Experimental Techniques

The tetraphenyl porphyrin (TPP), Tetrasodium meso-tetra(p-sulphophenyl) porphyrin (TPPS₄) and their corresponding metalloporphyrins with di, tri and tetravalent metals are found to be low band gap semiconductors. Further their photo catalytic activity was studied employing heterogeneous catalysis with solar radiations. The temperature range observed during the course of photolysis was 30 °C to 38 °C. Respective porphyrins were synthesized, purified, characterized using suitable methods and employed for photodegradation reactions.

3.1 Synthesis of porphyrins

The two different series of porphyrins were synthesized 1) Water insoluble or non-aqueous porphyrins 2) Water soluble or aqueous porphyrins. The metals used for synthesis of metalloporphyrins of both the series were M = Co, Ni, Cu, Zn, Ag, Mn, Fe and Sn.

3.1.1 Water insoluble or non-aqueous porphyrins

In this context the tetraphenyl porphyrin (TPP) and its metalloporphyrins (MTPP) with above mentioned metals were synthesized. This involves following two steps :

a) Synthesis of TPP and b) Synthesis of metalloporphyrins (MTPP).

a) Synthesis of TPP

The free base tetraphenyl porphyrin (TPP) was synthesized by suitable method. Equimolar quantities of AR grade pyrrole and bezaldehyde were refluxed in propionic acid for half an hour. The reaction mixture was cooled and washed with hot methanol followed by hot water. The product was completely dehydrated and dried in a vacuum.
desiccator for more than two hours. The purple shiny crystals of TPP were obtained with 17% yield. Purification of TPP was carried out using dry column chromatography. TPP was dissolved in AR grade CHCl₃ and silica gel (100-200 mesh) was added. The mixture was thoroughly stirred and the excess of CHCl₃ was evaporated on water bath. At this point, the silica becomes free flowing which is then loaded on the column of 45 cm × 3 cm diameter, already containing silica gel (100-200 mesh). The top of the column was covered with cotton and AR grade CHCl₃ was used as a mobile phase. At a time 1 g TPP was purified. The impurity of tetraphenyl chlorin (TPC) remains at the top and entire TPP gets eluted in the course of time. The recovered yield of purified TPP was found around 90%. The purity of TPP was checked on thin layer chromatography (TLC) using petroleum ether and chloroform (80%: 20%) and found to be pure.

b) Synthesis of metalloporphyrins (MTPP)

The above purified TPP was used to synthesize metalloporphyrins (MTPP) by suitable method. The divalent metals used were Co, Ni, Cu, Zn and Ag. During the synthesis of metalloporphyrins of cobalt tetraphenyl porphyrin (CoTPP), Nickel tetraphenyl porphyrin (NiTPP), Copper tetraphenyl porphyrin (CuTPP), Zinc tetraphenyl porphyrin (ZnTPP) and silver tetraphenyl porphyrin (AgTPP) the salts of metals in more than double the amount of stoichiometry was used and refluxed with dimethyl formamide (DMF) at 153 °C. All reactions were refluxed for 10-15 minutes. Further, synthesis of metalloporphyrins containing trivalent metals Mn and Fe and tetravalent Sn was carried out by the above method.

52
The monomers tetraphenylporphinatomanganese(III)chloride (MnTPPCl) and
tetraphenylporphinatoiron(III)chloride (FeTPPCl) were synthesized by above mentioned
method and the refluxing time for the reactions was modified to more than one hour. The
dimer of Mn i.e. \( \mu\)-Oxo-bis[tetraphenylporphinatomanganese(III)] \(O-(\text{MnTPP})_2\) was
synthesized by dissolving purified MnTPPCl in pyridine and then 30% KOH was added.
Then the reaction mixture was evaporated to dryness on a steam bath. The alkali was
removed by washing the solid with water. This process was repeated for two times. The
final dried product was recrystallized from benzene. The crystals were collected and
dried in a vacuum desiccator. The dimer \( \mu\)-Oxo-bis[tetraphenylporphinatoiron(III)] \(O-
(\text{FeTPP})_2\) was synthesized using suitable method \(^{33}\) by dissolving purified FeTPPCl in
CHCl₃ and adding 25% KOH and the solution was stirred for one hour. The chloroform
layer was separated from water layer and further purified by column chromatography.
The synthesis of tetraphenylporphinatotin(IV)chloride (SnTPPCl₂) was carried out by
above method and the refluxing time was extended to three hours for complete insertion
of metal. The completion of all the above metallation reactions was confirmed by
withdrawing aliquots from time to time and checking spectrophotometrically. Further, the
reaction mixture was allowed to cool and then cold water was added as much of the
reaction mixture. This was further filtered and dried in a vacuum desiccator. The
synthesized CoTPP, NiTPP, CuTPP, ZnTPP and AgTPP were purified by dry column
chromatography. For the purification of divalent metal porphyrins the method was
modified by introducing gradient elution which comprised of chloroform and petroleum
ether (50% : 50%) followed by evaporation of the solvent mixture. NiTPP purification
process was repeated twice with the same mobile phase. In CoTPP, CuTPP, ZnTPP and
AgTPP the recovery of pure compounds was more than 90% whereas in NiTPP it was less than 70%. The monomers and dimers of trivalent metals MnTPPCI, O-(MnTPP)₂, FeTPPCI, O-(FeTPP)₂ and the monomer of tetravalent Sn i.e. SnTPPCI₂ were purified by dry column chromatography as mentioned above. The mobile phase was modified to a gradient mixture of chloroform and methanol (50% : 50%). This type of mobile phase was used because axial ligands present in the structure of a molecule are strongly adsorbed on the column which requires sufficiently mobile gradient mixture for the movement of the desired fraction on the column. The purity of above metalloporphyrins was checked on TLC using petroleum ether and chloroform (80% : 20%) and found to be very satisfactory. At a time only 1 g of MTPP was purified.

3.1.2 Water soluble or aqueous porphyrins

The water soluble porphyrins were synthesized by substitution of sulphonic acid groups at the para position of the phenyl rings of TPP and then converted into its sodium salt. The new porphyrin thus obtained is called tetrasodium meso-Tetra (p-sulphophenyl)porphyrin (TPPS₄) which is subsequently used as a precursor for the synthesis of all water soluble metalloporphyrins.

a) Synthesis of TPPS₄

The synthesis of free-base TPPS₄ was carried out using standard methods which was further modified to required experimental conditions. Finely ground pure TPP (0.003mole) and Conc. H₂SO₄ (0.5 mole) were refluxed in a two neck flask for eight hours and the reaction mixture was kept aside for forty eight hours without any disturbance. Further, it was diluted with distilled water, heated and lime (CaO) was added until the
solution acquires permanent purple colour. The solution was filtered to remove CaSO₄, washed with hot water and the filtrate was concentrated to small volume (150-200 mL). Then concentrated solution of Na₂CO₃ was added and the pH of the solution was adjusted to 8-10. The precipitated CaCO₃ was removed by filtration and 90% C₂H₅OH was added periodically. The filtrate was concentrated on the steam bath and further dried in oven at 100 °C for two hours. At this stage, TPPS₄ crystals were collected and preserved in air tight capsule on account of its highly hygroscopic nature. Purification of TPPS₄ was accomplished by dry column chromatography using basic alumina as the stationary phase. The concentrated aqueous solution of TPPS₄ was added to alumina, stirred well and excess of water was removed on the steam bath until alumina becomes free-flowing. Further, it was loaded on the column of above mentioned dimension and covered with cotton plug. The mobile phase selected was a gradient solution of water, methanol and acetone in the ratio 7 : 2 : 1. During the process of elution, only a purple fraction due to TPPS₄ was collected and other fractions were rejected.

b) Synthesis of metalloporphyrins (MTPPS₄)

The above purified TPPS₄ was used to synthesize aqueous soluble metalloporphyrins (MTPPS₄) by independently devised methods. The divalent metals used were Co, Ni, Cu, Zn and Ag. For the synthesis of CoTPPS₄, NiTPPS₄, CuTPPS₄, ZnTPPS₄ and AgTPPS₄ the stoichiometric amounts of TPPS₄ and respective metal salts dissolved in ethyl alcohol, were added together with minimum amount of water and the reaction mixture was refluxed on steam bath for half an hour. It was also observed that if metal salts added are more than the stoichiometric amount then the concentration of green coloured dication
[H₄(TPPS₄)⁺²] was correspondingly increasing. The reason for this may be the reaction between TPPS₄ and the acid evolved during the course of synthesis. The synthesis of trivalent metal porphyrin FeTPPS₄Cl and its dimer [O-(FeTPPS₄)₂] was carried out using method³³ whereas synthesis of MnTPPS₄Cl was done by addition of slight excess of metal salt than stoichiometric requirement in the above procedure. The synthesis of tetravalent metal porphyrin SnTPPS₄Cl₂ was accomplished by addition of ten fold excess of metal salt to the aqueous solution of TPPS₄ and then above procedure was repeated.

The purification of all above mentioned metalloporphyrins was carried out using dry column chromatography as described above for purification of TPPS₄. During the course of elution, the colourless fraction, green coloured fraction and the fraction due to respective metalloporphyrin were collected. The colourless fraction is containing unreacted or excess of metal salt whereas green coloured fraction corresponds to dication [H₄(TPPS₄)⁺²]. Both of these fractions were checked spectrophotometrically and rejected. The fraction due to corresponding metalloporphyrin was checked on the spectrophotometer and selected. In general the recovery of purified metalloporphyrins was found in the range of 80-85%. For divalent metal porphyrins when stoichiometric amounts of metal salts and TPPS₄ were used, the yield of the corresponding metalloporphyrins was more than 85% otherwise it was in the range of 50-60%. The tri and tetravalent metal porphyrins required metal salts in excess quantities than stoichiometric requirement. The purity of above metalloporphyrins was checked on TLC using a mixture of methanol, ammonia and petroleum ether in the ratio 5 : 40 : 55. The recovered compounds exhibited satisfactory purity.
3.2 Characterization

The above synthesized free-base porphyrins and metalloporphyrins from non-aqueous and aqueous series were characterized by UV-Visible spectroscopy, infrared spectroscopy (FTIR), proton magnetic resonance spectroscopy (\textsuperscript{1}Hnmr), elemental analysis, mass spectroscopy (MS), high resolution mass spectroscopy (HR-MS), fluorescence spectroscopy, X-ray diffraction technique (XRD), image analysis (IA), thermal studies (TG-DSC), magnetic measurements, electron spin resonance (ESR) and diffused reflectance spectroscopy (DRS).

3.2.1 UV-visible spectroscopy

The UV-visible absorption spectra were recorded for $10^{-4}$ M and $10^{-5}$ M concentrations for each porphyrin. The solvents used for non-aqueous and aqueous porphyrins were chloroform and distilled water respectively. The results were recorded using quartz cuvettes of 10 mm width and the wavelength range was selected from 300-800 nm on Shimadzu visible spectrophotometer (model uv/2450uv).

3.2.2 Infrared spectroscopy (FTIR)

The infrared spectra of all solid porphyrins were recorded in the range 4000-400 cm\textsuperscript{-1} on Shimadzu IR spectrometer (model prestige/ 21 FTIR). The respective porphyrin and dehydrated powdered KBr were mixed in the ratio 1 : 100, sufficiently ground to make the mixture homogenous and the results were recorded.
3.2.3 Proton magnetic resonance spectroscopy ($^1$Hnmr)

$^1$Hnmr spectra of non-aqueous porphyrins TPP, CoTPP, NiTPP, CuTPP, ZnTPP, AgTPP, MnTPP, FeTPP and SnTPP were recorded in CDCl$_3$ whereas for aqueous- porphyrins TPPS, CoTPPS and MnTPPS$_4$Cl the solvent used was D$_2$O. The chemical shifts were recorded with respect to tetra methyl silane (Me$_4$Si) as a reference material. The NMR model used was Varian 300 MHz spectrometer.

3.2.4 Elemental analysis

The results of elemental analysis of non-aqueous and aqueous porphyrins were recorded on Prostar Varian C, H, N analyzer (model Flash 1112 series EA). TPP and CuTPP from non-aqueous porphyrins and MnTPPS$_4$Cl from aqueous porphyrins were selected as representative samples.

3.2.5 Mass spectroscopy

The mass spectrum of MnTPPS$_4$Cl was recorded as relative base peak intensity versus mass to charge (m/e) ratio. The fragmentation pattern of the compound gave the molecular ion peak from which molecular weight and molecular formula of the compound were calculated. The instrument used to record the results was IT mass spectrometer (model Varian 500-MS) with APCI source.
3.2.6 High-resolution mass spectroscopy (HR-MS)

High resolution mass spectrum for aqueous porphyrins TPPS₄ and FeTPPS₄Cl were recorded as representative samples of the series. The relative intensity of the base peak versus m/z ratio gave mass spectrum, which gave molecular ion peak and thus molecular weight of a respective porphyrins were determined.

3.2.7 Fluorescence spectroscopy

The fluorescence intensities of non-aqueous and aqueous porphyrins were recorded as a function of wavelength in nm. The excitation wavelengths used for the non-aqueous and aqueous porphyrins were 420 nm and 300 nm respectively. The λ_max value for each porphyrin was determined for 10⁻⁴ M concentration. The results were recorded on single beam Shimadzu spectrofluorimeter (model RF-5301PC).

3.2.8 X-ray diffraction spectroscopy (XRD)

The X-ray diffractograms of TPP and ZnTPP were recorded a representative samples on ITAL X-ray diffractometer using Cu Kα radiation, filtered through Ni absorber, at a scanning rate of 0.1°/min. This was necessary to understand the nature and existing phases in the synthesized porphyrin materials.

3.2.9 Image analysis (IA)

The non-aqueous porphyrins TPP and SnTPPCl₂ and aqueous porphyrins TPPS₄ and CoTPPS₄ were subjected to image analysis for the knowledge of average size of the
particles. The areas of all particles of a given sample were converted into equivalent circular diameter (ECD) and measured in micrometer. The results were recorded on optical microscope from 'Leica' model MPS-30.

3.3 Magnetic susceptibility measurements

The magnetic susceptibility $\chi_g$ of all porphyrins was measured in air at room temperature using Gouy method. The magnetic field employed was 8000 Gauss and the single pan analytical balance of DONA was used. Mercury tetra thiocyanatocobaltate(II) \(\text{Hg}[\text{Co(SCN)}_4]\) was used as a standard material. The sample tube was washed, dried and filled with respective material for each operation. In case of aqueous porphyrins since they are highly hygroscopic filling of the sample is done in air cooled atmosphere. The procedure adopted involved loading the filled sample tube in between two electromagnets of Gouy balance and the readings are recorded without and with magnetic field. The magnetic susceptibility $\chi_g$ was calculated as given below.

In the first part of the calculation the tube constant ($\beta$) was evaluated and then magnetic susceptibility ($\chi_g$) was obtained using following relation

$$\chi_g = \beta \times \Delta W/W$$

Where, $\beta$ = tube constant

$\Delta W = \Delta W_1 + \Delta W_2$ (+ve for paramagnetic and -ve for diamagnetic)

$\Delta W_1 = W_4 - W_3$ and $\Delta W_2 = W_1 - W_2$

Where,

$W_1$ = weight of the empty tube (without field)

$W_2$ = weight of the empty tube (with field)
\[ W_3 = \text{weight of the tube + standard (without field)} \]

\[ W_4 = \text{weight of the tube + standard (with field)} \]

\[ W = W_3 - W_1 = \text{weight of the substance} \]

The value of tube constant (\( \beta \)) is then substituted in the above relation to get \( \chi_b \). Further, molar susceptibility is calculated by relation

\[ \chi_m = \chi_b \times \text{molecular weight} \]

Where \( \chi_m \) = molar susceptibility

\[ \chi_b = \text{gram susceptibility} \]

The magnetic moment \( \mu \) effective (\( \mu_{\text{eff}} \)) of the sample is calculated by using following equation.

\[ \mu_{\text{eff}} = 2.84 \sqrt{\chi_b \times T} \quad \text{B.M. where } \mu_{\text{eff}} \text{ is the magnetic moment and } T \text{ is absolute temperature.} \]

3.4 Electron spin resonance spectroscopy (ESR)

In the case of paramagnetic porphyrins, one or more unpaired electrons may reside either on the porphyrin ring or in the central metal system, or in both. The basic features of ESR spectra are strongly dependent on the number as well as the location of the unpaired electrons in a system. The ESR spectra of non-aqueous porphyrins CuTPP, AgTPP and MnTPPCI were recorded at room temperature at magnetic field 3000 Gauss. In case of CoTPP, FeTPPCI and O-(FeTPP)\textsubscript{2} there were no observable signals at room temperature therefore ESR signals of these compounds were recorded at liquid nitrogen temperature. From aqueous porphyrins, CoTPPS\textsubscript{4}, CuTPPS\textsubscript{4}, AgTPPS\textsubscript{4}, MnTPPS\textsubscript{4}Cl, FeTPPS\textsubscript{4}Cl and O-(FeTPPS\textsubscript{4})\textsubscript{2} were used to record ESR spectra. Further, ESR signals were used to calculate g-factor or Lande’s splitting factor, number of unpaired electrons.
and line width. Hyperfine splitting constant (A) was calculated in case of CoTPP, CuTPP, AgTPP, MnTPPCI and MnTPPS₄. The results were recorded on Varian E-112 X-band ESR spectrometer.

3.5 Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectra of non-aqueous and aqueous porphyrins were recorded on Shimadzu visible spectrometer (model uv/2450) using wavelength range from 300 to 800 nm and BaSO₄ as a reference material. Reflectance data are usually expressed in terms of percent reflectance (%R) which is analogous to percent transmission in absorption spectroscopy. When wavelength in nm was made a function of %R then the spectrum is obtained which was used to calculate band gap energy for synthesized porphyrins.

3.6 Thermal studies

The thermal studies were carried out with reference to a) TG-DSC studies and b) TG-EGA-MS studies.

a) Thermogravimetry-Differential scanning calorimetry (TG-DSC)

These studies for aqueous and non-aqueous porphyrins were carried out in synthetic air and argon atmospheres using NETZSCH-Geratebau GmbH Thermal Analyser (STA 409 PC) from room temperature to 800 °C. The rate of heating the sample was maintained to 10 °C/minute. TG furnishes information about percent weight loss of a sample and physical processes such as vaporization, sublimation and decomposition. DSC gives information about melting point, loss of ligand and different decomposition
temperatures at different stages. It is also used as a tool for characterization and to distinguish between monomers and dimers. The sample quantity required was 10-15 mg.

b) Thermogravimetry-evolved gas analysis-mass spectroscopy (TG-EGA-MS)

The TG-EGA-MS results were recorded on some selective porphyrins in argon atmosphere from room temperature to 900 °C. The non-aqueous porphyrins like CoTPP, FeTPPCl and SnTPPCl₂ and aqueous porphyrins like TPP₄ and CoTPPS₄ were selected for the study. For detection of the gases from the sample, the mass spectrometer was calibrated to some desired gases as can be expected from the structure of the compound. During the course of experiment, as the TG process advances, the respective gases are evolved which were subsequently detected by mass spectrometer. The temperature of delivery tube which carries the respective gases to the mass spectrometer was maintained below 125 °C.

3.7 Photocatalytic studies

It was necessary to select the suitable dyes for photodegradation studies in aqueous medium and organic medium. The criterion of suitability for dye was determined based on its self degradation in solar radiations. When it was observed that 10⁻⁵ M solution of a dye degrades comparatively faster in sunlight without the presence of a photocatalyst, then such dyes were not selected for the studies. The list of water soluble dyes which were tested were 1) Amaranth 2) Amido Black 10B 3) Tartrazine 4) Carmosine 5) Ponceau S 6) Indigo Camine 7) Xylenol Orange 8) Eriochrome Black T 9) Phenol Red 10) Methylene Blue 11) Rose Bengal 12) Methvl Violet 13) Murexide 14) Alizarin
Red 15) Thymol Blue 16) Methyl Orange and 17) Bromocresol Green. Depending on our experimentation it was seen that following dyes were suitable for our undertaken studies. 1) Amido Black 10B 2) Methyl Orange and 3) Ponceau S.

Further the dyes soluble in different organic solvents were tested. The list of the tested dyes was 1) Fluorescein 2) Methyl Red 3) Thymolphthalein 4) Rhodamin B.

Among these dyes Rhodamin B was selected for our photodegradation study.

The focus of our study was photocatalytic degradation of the dyes. The synthesized porphyrins were used as photocatalysts. Therefore, photocatalysis was carried out in two different ways.

a) Photodegradation of aqueous solution of dye by non-aqueous porphyrins and

b) Photodegradation of non-aqueous solution of dye by aqueous porphyrins

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a) Photodegradation of aqueous solution of dye by non-aqueous porphyrins

The dyes used under this category were 1) Amido Black 10 B 2) Methyl Orange and 3) Ponceau S.

The stock solution of $10^{-4}$ M concentration of each dye was prepared and then it was diluted to $10^{-5}$ M concentration for actual experiment. To develop the optimum conditions for photolysis the solutions of above dyes were tested with and without oxygen, varying amounts of photocatalysts and at different pH conditions. Based on these observations the ideal condition was developed. The 100 mL of concerned dye solution was taken and saturated with oxygen for five minutes. Further, depending upon the results of optimum amount of photocatalyst, it was seen that Amido Black 10B and
Ponceau S required 25 mg and Methyl Orange required 20 mg of the photocatalysts for degradation of the solution. Thus required amount of synthesized photocatalyst was added, the solution was stirred thoroughly and closed assembly of the reaction was kept in solar radiations during the period 11.30 am to 3.30 pm within a temperature range of 30 °C to 40 °C. The aliquots of the reaction mixture were withdrawn with the help of a syringe at the regular intervals of one hour and the course of photodegradation reaction was monitored using Shimadzu visible spectrophotometer (model uv/2450uv). The photolysis reactions for selected dyes were studied at pH 6, 7 and 10 respectively for comparative studies.

b) Photodegradation of non-aqueous solution of dye by aqueous porphyrins

This type of experiment required selection of a suitable organic solvent, its non-carcinogenic nature, solubility of a dye in the solvent, insolubility of a photocatalyst in solvent and easy availability at a cheaper rate. As per our observations, it is seen that acetone is satisfying all these conditions. Thus acetone was selected as a non-aqueous solvent for photocatalysis. To acquire acetone of high purity, AR grade acetone was refluxed with KMnO₄ for two hours until the colour of KMnO₄ persists and then it was distilled. The stock solution of 10⁻⁴ M concentration of Rhodamin B was prepared in acetone and then it was diluted to 10⁻⁵ M concentration for actual experiment. For optimum conditions of experiment, the dye solution was tested with oxygen, without oxygen and varying amount of photocatalysts in solar radiations. Based on these observations, it was seen that the amount of photocatalyst required was 5 mg for 50 mL dye solution. Therefore, 50 mL of 10⁻⁵ M solution of Rhodamin B was taken in a conical
flask and 5 mg of above synthesized photocatalyst was added. The solution was stirred thoroughly and the closed reaction assembly was kept in sunlight. Since, the rate of degradation was much faster, therefore, the aliquots were withdrawn at every five minute or ten minute with the help of a syringe. The course of photodegradation was monitored using Shimadzu visible spectrophotometer (model uv/2450uv).

In addition to UV-visible spectroscopy the above degradation processes were studied with the help of

i) Liquid chromatography-Mass spectrometry (LC-MS), where mass fragmentation pattern of a particular dye was obtained. This was helpful in predicting probable reaction mechanism in the course of dye degradation process. The degraded dye solution at pH 7 was selected for the study. The results were recorded on IT mass spectrometer (model Varian 500-MS) with APCI source.

ii) High performance liquid chromatography (HPLC)

This was helpful to resolve the number of components after the photodegradation process was completed. The results were recorded on HPLC unit Perkin Elmer SERIES-200. The column used for this was C18 with dimensions 250 mm × 4.6 mm and particle size diameter 5 micrometer. The solvent system selected was methanol and water (80%:20%) with UV detector which functions at 254 nm. The degraded dye solutions of Amido Black 10B and Methyl Orange at pH 6 and 7 were used. The solution of Rhodamine B was also studied for the number of components after degradation reaction.
iii) The qualitative and quantitative study of mineralization of dyes during the course of phodegradation was studied using ion-chromatography. The equipment required for this involves cation and anion exchangers with suitable stationary and mobile phases. The degraded solution of Amido Black 10B and Methyl Orange at pH 7 and Rhodamine B solution were used for study.