is not much as is seen in SnTPPCl$_2$ and Sn(IV) is at the centre.

2.5.7 Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectroscopy (DRS) is a more convenient technique to characterize the materials under consideration than UV-Visible absorption spectroscopy, since it can be used in the solid state where an enhanced scattering of light is taken into account. The technique is non-destructive and is used to determine the energy gap ($E_g$) in semiconductors in optoelectronics$^{120-123}$. A common way of determining band gap from absorption spectra is the percent reflectance ($\%R$) is made function of wavelength and from the corresponding graph $E_g$ is calculated. To arrive at more certain $E_g$ values, the usual spectra are given Kubelka-Munk treatment, which involves intersection between the linear fit and the photon energy axis. This method of calculating $E_g$ is also helpful when
there are erroneous results from usual UV-visible absorption peaks. The absorption peaks are obtained by plotting absorbance as a function of photon energy in electron volts (eV). A more common way of getting $E_g$ is first derivative of absorption with photon energy and finding the maxima in the derivative spectra at the lower energy side\textsuperscript{124}. The $E_g$ is associated to the maximum in the spectrum, i.e. where the absorbance has a maximum increase with respect to photon energy. The first derivative method is convenient when the absorption peak dominates the spectrum as is observed in colloidal samples\textsuperscript{125}. If the scattering effect is as high as the optical absorption process, it screens the absorption peak and makes calculation of $E_g$ difficult. To avoid the difficulties in obtaining $E_g$ from UV-Visible absorption spectroscopy in dispersed samples, diffuse reflectance spectroscopy (DRS) of dry powders can be performed. DRS values are calculated by plotting $\%R$ versus wavelength or Kubelka-Munk transformed reflectance versus photon energy. The latter method of plotting confirms the assignment of $E_g$ with more certainty.

The theory which makes possible to use DRS was proposed by Kubelka and Munk. In the limiting case of infinitely thick sample, thickness and sample holder have no influence on the value of reflectance ($R$). In this case, the Kubelka-Munk equation at any wavelength becomes:

$$K/S = (1 - R_{\infty})^2 / 2 R_{\infty} = F(R_{\infty}) \quad \text{********} (1)$$

K and S are called K-M absorption and scattering coefficients respectively.

$F(R_{\infty})$ is the so called remission or Kubelka-Munk function, where

$$R_{\infty} = R_{\text{sample}} / R_{\text{standard}} \text{\textsuperscript{126}}$$
In the parabolic band structure, the band gap $E_g$, and absorption coefficient $\alpha$ of a direct band gap semiconductor are related through well-known equation\(^{127}\).

$$\alpha h\nu = C_1 (h\nu - E_g)^{1/2} \quad \text{(2)}$$

Where $\alpha$ is the linear absorption coefficient of the material, $h\nu$ is the photon energy and $C_1$ is proportionality constant. When the material scatters in perfectly diffuse manner (or when it is illuminated at $60^\circ$ incidence), the K-M absorption coefficient $K$ becomes equal to $2\alpha$. In this case, considering the K-M scattering coefficient $S$ as constant with respect to wavelength, and using the remission function in Eq. (2), we obtain the expression:

$$[F(R_\infty)h\nu]^2 = C_2 (h\nu - E_g) \quad \text{(3)}$$

Therefore, obtaining $F(R_\infty)$ from Eq. (1) and plotting the $[F(R_\infty)h\nu]^2$ against $h\nu$, the band gap $E_g$ of a powder sample can be determined easily.

A simple diffuse reflectance UV-visible spectroscopic determination was used\(^{128}\) for screening organic pigments like fringelites or porphyrins, in sediments and fossil specimen. In contrast to common inorganic pigments, like Fe$_2$O$_3$, these pigments exhibit well-structured characteristic absorption peaks which allow their recognition.

### 2.5.8 Electron spin resonance (ESR) studies:

The ESR technique enables one to detect and in many cases to characterize systems with one or more unpaired electrons. In the context of paramagnetic porphyrin system, one or more unpaired electrons may reside either on the $\pi$-ligand system or in the central metal atom, or in both. The underlying principle of
ESR depends upon the number as well as the location of the unpaired electrons in a system, thus making the technique very useful in porphyrin radical chemistry.

The magnetic moment $\mu$ of an unpaired electron is given by

$$\mu = g \beta S$$

where $'g'$ is the ratio of the magnetic moment to the total angular momentum, 'S' is the spin angular momentum in units of $h/2\pi$, and $'\beta'$ is the Bohr magneton. In the presence of an external magnetic field $H$, the component of $S$ in the direction of $H$ is quantized and can have two values $M_s = \pm 1/2$. Thus there are two energy levels $\pm (1/2)\beta H$, and the frequency of electromagnetic radiation required to induce transitions between the two states is $\nu = (g\beta/h)H$.

The $g$-value is a dimensionless parameter which can be determined from the experimental ESR spectrum. It is determined solely by the spin and orbital angular momenta of the unpaired electron. In a spherically symmetric environment (S-state) the orbital angular momentum is zero, and the $g$ has the free-spin value 2.0023. In solids, the $g$-value depends on the orientation of the magnetic field to the symmetry axes of the electric field about the ion, leading to anisotropy in the $g$-values. A major absorption takes place when the external magnetic field is perpendicular to the symmetry axis (say $z$), ($g_x = g_y = g_\perp$) and minor absorption takes place if the applied magnetic field is parallel to the symmetric axis ($g_z = g_\parallel$). This situation is observed in most of the metalloporphyrins since the square-planar ligand field possesses an axial symmetry. When the environment is orthorhombic, one observes three different $g$-
values in the solid state. With solutions where the tumbling motions of molecules produce an average electric field, only a single g-value, i.e. \( g_{\text{avg}} = \frac{1}{3} (g_x + g_y + g_z) \) or \( g_{\text{avg}} = \frac{1}{3}(2g_\perp + g_\parallel) \) is observed. The g-value is characteristic of the metal ion, its oxidation state and its molecular environment\(^{130,131,132}\).

It is to be noted that if the electron spin and the nuclear spin are parallel prior to an ESR transition, they will be antiparallel after the transition and vice versa. A splitting of an ESR line due to interaction between the nuclear spin and the electron spin of the same atom is known as hyperfine splitting. The number of hyperfine splitted lines is given by the total number of orientations of the nuclear spin, i.e. \( (2I + 1) \). These lines are equally separated with a spacing of ‘A’ called as hyperfine splitting constant. If there are \( n \) equivalent nuclei of nuclear spin ‘I’, then the number of lines obtained\(^{133}\) is \( (2nI + 1) \). An important characteristic of Fe(III) porphyrins is that they do not give any ESR spectra at room temperature because the spin-lattice relaxation times are very short. Therefore, for a reasonably good ESR spectra are obtained at liquid nitrogen temperature and sharper and more intense lines are observed at liquid helium temperature.

Co(II) porphyrins are extensively studied by ESR because of their importance in oxygen adsorption. The three distinct types of ESR spectra of Co(II) are i) the adducts of Co(II) porphyrins with \( \pi \)-acceptors ii) the complexes of Co(II) porphyrins with Lewis bases (generally a five coordinate complex) iii) the molecular oxygen adducts of Co(II) porphyrins\(^{134}\).
Copper porphyrins are most extensively studied and best understood class of metalloporphyrin. There are two reasons for this: i) they can be studied at room temperature and ii) it is simpler to interpret the electronic structure of d^9 system\textsuperscript{135}.

Silver porphyrins were not studied as extensively as copper porphyrins because of uncertainties in interpretations and experimental difficulties. The careful study of AgTPP in TPP single crystals\textsuperscript{136} provided some reliable data.

### 2.5.9 Magnetic studies

The aim of magnetic susceptibility measurements of metalloporphyrins is to confirm or establish the oxidation state of the metal ion and to find if any peculiar magnetic interactions are present\textsuperscript{137}. The experimental distinction between high-spin and low-spin complexes is based on the determination of their magnetic properties. Complexes are classified as diamagnetic if they tend to move out of a magnetic field and paramagnetic if they tend to move into a magnetic field. The extent of the paramagnetism of a complex is commonly reported in terms of the magnetic dipole moment it possesses. If higher the magnetic dipole moment of the complex, the greater the paramagnetism of the sample is observed\textsuperscript{138}. For his purpose, $\mu_{\text{eff}}$ is compared with the ‘spin only’ value computed from the equation $\mu_{\text{so}} = \sqrt{N(N + 2)}$, where N is the number of unpaired electrons. Many tabulations show the range of $\mu_{\text{eff}}$ values to be expected from a particular magnetically dilute
metal ion in a given environment. More information can also be obtained from susceptibility measurements at low temperatures and high field strengths, using single crystals. The susceptibility of solids or solutions can be measured on large scale by Gouy method when sample size is greater than 100 mg. The Faraday method, however, is more useful for porphyrin studies, where only a limited amount of solid material is available i.e. less than 5 mg. Balances for measurements from ambient temperatures to 77 °K can be inexpensively constructed\textsuperscript{139,140}. Either method requires a standard of known susceptibility and Hg[Co(SCN)\textsubscript{4}]\textsuperscript{141} has been most widely used. Different groups of research workers\textsuperscript{142} have shown that the temperature dependence of the susceptibility of this complex when measured by the Faraday method differs from that obtained by the Gouy method. Many workers determine metalloporphyrin susceptibilities in solution by Evans PMR method\textsuperscript{143,144}. The shift of a proton resonance line of an inert reference substance due to a paramagnetic species given by \((\Delta H / H) = (2\pi/3)\Delta \kappa\), where \(\Delta \kappa\) is the change in volume susceptibility. The same precision\textsuperscript{145} in the measurement of the paramagnetic susceptibility can be obtained by a PMR study on 50 mg of material at 60 MHz where Gouy method requires 400 mg of the sample. Further, it is an observed fact that magnetic susceptibility measurements are routinely used by chemists to probe the stereochemistry and electronic state of metal ions in coordination compounds.

The magnetic susceptibilities of FeTPPCl and [O-(FeTPP)\textsubscript{2}] were determined by Faraday method\textsuperscript{146} at 293 \(K\), 194 \(K\) and 77 \(K\) respectively. The magnetic susceptibility of FeTPPCl follows the Curie-Weiss law. This indicates iron has a

37
spin of 5/2 and is in a high spin state. This has been observed for other Fe(III) porphyrins\textsuperscript{147}. The dimer's magnetic properties definitely indicate an antiferromagnetic interaction between the two iron ions of the dimer. The magnetic susceptibility values were determined for MnTPPCl, \([\text{O-}(\text{MnTPP})_2]\) by Faraday method whereas for FeTPPS\textsubscript{4} and \([\text{O-}(\text{FeTPPS})_2]\), Evan's method was used. It was also seen that the water-soluble porphyrins of Fe(III) showed higher magnetic moment than carefully dried porphyrins. This has differentiated between the structural aspects of hydrous and anhydrous porphyrins\textsuperscript{33}.

2.6 Thermal studies

Edwards et. al.\textsuperscript{148} determined the heats of sublimation for both porphyrins and phtahalocyanines. It was also revealed that these values of heats of sublimation were higher in magnitude for the above compounds and it certainly reflected upon the relatively strong interactive tendencies of these structures seen in so many of their other physical properties\textsuperscript{149}. A series of porphyrin polymers containing different groups was synthesized and studied\textsuperscript{150} using TG, DSC, and FTIR. The thermal behaviours including the possible conformation transition and phase transition of porphyrins were studied during the heating process at lower temperature. It was observed that porphyrins with spacer groups exhibited higher thermal stability than that without spacer group.
2.6.1 Photocatalytic studies

The heterogeneous catalysis is one of the powerful techniques which can be employed for the total oxidation of organic and inorganic water pollutants and various dyes used by different types of industries. The photoassisted catalytic decomposition employing semiconductors has been a promising method for the same purpose\textsuperscript{151,152,153}. The main steps which can be envisaged in a photocatalytic processes are\textsuperscript{154}:

i) Photogeneration of electron-hole pairs and their trapping by suitable reducible-oxidable species to avoid recombination;

ii) Chemical transformation of these species into suitable products and their separation (desorption) from the reacting media;

iii) Restoration of the initial conditions to photocatalysts

The photolytic process may occur with any type of solids but more favourably with semiconductors. The only condition is the formation of species containing chromophore groups and the use of suitable light irradiation. When semiconductors solids are used, the redox reaction mechanisms, specific for the semiconductors, may mix up with photolytic processes. Many different photocatalysts have been used in the field of photocatalysis. Among the various inorganic semiconductors TiO\textsubscript{2}, ZnO, CdS and SnO\textsubscript{2} are widely employed as photocatalysts for the degradation of variety of environmental contaminants due to their high photosensitivity and large bandgap, i. e. high driving force for
reduction and oxidation processes respectively\textsuperscript{155,156,157}. Despite the positive aspects of these photocatalysts, there are some drawbacks associated with their use: i) the combination of charge carriers occurs within nano seconds and ii) the band edge absorption threshold does not allow the utilization of visible light\textsuperscript{158}. To overcome these difficulties, many strategies have been proposed to improve the light absorption features and lengthen the carrier life time characteristics of the photocatalysts. It has been observed that the photocatalytic activity of a catalyst can be influenced by crystal structure, surface area, size distribution, porosity, bandgap and surface hydroxyl group density\textsuperscript{159}. Further, it is also proposed that the rate of photo-oxidation of organic compounds on the surface of a catalyst is confined by the rate of electron transfer to molecular oxygen. It was also reported that a modification of the catalyst surface by incorporation of noble metals can increase the efficiency of photoassisted oxidation. Another approach to increase the efficiency of charge separation involves bringing the contact of one semiconductor particle with another semiconductor\textsuperscript{160}.

In semiconductors the highest occupied and lowest unoccupied bands are important. The highest occupied band is called valence band whereas lowest unoccupied band is called conduction band. The difference of energy between these bands is called bandgap energy $E_g$. Semiconductors can be made more conductive by addition of electrons into conduction band or by removal of electrons from valance band. When an electron is removed from a valence band ‘a positive hole’ or simply a hole is created, which can be taken as a mobile entity. Thus electric current can be carried either by electrons in the conduction band or
holes in the valance band, or by both types of charge carriers. Mobile charge carriers can be generated by three different mechanisms:

i) Thermal excitation where a sufficiently small amount of thermal energy can promote electron from valence band to conduction band.

ii) The absorption of light radiations promotes electron from valence band to conduction band provided that $hv > E_g$ and

iii) By doping new energy levels are introduced into the bandgap. This brings about two types of semiconductors, n-type and p-type. For n-type doping, occupied donor levels are created very near to the conduction band edge and current is mainly carried by negative charge carriers. Similarly, in p-type doping empty acceptors levels are formed near the valence band, creating positive charge carriers. The current is carried by positive charge carriers.

The various inorganic semiconductors acting as photocatalysts are used of which TiO$_2$, ZnO and CdS are employed very widely. The bandgap energies for the corresponding semiconductors are 3.2 eV, 3.2 eV, and 2.4 eV respectively. In the context of photodegradation of several dyes different research workers have made attempts in different directions by varying experimental conditions.

Qumar M et. al.\textsuperscript{161} carried out photocatalytic degradation of Amido Black 10B and Chromotrope 2B in aqueous suspensions of TiO$_2$ under a variety of conditions such as reaction pH, catalyst concentration, substrate concentration and in presence of different electron acceptors such as H$_2$O$_2$, KBrO$_3$ and ammonium
per sulphate besides molecular oxygen. Shen-Peng et. al.\textsuperscript{162} used Fenton-oxidation process for the degradation of Amido Black 10B. Under optimal conditions 99.2\% degradation efficiency was observed in aqueous solution of dye after 60 minutes reaction. It was also seen that, chromophoric group was easier to destruct than the aromatic ring of Amido Black 10B. Degradation of 'Reactive Black 5' (RB 5) by Fenton/UV-C and ferrioxalate/H\textsubscript{2}O\textsubscript{2}/solar light was carried out by Lucas et. al.\textsuperscript{163}. The experiment indicates that RB5 can be effectively decolorized to 98.1\% by Fenton /UV-C and 93.2\% by ferrioxalate/H\textsubscript{2}O\textsubscript{2}/solar light after 30 minutes. Jian-Qiu Chen et. al.\textsuperscript{164} used 'Pelagite', a photocatalyst for the first time to degrade Methyl Orange, where total degradation and decolourization was observed within 120 minutes. Rashed et. al.\textsuperscript{165} carried out photocatalytic degradation of Methyl Orange in aqueous TiO\textsubscript{2} under different sources like tungsten halogen, fluorescent light and sunlight. It was observed that the rate of photo-oxidation of a dye depended upon initial dye concentration, irradiation time and irradiation intensity. It was concluded that dye undergo fast degradation with the natural sun light than other two sources. Methyl Orange was degraded in a neutral phosphate buffer solution by means of contact glow discharge electrolysis (CGDE) by Gong Jianying and Cai Weimin\textsuperscript{166}. Based on the analysis of ultraviolet (UV) spectra of the solution and the intermediate products from High Pressure Liquid Chromatography-Mass Spectrum (HPLC-MS), the reaction pathway was proposed. The attack of hydroxyl radicals was considered to be a key step to start the whole oxidation process. Sadik et. al.\textsuperscript{167} carried out photodecolourization of Ponceau 4R dye by combination of TiO\textsubscript{2} and UV
irradiation at a pH of 6. The catalytic systems used were UV/TiO₂/Na₂S₂O₈ and UV/TiO₂/NaIO₄. It was also observed that the most effective catalytic system for the dye decolourization was UV/TiO₂/NaIO₄. It was concluded that degradation increases with the increase in dye concentration. Wu and Zhang¹⁶⁸ found that well-crystallized anatase thin films of TiO₂ induced complete degradation of Rhodamin B (RB) dye in water with an initial concentration of less than 0.02 mM after 4-5 hours of illumination under a high-pressure mercury lamp. The RB decayed directly to colourless end products of water and mineral acids. Li et. al.¹⁶⁹ carried out TiO₂ assisted photocatalytic degradation of Rhodamin B dye under visible light irradiation. The degradation intermediates were identified using infrared (IR) spectra, proton magnetic resonance (PMR) spectra, and gas chromatography-mass spectroscopy (GC-MS). The IR and PMR results showed that the large conjugated chromophore structure of RB was efficiently destroyed under visible light irradiation. Byrappa et. al.¹⁷⁰ carried out photocatalytic degradation of RB dye using hydrothermally prepared ZnO. In this regard, actual textile effluent containing RB as a major constituent along with other dyes and dyeing auxiliaries were treated using hydrothermally synthesized ZnO and the reduction in the chemical oxygen demand (COD) of the treated effluent revealed a complete destruction of the organic molecules along with colour removal. Jin-Ming Wu¹⁷¹ showed photodegradation of RB in water assisted by titania nano-rod thin films subjected to various thermal treatments. It was found that photocatalytic activity of the titania nanorod film is found to increase with an increasing heating temperature up to 450 °C.
Heterogeneous photocatalysis was also effectively used by Sakthivel\textsuperscript{159} for the determination of photocatalytic activity of $\alpha$-Fe$_2$O$_3$, WO$_3$ and CdS deposited on ZnO for the photo-oxidation of dichloro acetic acid in aqueous solution illuminated under medium pressure mercury lamp. The experiment was conducted under following conditions.

i) under continuous purging with molecular oxygen ii) in the presence of naturally dissolved oxygen, and iii) in the absence oxygen. It was observed that in the presence of oxygen, there was a three fold enhancement in the rate of photocatalytic degradation of dichloro acetic acid. This was explained by an increased scavenging of the photogenerated electrons by $O_2$. Ollis\textsuperscript{172} adopted water purification process by destruction of halogenated hydrocarbon contaminants with the help of TiO$_2$. This idea was further extended by Piscopo et al.\textsuperscript{173} for photocatalytic degradation of benzamide and para-hydroxy benzoic acid with TiO$_2$. Borgarello et al.\textsuperscript{174} showed the application of photocatalysis to some of the important environmental problems such as i) the photocleavage of hydrogen sulphide ii) the treatment of wastes, and iii) the photoreduction and recovery of metals on TiO$_2$. Serpone et al.\textsuperscript{175} used n-type semiconductors such as CdS and TiO$_2$ for the photocleavage of water, hydrogen sulphide and in the photo-oxidation of alcohols including carboxylate compounds.
2.6.2 Organic semiconductors

In the last 50 years, inorganic semiconductors have offered an interesting ground for investigation of the physics in solid state and also for development of the optoelectronic devices which have become basis of the information technology. So far optoelectronics has been dominated by inorganic materials (Ti, Ge, Si, Ga and As or other III/V or II/VI group compounds) with organics to carry out role of insulators. In the last 20 years, however, conjugated molecules and macromolecules in particular have been proposed as a novel class of semiconductors with technological potential for the treatment of information.

Organic semiconductors are carbon-based materials capable of transporting charged excitations and interacting with visible radiation. For this reason they can replace conventional inorganic semiconductors in optoelectronic devices such as light-emitting diodes (LED), photovoltaic cells and field-effect transistors (FET). Metal-organic compounds offer a wide variety of tools for these materials on account of substitution of carefully designed chemical groups. This also provides the opportunity for transduction of chemical or biochemical interactions into optoelectronic signals, and hence for the fabrication of chemo- and bio-sensors. The organic semiconductors possess very cheap manufacturing cost; cover large area and flexible substrates with an immense freedom for the observation of electronic and optical properties.
2.6.3 Porphyrins as photocatalysts

More recently porphyrins are used as model structures for explaining the general behaviour of the organic solid state itself and, more particularly, on their technological possibilities in various types of devices, electrodes, or solid catalysts for dealing with pollution problems or energy generating processes\textsuperscript{36, 37}.\textsuperscript{38}

Hequet et. al.\textsuperscript{177} showed the photocatalytic degradation of a pesticide ‘atrazine’ by porphyrin and phthalocyanine complexes. The study sought to assess an efficiency of the reaction in a mercury lamp reactor and under solar irradiation. These catalysts exhibit particular oxidation activities and the degradation rates have been found different between the semi-conductor and the metallic complexes. It was also observed that these complexes are able to cleave the triazinic ring more efficiently than the titanium dioxide. Mele et. al.\textsuperscript{178} carried out photocatalytic degradation of 4-nitrophenol in aqueous suspensions by using polycrystalline TiO\textsubscript{2} impregnated with functionalized Cu(II)-porphyrin or Cu(II)-phthalocyanine. The results indicated that the presence of the sensitizers is beneficial for the photoactivity and suggest an important role of Cu(II). A comparison with similar samples impregnated with modified Cu(II)- and metal-free phthalocyanines showed that the presence of porphyrin is more beneficial both for the decomposition rate of 4-nitrophenol and for the disappearance of nonpurgeable organic carbon (NPOC). The extension of this study\textsuperscript{179} was done for the degradation of 4-nitrophenol which contained TiO\textsubscript{2} based
photocatalysts impregnated with metallporphyrins. In this context, the photocatalytic polycrystalline TiO$_2$ systems were impregnated with sensitizers, i.e. copper, iron or manganese porphyrins and their photoactivity for 4-nitrophenol oxidation compared with that of bare TiO$_2$. A significant improvement of the photoreactivity was observed in the case of TiO$_2$ impregnated with copper porphyrin, while only a slight beneficial effect was observed in the case of iron porphyrin. The effect produced by the presence of manganese porphyrin appeared to be detrimental. Kalyanasundaram et. al.$^{180}$ carried out the experiment where efficient charge injection from the excited state of a zinc porphyrin to the conduction band of TiO$_2$ has been observed during the visible light irradiation of TiO$_2$ electrodes coated with a film of [tetrakis(4-carboxyphenyl)porphinatozinc(II)] (ZnTPPC). The mechanism of charge injection process has been studied in dye-adsorbed TiO$_2$ dispersions and colloids, using steady-state and time-resolved photolysis techniques. The process was found extremely sensitive to pH. Furuto et. al.$^{181}$ showed that oxygen sensing system using triplet-triplet reflectance of zinc porphyrin immobilized in polymer membrane studies by laser flash photolysis. The photosensitizers, zinc tetraphenylporphyrin (ZnTPP), zinc tetrakis(pentafluorophenyl)porphyrin (ZnTFPP), zinc etioporphyrin (ZnEtioP), zinc octaethylporphyrin (ZnOEP), zinc tetrabenzoporphyrin (ZnTBP) were suitable for oxygen sensing.

2.6.4 Mechanism

When energy of a photon matches with or exceeds the band gap energy $E_g$ in a semiconductor then the electron from valence band is excited to conduction
band and hole is formed in the valence band. If this excited electron from conductance band comes to the ground state then it combines with hole producing heat. Therefore, recombination of hole and electron is prevented by introducing electron scavenger and subsequently photocatalytic activity of semiconductor is enhanced. In the process of dye degradation different groups of research workers have different mechanisms.

1) Rashed et. al.\textsuperscript{165} carried out degradation of Methyl Orange on the surface of TiO\textsubscript{2} as below:

\[
\begin{align*}
\text{TiO}_2 + \text{hv (UV)} & \rightarrow \text{TiO}_2 (e_{\text{CB}}^- + h_{\text{VB}}^+) \\
\text{TiO}_2 (h_{\text{VB}}^+) + \text{H}_2\text{O} & \rightarrow \text{TiO}_2 + \text{H}^+ + \text{OH}^- \\
\text{TiO}_2 (h_{\text{VB}}^+) + \text{OH}^- & \rightarrow \text{TiO}_2 + \text{OH} \\
\text{TiO}_2 (e_{\text{CB}}^-) + \text{O}_2 & \rightarrow \text{TiO}_2 + \text{O}_2^- \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{HO}_2^- \\
\text{Dye} + \text{OH}^- & \rightarrow \text{degradation products}
\end{align*}
\]

It was also seen that resulting OH\textsuperscript{-} radical, being a very strong oxidizing agent (standard redox potential +2.8V) can oxidize most of methyl orange dye to the mineral end-products.

2) Byrappa et. al.\textsuperscript{170} showed photodegradation of aqueous solution of Rhodamine B on the surface of ZnO as shown by

\[
\begin{align*}
\text{ZnO} + \text{hv} & \rightarrow \text{ZnO}^* \\
\text{ZnO}^* + \text{H}_2\text{O} & \rightarrow \text{ZnO}^* + \text{H}^+ + \text{OH}^- \\
\text{OH}^- + \text{dye molecule} & \rightarrow \text{intermediates} \rightarrow \text{CO}_2 \uparrow + \text{H}_2\text{O} + \text{mineral acids}
\end{align*}
\]
This proposed reaction mechanism was also supported by the fairly high positive values of the free energy of activation and enthalpy of activation which indicated that the transition state was highly solvated. While the small value of entropy of activation $\Delta S^*$ suggested that the intermediate complex was less ordered than the reactants, which supported higher degree of the dye molecule into simple products.

3) For photodegradation of Methyl Orange on ZnO, Daneshvar et. al.\textsuperscript{182} proposed the following reaction mechanism.

The high oxidative potential of the hole ($h^+_{vb}$) in the catalyst permits the direct oxidation of the dye to reactive intermediates.

$$h^+_{vb} + \text{dye} \rightarrow \text{dye}^+ \rightarrow \text{oxidation of the dye}$$

Another reactive intermediate which is responsible for the degradation is hydroxyl radical (OH'). It is either formed by the decomposition of water or by reaction of the hole with OH'. The hydroxyl radical is an extremely strong, non-selective oxidant ($E^o = +3.06$ V) which leads to the partial or complete mineralization of several organic chemicals.

$$h^+_{vb} + H_2O \rightarrow H^+ + OH'$$

$$h^+_{vb} + OH^- \rightarrow OH'$$

$$\text{OH}^+ + \text{dye} \rightarrow \text{degradation of the dye}$$

4) The Fenton reaction system is based on the capture of a photon by a ferric hydroxyl with its conversion to a ferrous ion plus a hydroxyl radical\textsuperscript{183}. This
reaction can be energized by photons from the ultra-violet into the violet and blue.

The ferrous ion can be oxidized by molecular O₂ to restore the original ferric complex.

\[
\begin{align*}
\text{Fe(OH)}^{2+} + \text{photon} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{OH}^- + \text{Fe(OH)}^{2+}
\end{align*}
\]

Target molecule + OH⁻ → reaction products

Two OH⁻ radicals are generated for each H₂O₂ and for each photon absorbed, two H₂O₂ are needed to oxidize one carbon atom to CO₂.