CHAPTER-2
SYNTHE\textsc{i}s\& CHARACTERIZATION

Experimental section
Preparation of tetraphenylporphyrin
Preparation of tetrasodium tetra (p-sulfophenyl) porphyrin
\((\text{Na}_4\text{TPPS})\)
Preparation of tetratolylporphyrin
Preparation of water- soluble tetrasodium tetra (p-sulfo tollyl)(\text{Na}_4\text{TPPS})
Preparation of Tetrapyridylporphyrin (TPyP):
Preparation of Tetra(methylpyridyl) porphyrine iodide: (TMPyP) \text{I}_4
Preparation of Tetra- (p-methylpyridyl) porphyrine chloride: (TMPyP) \text{Cl}_4
Metallation of TPPS with NiCl\textsubscript{2} \cdot 6\text{H}_2\text{O}
Metallation of TPPS with CoCl\textsubscript{2} \cdot 6\text{H}_2\text{O}
Metallation of TPPS with CuSO\textsubscript{4} \cdot 5\text{H}_2\text{O}
Metallation of TPPS with NiCl\textsubscript{2} \cdot 6\text{H}_2\text{O}
Metallation of TPPS with CoCl\textsubscript{2} \cdot 6\text{H}_2\text{O}
Metallation of TPPS with CuSO\textsubscript{4} \cdot 5\text{H}_2\text{O}
Metallation of TMPyP with NiCl\textsubscript{2}
Metallation of TMPyP with CoCl\textsubscript{2} \cdot 6\text{H}_2\text{O}
Metallation of TMPyP with CuSO\textsubscript{4} \cdot 5\text{H}_2\text{O}
IR spectroscopy
UV-visible spectroscopy
Reaction with different substrate
X-Ray Diffraction study
Nuclear Magnetic Resonance
Electron Para magnetic Resonance
Mass Spectrometry
EXPERIMENTAL SECTION:

All chemicals were procured from commercial sources and used as it is as obtained. Commercially obtained pyrrole, benzaldehyde and acetone were distilled prior to its usage in experimental preparations. Column chromatography was performed on silica gel (100-200 mesh). UV-Vis spectra were recorded on Cintra 10 UV-Visible spectrometer. Samples were prepared by dissolving the complexes in water or acetate buffer solution of definite conc. at different pH in water. The spectra were recorded in the range of 300-1000nm. The infrared spectra of the complexes synthesized for this work were recorded on Bukaer FT-IR Spectrometer Vector 22. The samples were prepared as KBr pellets and the absorbance frequencies have been referenced to KBr bands, at 120 scans. All the values given are in cm$^{-1}$. The X-ray diffractometer used to analyze the synthesized crystalline complexes was Richseifert X-ray diffractometer (model Isodebyeflex 2002). The samples were prepared in powder form and mounted on slide by small amount of methanol. The range between spectra were collected was 56° to 506° angel, sweep 3.0°/min, range (CPM) 20k, time constant(s) 3.0, Target-Cu. Electron spin resonance (ESR) data were recorded on a Bruker EMX ESR Spectrometer at a typical microwave frequency of 9.8 GHz and a microwave power of 0.200mW. The modulation amplitude was 5 G and the time constant 10ms. To record temperature dependent ESR data, we used liquid N$_2$ to vary temperature upto 115K. For the
measurements, powdered samples were placed into EPR Wilmad 5mm o.d. quartz tubes centered into the rectangular cavity. Spectra processing (numerical integration, digital filtering, baseline correction, parameter calculation, etc.) were performed by using Bruker WIN-EPR and SimFonia Software. $^1$H NMR spectra (400 MHz) were recorded in CDCl$_3$. All NMR spectra were obtained on a JEOL-JNM LAMBDA 400 FT-NMR at 298 K. $^1$H NMR spectra were recorded at 399.65 MHz and the range was set from -4 to 12 ppm.

2.1 SYNTHESIS OF BASE COMPOUND

PREPARATION OF TETRAPHENYLPORPHYRIN$^{1,2}$

Approximately 500 ml of dry dichloromethane was taken in a three-necked round bottom flask and one of the necks was closed with rubber septum. The central neck was fitted with a water condenser and from the other neck argon was passed in DCM for about 10 min to remove the dissolved oxygen. After the neck was closed with stopper argon was allowed to pass through the top of the condenser throughout the reaction. One equivalent each (3:4.4 ml) of pyrrole and benzaldehyde were added into stirred for about 15 minutes. The setup was covered with black paper to avoid photochemical reaction. Then 1ml boron trifluoroetherate was added rapidly using a syringe and the reaction mixture was stirred for about an hour. Calculated amount of p-chloranil was added as an oxidant then refluxing was carried out for an hour. The solvent was then evaporated and the product was separated by using column chromatography using initially 1:2 ratio of DCM and petroleum ether and gradually changing ratio to 1:1.
Another alternative method of preparation of TPP was used. Freshly distilled pyrrole and benzaldehyde in equimolar amount were added to 3 times of refluxing reagent grade propionic acid. After refluxing for 30 min., the solution is cooled to room temperature and filtered; the filter cake is washed with methanol. After a hot water washing, the resulting purple crystals were dried, and finally dried in vacuo to remove absorbed acid to yield 20% of TPP.

**Analytical data:** \( \text{C}_{44}\text{H}_{30}\text{N}_4; \) C, 85.90; H, 4.92; N, 9.12; \(^1\text{H NMR (400 MHz)}\) (CDCl\(_3\)) \( \delta -2.62\) (br s, 2H, NH), 8.1-8.2(dd, 8H, pyrrole), 7.6-7.7(s, 20H, phenyl); UV -vis 417,513,546,589,642nm.

![Chemical structure of tetraphenylporphyrin](image.png)

**Fig. 2.1.1: Preparation of tetraphenylporphyrin**

**PREPARATION OF WATER- SOLUBLE TETRASODIUMTETRA(p-SULFOPHENYL)PORPHYRIN (Na\(_4\)TPPS)**

TPPS was synthesized according to the literature procedure published by Fleischer et.al.\(^5\) Pure TPP (2 gm) and concentrated \( \text{H}_2\text{SO}_4 \) were grounded into a homogenous paste using mortar and pestle. The paste was transferred to a 250ml flask and 50ml of
concentrated H$_2$SO$_4$ was added. The mixture was heated in a steam bath for 4 hours and allowed to stand at room temperature for 48 hours. The filtrate was cautiously diluted with two volumes of distilled water and salt was precipitated by the addition of acetone. The resulting bright green ppt. is of the HSO$_4^-$ salt of the para sulfonated of TPP since earlier method to filter the mixture after steam bath heating was resulting in the low yield. The diacid was washed several times with acetone and then dissolved in distilled water and NaOH (4 eq.) was added to the solution of H$_2$TPPS to obtain Na$_4$TPPS. The reaction was complicated and yield was very less.

**Analytical data** - UV-Vis (in H$_2$O) are 411, 515, 552, 580, 633 nm. IR (N-H stretch 3454; -CH$_3$, -C-H, - C=N stretch 1394, 1365; C-H (pyrrole) 990,964). NMR $^1$H in ppm (pyrrole-H 8.32; pyrrole-H 6.9; phenyl-H 7.9; phenyl-H 7.1) 13 C (SO$_3$-C 135.8; pyrrole -C 124.7; meso-C 118.7; phenyl-C143.7, 142.6)

![Fig.2.1.2: Preparation of tetrasodiumtetra(p-sulfophenyl)porphyrin](image-url)
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PREPARATION OF TETRATOLYLPORPHYRIN (TTP)

1. Approximately 500 ml of dry dichloromethane was taken in a three-necked round bottom flask and one of the necks was closed with rubber septum. The central neck was fitted with a water condenser and from the other neck argon was passed in DCM for about 10 min to remove the dissolved oxygen. After the neck was closed with stopper, argon was allowed to pass through the top of the condenser throughout the reaction. One equivalent each (3:4.4 ml) of pyrrole and 4-methyl benzaldehyde were added and stirred for about 15 minutes. The setup was covered with black paper to avoid photochemical reaction. Then 1ml borontrifloroetherate was added rapidly using the syringe and the reaction mixture was stirred for about an hour. Calculated amount of p-chloranil was added as an oxidant and then refluxing was carried out for an hour. The solvent was then evaporated and the product was separated by column chromatography using initially 1:2 ratio of DCM and petroleum ether and gradually changing ratio to 1:1.

2. Freshly distilled pyrrole and 4-methyl benzaldehyde in equimolar amount are added to 300 ml of refluxing reagent grade propionic acid. After refluxing for 30 min., the solution is cooled to room temperature and filtered; the filter cake is washed with methanol. Washing with hot water, the resulting purple crystals were finally dried in vacuo to remove absorbed acid to yield 20% of TPP.
**PREPARATION OF WATER-SOLUBLE TETRASODIUMTETRA(p-SULFO TOLYL)(Na₄TTPS)**

TTPS was synthesized according to the literature procedure published by Fleischer et.al.² Pure TTP (2 gm) and concentrated H₂SO₄ were grounded into a homogenous paste using mortar and pestle. The paste was transferred to a 250ml flask and 50ml of concentrated H₂SO₄ was added. The mixture was heated in a steam bath for 4 hours and allowed to stand at room temperature for 48 hours. The filtrate was cautiously diluted with two volumes of distilled water and salt was precipitated by the addition of acetone. The resulting bright green ppt. is the HSO₄⁻ salt of the para sulfonated of TTP since earlier method to filter the mixture after steam bath heating was resulting low yields. The diacid was washed several times with acetone and then dissolved in distilled water, NaOH (4 eq.) was added to the solution of H₂TPPS to obtain Na₄TPPS was complicated and yield was very less.
**Analytical data:** UV-vis (H₂O) 411, 515, 552, 580, 633. IR (N-H stretch 3469; -CH₃, -C-H, -C=N stretch 1188; C-H (pyrrole) 975, 901). NMR ¹H in ppm (pyrrole-H -2.5; pyrrole-H 6.5; phenyl-H 7.26; CH₃ 2.5) ¹³C in ppm (SO₃-C 135.8; pyrrole-C 125; meso-C 137; phenyl-C 130-143; CH₃ 16.5)

Fig. 2.1.4: Preparation of tetrasodiumtetra(p-sulfonatolyl)porphyrin

**PREPARATION OF TETRAPYRIDYL PORPHYRIN (TPyP):**

500 ml of Propionic acid were taken in a round bottom flask and equimolar amount of both pyridine-4-carboxaldehyde and pyrrole were added and the solution was refluxed up to 45 minute. The solvent was flashed off and the residue was washed with DMF, which dissolves the tarry byproduct and leaves purple crystals: yield 28%
Analytical data: The visible absorption spectrum in chloroform consists of five peaks centered at 418 (Soret band), 514, 549, 588 and 616 nm (Q-bands). The mass spectrogram gives a parent peak m/e = 618

PREPARATION OF TETRAMETHYL PYRIDYL)PORPHRYNE IODIDE (TMPyP) I₄:

TPyP(1.0) was taken in a 20ml of DMF and heated for 1hr with simultaneous stirring on the oil-bath. The suspended solution was cooled at room temperature and methyl iodide (8 ml) was added and slurry was heated to reflux for 30 minute. As the slurry became thicker and hard to stir, it was cooled and acetone 1.0 g of iodide salt of TMPyP was taken in 20 ml of water was added along with 5 ml of conc. HCl into this and solution turns green. The solution was heated on water bath for 1hr and most of the water was evaporated off, then addition of acetone, precipitates out chloride salt of TMPyP. The fine precipitate was filtered, washed with acetone and dried in a vacuum desiccators: yield 1.24 g (95%)
PREPARATION OF TETRA(P-METHYLPYRIDYL)PORPHYRINCHLORIDE (TMPyP) Cl₄:

1.0g of iodide salt of TMPyP was taken in 20 ml of water and shaken with carbon tetrachloride saturated with Cl₂ gas, the solution turns green then and washed 2-3 times with CCl₄ to washed out with iodine. Excessive of water was then removed on water bath and compound was extracted by methanol and precipitated out by acetone. It was then Filtered and vacuum dried. Another method was also adopted to make chloride salt of TMAP where it was passed through anion exchanger resin. Yield 95%

Analytical data: The visible absorption spectrum (in water) consists of peaks centered at 411,513,582.5,629 nm. IR (N-H stretch 3382; -CH₃, -C-H, - C=N stretch 1354, 1328; C-H (pyrrole) 969). NMR ¹H in ppm (pyrrole-H 8.84; phenyl-H 8.5; N-H 9.1). ¹³C
in ppm (SO₃-C 135.8; α pyrrole -C 145.65; β pyrrole -C 135; meso-C 117.05; phenyl-C 158.5; N-CH₃-50)

METALATION OF TPPS WITH NiCl₂·6H₂O

1gm of TPPS and 1.5 equivalent of anhydrous NiCl₂ were taken in a 250 ml beaker containing 50 ml distilled water and it was kept on a water bath for several hours. The completion of metatillation was checked spectrophotometrically. Free radical was removed by passing aqueous solution of metalloporphyrin through cation exchange column.
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Fig. 2.1.8: Metallation of TPPS with NiCl₂·6H₂O

**Analytical data:** visible absorption spectrum (in water) 410,526 nm. IR (-CH₃, -C-H, - C=N stretch 1389, 1355; C-H (pyrrole) 856).

**METALATION OF TPPS WITH CoCl₂·6H₂O**

1gm of TPPS and 1.5 equivalent of CoCl₂ were taken in a 250 ml beaker containing 50 ml of distilled water and it was kept on a water bath for several hours. The completion of metallation was checked spectrophotometrically. Free radical was removed by passing aqueous solution of metalloporphyrin through cation exchange column.

Fig. 2.1.9: Metallation of TPPS with CoCl₂·6H₂O

**Analytical data:** UV (in water) 410,526 nm. IR (-CH₃, -C-H, - C=N stretch 1391, 1351; C-H (pyrrole) 853).

**METALATION OF TPPS WITH CuSO₄·5H₂O**
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1gm of TPPS and 1.5 equivalent of CuSO₄ were taken in a 250 ml beaker containing 50 ml of distilled water and it was kept on a water bath for several hours. The completion of metallation was checked spectrophotometrically. Free radical was removed by passing aqueous solution of metalloporphyrin through cation exchange column.

![Metallation of TPPS with CuSO₄ 5H₂O](image)

**Fig.2.1.10: Metallation of TPPS with CuSO₄ 5H₂O**

**Analytical data:** UV (in water) 411,537 nm. IR (-CH₃, -C-H, - C=N stretch 1389, 1345; C-H (pyrrole) 856).

**METALATION OF TTPS WITH NiCl₂ 6H₂O**

1gm of TTPS and 1.5 equivalent of anhydrous NiCl₂ in a 250 ml beaker containing 50 mL distilled water and kept on water bath for several hours. The completion of metallation was checked spectrophotometrically. Free radical was removed by passing aqueous solution of metalloporphyrin through cation exchange column.

**Analytical data:** UV (in water) 424,543 nm. IR (-CH₃, -C-H, - C=N stretch 1388, 1352; C-H (pyrrole) 856).
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Heating on waterbath with NiCl₂

Fig. 2.1.11: Metallation of TTPS with NiCl₂·6H₂O

METALATION OF TTPS WITH CoCl₂·6H₂O

1gm of TTPS and 1.5 equivalent of CoCl₂ were taken in a 250 ml beaker containing 50 ml of distilled water and it was kept on a water bath for several hours. The completion of metallation was checked spectrophotometrically. Free radical was removed by passing aqueous solution of metalloporphyrin through cation exchange column.

Fig. 2.1.12: Metallation of TTPS with CoCl₂·6H₂O
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Analytical data: UV (in water) 410,526 nm. IR (-CH₃, -C-H, - C=N stretch 1385, 1353; C-H (pyrrole) 912).

METALATION OF TTPS WITH CuSO₄·5H₂O

1gm of TTPS and 1.5 equivalent of CuSO₄ were taken in a 250 ml beaker containing 50 ml of distilled water and it was kept on water a bath for several hours. The completion of metallation was checked spectrophotometrically. Free radical was removed by passing aqueous solution of metalloporphyrin through cation exchange column.

Fig. 2.1.13: Metallation of TTPS with CuSO₄·5H₂O

Analytical data: UV (in water) 411,539 nm. IR (-CH₃, -C-H, - C=N stretch 1381, 1343; C-H (pyrrole) 907).
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METALATION OF TMPyP WITH NiCl₂

1.0 g of chloride salt of TMPyP was taken in a 250 ml beaker and dissolved into 10 ml of water. The solution was heated and in this hot condition 2 equiv. of NiCl₂ were added and pH of the solution was maintained around 6 to 6.5. UV-Vis spectrophotometer monitored completion of metallation. Excess sodium sulfate and chloride present for dissolving the crude product in methanol and precipitating metallated product from the solution with acetone could remove impurities. By this method, the yield can be improved from reported 85% to 90% of pure product.

Analytical data: UV (in water) 416,534 nm. IR (-CH₃, -C-H, - C=N stretch 1354; C-H (pyrrole) 861).

METALATION OF TMPyP WITH CoCl₂.6H₂O

1 g of chloride salt of TMPyP was taken in a 250 ml beaker and dissolved into 10 ml of water. The solution was heated and in
this hot condition 2 equiv. of CoCl$_2$.6H$_2$O were added and pH of the solution was maintained around 6 to 6.5. UV-Vis Spectrophotometer monitored completion of metallation. Excess sodium sulfate and chloride present as dissolving the crude product in methanol and precipitating metallated product from the solution impurities can be removed by washing with acetone. By this method, we could improve the yield of the pure product from the reported 85% to 90%.

![Metalation of TMPyP with CoCl$_2$.6H$_2$O](image)

Fig.2.1.15: Metalation of TMPyP with CoCl$_2$.6H$_2$O

**Analytical data:** UV(in water) 425,548 nm.

**METALATION OF TMPyP WITH CuSO$_4$.5H$_2$O**

1.0 g of chloride salt of TMPyP was taken in a 250 ml beaker and dissolved into 10 ml of water. The solution was heated and at 2 equiv. of CuSO$_4$.5H$_2$O was added at this hot condition and pH of the solution was maintained around 6 to 6.5. UV-Vis Spectrophotometer monitored completion of metallation. Excess sodium sulfate and chloride present as dissolving the crude product in methanol and precipitating metallated product from the solution
impurities can be removed by washing with acetone. This method provides better and improved yield of the pure product as compared to the reported 85%-90%.

![Metallation of TMPyP with CuSO₄·5H₂O](image)

Fig. 2.1.16: Metallation of TMPyP with CuSO₄·5H₂O

**Analytical data:** UV (in water) 424,548 nm. IR (-CH₃, -C-H, -C=N stretch 1354; C-H (pyrrole) 861).

### 2.2. INFRARED (IR) SPECTROSCOPY:

Infrared Spectroscopy is a spectroscopic technique where molecular vibrations are analyzed. In IR spectroscopy the studies were carried out in the region 4000-500 cm⁻¹. Every particular bond has its characteristic vibrational frequency. The basic criteria of a molecule to be IR active is that any of its vibrational modes should undergo a change in dipole moment.

The infrared spectra of the complexes synthesized in this work were recorded on Boker FT-IR Spectrometer Vector 22. The samples were prepared as KBr pellets and the absorbance frequencies have been referred to KBr bands, at 120 scans. All the values given here are in cm⁻¹.
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The starching frequencies at different vibrations of porphyrin and metalloporphyrins have been tabulated in the table 2.1.

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<th>N-H Stretch</th>
<th>C-H Stretch</th>
<th>C=C Stretch</th>
<th>C=C Pheny l</th>
<th>CH$_3$ H Bond &amp; C=N stretc h</th>
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Figure 2.2.1: Infrared Spectrum of TPPS in KBr

Figure 2.2.2: Infrared spectrum of NiTPPS in KBr
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Figure 2.2.3: Infrared spectrum of CuTPPS in KBr

Figure 2.2.4: Infrared Spectrum of Cotppps in KBr
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Figure 2.2.5: Infrared spectrum of TPPSMe in KBr

Figure 2.2.6: Infrared Spectrum of NiTPPSMe in KBr
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Fig. 2.2.7: Infrared Spectrum of CuTPPSMe in KBr

Fig. 2.2.8: Infrared Spectrum of CoTPPSMe in KBr
Fig. 2.2.9: Infrared Spectrum of TMPyP in KBr

Fig. 2.2.10: Infrared Spectrum of NiTMPyP in KBr
2.3 UV-VISIBLE SPECTROSCOPY:

UV-Visible spectroscopy is the measurement of the wavelength and intensity of absorption of near-ultraviolet and visible light by a molecule. Ultraviolet and visible light is energetic enough to promote outer electrons to move to higher energy levels. This is an absorption spectroscopy where absorption occurs that is the characteristic of a particular molecule or chromophore or auxochromes. The spectra have been divided into two groups; the first in the region of 700-450 nm and the other from 450-350 nm. The absorption bands in the 700-450nm region can be regarded in vibrational terms of a common electronic transition while the intense band falls in the near ultraviolet region. The so called Soret
band can correspond to a different electronic transition. As the metal gets inserted into cavity of a porphyrin ring, the four Q bands in the region 700-450nm shifts to two Q bands which leads a bathochromic shift occurs in the Soret band.

UV-VIS spectra were obtained with a Citra 20 UV-VIS spectrometer. Samples were prepared by dissolving complexes in water or acetate buffer solution of definite conc. at different pH values in water. The spectrums was recorded in the range of 300-1000nm. The UV-Visible spectra of the synthesized complexes were recorded in chloroform. In case of metalloporphyrin synthesized with p-hydroxybenzaldehyde, the UV-Visible spectrum was recorded in methanol. The concentration of $10^{-6}$ M was taken to record the spectrum from 350-1000 nm.

The electronic spectra values obtained for nickel, copper and cobalt metalloporphyrins are tabulated in the table no. 2.2.

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<th>S.No.</th>
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Fig. 2.3.1

Electronic spectra of Nlppps(25x10^-6) with 3.6 pH acetate
buffer solution(0.2molar) in water
**Chapter II**

Electronic spectra of Nitpps ($25 \times 10^{-6}$) with 4.0 pH acetate buffer solution (0.2 molar) in water

**Fig. 2.3.2**

Electronic spectra of Nitpps ($25 \times 10^{-6}$) with 5.0 pH acetate buffer solution (0.2 molar) in water

**Fig. 2.3.3**
Chapter II

Fig. 2.3.4

Electronic spectra of Nitpps(25×10⁶) with 5.6 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.5

Electronic spectra of Nitppsme(25×10⁶) with 3.6 pH acetate buffer solution (0.2 molar) in water
Chapter II

**Fig. 2.3.6**

Electronic spectra of Nitppsm(25x10^{-6}) with 4.0 pH acetate buffer solution (0.2 molar) in water

**Fig. 2.3.7**

Electronic spectra of Nitppsm(25x10^{-6}) with 5.0 pH acetate buffer solution (0.2 molar) in water
Chapter II

Electronic spectra of Nitppane (25x10⁻⁵) with 5.6 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.8

Electronic spectra of Cutpps (8.3x10⁻⁵) with 3.6 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.9
Chapter II

Electronic spectra of Cutpps (8.3x10^4) with 4.0 pH acetate buffer solution (0.2 molar) in water

Fig 2.3.10

Electronic spectra of Cutpps (25x10^-6) with 5.0 pH acetate buffer solution (0.2 molar) in water

Fig 2.3.11
Electronic spectra of Cutpps (25x10^5) with 5.6 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.12

Electronic spectra of Cutppsme (25x10^5) with 3.6 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.13
Chapter II

Fig. 2.3.14

Electronic spectra of Cutppsm (25×10⁻⁶) with 4.0 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.15

Electronic spectra of Cutppsm (25×10⁻⁶) with 5.6 pH acetate buffer solution (0.2 molar) in water
Chapter II

Electronic spectra of Cu(tppsme)(25x10^-6) with 5.6 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.16

Electronic spectra of Cu(tpyp)(25x10^-6) with 3.6 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.17
Electronic spectra of Cutmpyp\((25\times10^{-5})\) with 4.0 pH acetate buffer solution (0.2 molar) in water

Fig 2.3.18

Electronic spectra of Cutmpyp\((25\times10^{-5})\) with 5.0 pH acetate buffer solution (0.2 molar) in water

Fig 2.3.19
Chapter 11

Electronic spectra of Cutmpyp(25x10^-5) with 5.6 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.20

Electronic spectra of Cotmpyp(25x10^-5) with 3.6 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.21
Chapter II

Electronic spectra of Co(II) with 5.0 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.22

Electronic spectra of Co(II) with 4.0 pH acetate buffer solution (0.2 molar) in water

Fig. 2.3.23
Chapter II

2.4. REACTION WITH DIFFERENT SUBSTRATE:

Effect of different substrate (imidazole, sod. azide, sod. thiocyanate) on different metalloporphyrins on their axial ligation property we studied by using four times concentration of substrate with respect to metalloporphyrins. The following table shows the change in Soret band after the addition of the substrate to the metalloporphyrin.

The wavelength values of different synthesized metalloporphyrins with respect to different substrates have been tabulated in table 2.3.
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Table no. 2.3
Chapter II

Electronic spectra of Nlpps (10⁻⁴ molar conc.) with imidazole (10⁻³ molar conc.) with water

Fig. 2.4.1
Chapter II

Electronic spectra of Ntpps (10⁻⁴ molar conc.) with Sod. azide (10⁻³ molar conc.) in water

Fig. 2.4.2

Electronic spectra of Ntpps (10⁻⁴ molar conc.) with Sod. thiocyanate (10⁻³ molar conc.) in water

Fig. 2.4.3
Chapter II

Electronic spectra of Nitppsme ($10^{-4}$ molar conc.) with Imidazole ($10^{-7}$ molar conc.) in water

Fig. 2.4.4

Electronic spectra of Nitppsme ($10^{-4}$ molar conc.) with Sod. azide ($10^{-7}$ molar conc.) in water

Fig. 2.4.5
Chapter II

Electronic spectra of Nitppsm (10^{-5} molar conc.) with Sod. thiocyanate (10^{-1} molar conc.) in water

Fig. 2.4.6

Electronic spectrum of Nitmpyp (10^{-5} molar conc.) with imidazole (10^{-3} molar conc.) in water

Fig. 2.4.7
**Chapter II**

Electronic spectra of Nitmpyp (10^{-4} molar conc.) with Sod. azide (10^{-1} molar conc.) in water

**Fig. 2.4.8**

Electronic spectra of Nitmpyp (10^{-4} molar conc.) with Sod. thiocyanate (10^{-1} molar conc.) in water

**Fig. 2.4.9**
Chapter II

Electronic spectra of Cutpps ($10^{-4}$ molar conc.) with Imidazole ($10^{-3}$ molar conc.) in water

Fig. 2.4.10

Electronic spectra of Cutpps ($10^{-4}$ molar conc.) with Sod. azide ($10^{-3}$ molar conc.) in water

Fig. 2.4.11
Electronic spectra of Cupps (10⁻⁴ molar conc.) with Sod. thiocyanate (10⁻¹ molar conc.) in water

Fig. 2.4.12

Electronic spectra of Cuppsme (10⁻³ molar conc.) with Imidazole (10⁻¹ molar conc.) in water

Fig. 2.4.13
Chapter II

Electronic spectra of Cutppsm(10^4 molar conc.) with Sod. azide (10^{-1} molar conc.) in water

Fig. 2.4.14

Electronic spectra of Cutppsm(10^4 molar conc.) with Sod. thiocyanate (10^{-1} molar conc.) in water

Fig. 2.4.15
Electronic spectra of Ctmpyp (10^{-4} molar conc.) with Imidazole (10^{-1} molar conc.) in water

Fig. 2.4.16

Electronic spectra of Ctmpyp (10^{-4} molar conc.) with Sod. azide (10^{-1} molar conc.) in water

Fig. 2.4.17
Chapter II

Electronic spectra of Cutmpyp ($10^{-3}$ molar conc.) with Sod. thiocyanate ($10^{-3}$ molar conc.) in water

Fig. 2.4.18

Electronic spectra of Cotpps ($10^{-4}$ molar conc.) with Imidazole ($10^{-5}$ molar conc.) in water

Fig. 2.4.19
Electronic spectra of C6pophs (10⁻⁴ molar conc.) with Sod. azide (10⁻¹ molar conc.) in water

Fig. 2.4.20

Electronic spectra of C6pophs (10⁻⁴ molar conc.) with Sod. thiocyanate (10⁻¹ molar conc.) in water

Fig. 2.4.21
Chapter II

Electronic spectra of Cotppsme(10^3 molar conc.) with Imidazole (10^3 molar conc.) in water

Fig. 2.4.22

Electronic spectra of Cotppsme (10^4 molar conc.) with Sod. azide (10^3 molar conc.) in water

Fig. 2.4.23
Chapter II

Electronic spectra of Cotppsm(10⁻⁴ molar conc.) with Sod. thiocyanate(10⁻¹ molar conc.) in water

Fig. 2.4.24

Electronic spectra of Cotmpyp (10⁻⁴ molar conc.) with Imidazole (10⁻¹ molar conc.) in water

Fig. 2.4.25
Chapter II

Electronic spectra of Cotmpyp (10^{-4} molar conc.) with Sod. azide (10^{-1} molar conc.) in water

Fig. 2.4.26

Electronic spectra of Cotmpyp (10^{-4} molar conc.) with Sod. thiocyanate (10^{-1} molar conc.) in water

Fig. 2.4.27
2.5 X-RAY DIFFRACTION STUDY:

As an x-ray beam travels through any substance, its intensity decreases with the distance traveled through the substance. Only a small range of characteristic x-rays are widely used for diffraction. When an X-ray is incident on a crystalline material reflections occur due to the interaction between X-ray with the periodically aligned atoms in various layers of crystal lattice. Since nanocrystalline materials contain particles of nanometer dimensions the relevant instruments for characterizing nanocrystalline materials are powder diffractometers. Here samples consist of a collection of many small crystallites with random orientations. Here an averaging is done over crystal orientations and diffraction pattern is measured as the scattered intensity vs. function of outgoing angle. The X-ray diffractometer used to analyze the synthesized crystalline complexes was powder X-ray diffraction were recorded on Richseifert X-ray diffrectometer(model Isodebyeflex 2002) operating in the Bragg configuration using Cu $\alpha$ radiation $\lambda$=1.541Å and nickel filter.

The samples were prepared in powder form mounted on slide by small amount of methanol. The range between spectrum were collected was 50° to 500° angel, sweep 3.0°/min, range (CPM) 20k, time constant(s) 3.0, Target-Cu.

The XRD spectra of different synthesized metalloporphyrins are shown in fig.2.5.1 to 2.5.11.
Chapter II

Fig. 2.5.1 XRD spectrum of NiTPPS

Fig. 2.5.2 XRD spectrum of NiTPPSMe
Chapter II

Fig. 2.5.3: XRD Spectrum of CuTPPS

Fig. 2.5.4: XRD spectrum of CuTPPSMe
Fig. 2.5.5: XRD spectrum of CuTMPyP

Fig. 2.5.6: XRD spectrum of CoTPPSMe
Chapter II

Fig.2.5.7: XRD spectrum of CoTMPyP

2.6 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY:

The $^1$H chemical shifts in porphyrins are very much dependent on the distance and orientation of the proton with respect to the delocalization pathway of the $\pi$ electrons of the porphyrin ring. Protons above or inside the porphyrin ring are in the shielding region of the ring current effect, whereas protons in the plane of the macrocycle but at the porphyrin periphery are in deshielding region. This orientation dependence is readily apparent in the $^1$H chemical shift of free base porphyrins where the NH protons are strongly shielded and the pyrrole protons are strongly deshielded compared to the corresponding protons in pyrrole. NH protons of pyrrole appear at -2 to 4 ppm while pyrrole $\beta$-H appears at 8 to 9 ppm. In the case of NMR of metalloporphyrin, the principal
changes observed in the $^1$H NMR spectra upon metalation are the loss of the high field signal for $-\text{NH}$ protons and any symmetry reduction associated with metalation. The number of signals observed for the substituents of a metalloporphyrin is dependent on the symmetry of metalloporphyrin and rotational barriers of the substituents. It has been noted that increasing in the oxidation state of the metal shows the general downfield shift. This suggests the presence of structural effects on the $^1$H chemical shifts caused by the macrocyclic rearranging to accommodate unusually large or small central atoms. The chemical shift change due to metal insertion is relatively small.

$^1$H NMR spectra (400 MHz) were recorded in CDCl$_3$. All NMR spectra were obtained on a JEOL-JNM LAMBDA 400 FT-NMR at 298 K. $^1$H NMR spectra were recorded at 399.65 MHz and the range was set from -4 to 12 ppm.
Fig. 2.6.1

1H NMR spectrum of TPPS
Fig. 2.6.2

13C NMR spectrum of TPPS
Chapter II

Fig. 2.6.3

13C NMR spectrum of TPPS
Chapter II

Fig. 2.6.4

$^1$H NMR spectrum of TMPyP
Fig. 2.6.5

$^1$H NMR spectra of TMPyP
Chapter II

Fig. 2.6.6

$^{13}$C NMR spectrum of TMPyP
2.7. ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY:

Electron spin resonance (ESR) data were recorded on a Bruker EMX ESR spectrometer at a typical microwave frequency of 9.8 GHz and a microwave power of 0.200 mW. The modulation amplitude was 5 G and the time constant 10 ms. To record temperature dependent ESR data, we used liquid N$_2$ to vary temperature up to 115 K. For the measurements, powdered samples were placed into EPR Wilmad 5 mm o.d. quartz tubes centered into the rectangular cavity. Spectra processing (numerical integration, digital filtering, baseline correction, parameter calculation, etc.) were performed using Bruker WIN-EPR and SimFonia software.

The $g_{||}$, $g_{\perp}$ and $a_{||}$, $a_{\perp}$ values are shown in tabular forming table 2.4.
<table>
<thead>
<tr>
<th>Name of complex</th>
<th>gⅡ</th>
<th>g┴</th>
<th>all</th>
<th>a┴</th>
<th>Remark</th>
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<td>2.071</td>
<td>202</td>
<td>29</td>
<td>RT</td>
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Table no. 2.4.
Chapter II

Fig. 2.7.1

EPR spectra of powdered CuTPPS at room temp.

Fig. 2.7.2

EPR spectra of powdered CuTPPS at room temp.
Chapter II

EPR spectra of powdered Cu(tpp) at 120K

Fig. 2.7.3

EPR spectra of powdered Cu(tpp) at 120K

Fig. 2.7.4
Chapter II

EPR spectra of powdered CuTPPS KBr at room temp.

Fig. 2.7.5

EPR spectra of powdered CuTPPS KBr at room temp.

Fig. 2.7.6
Chapter II

EPR spectra of powdered Cu(tpps) KBr at 120K

Fig. 2.7.7

EPR spectra of powdered Cu(tpps) KBr at 120K

Fig. 2.7.8
Chapter II

Fig. 2.7.9

EPR spectra of Cutpps solution in DMF at 120K

Fig. 2.7.10

EPR spectra of Cutpps solution in DMF at 120K
Chapter II

EPR spectra of powder Cutppsme at room temp.

Fig.2.7.11

EPR spectra of powder Cutppsme at room temp.

Fig.2.7.12
Chapter II

![Graph 1](image1.png)

**Fig. 2.7.13**

![Graph 2](image2.png)

**Fig. 2.7.14**
Chapter II

Fig. 2.7.15

EPR spectra of powdered in Culpppsme KBr at room temp.

Fig. 2.7.16

EPR spectra of powdered in Culpppsme KBr at room temp.
EPR spectra of powdered CuTPP in KBr at 120K

Fig. 2.7.17

EPR spectra of powdered CuTPP in KBr at 120K

Fig. 2.7.18
Chapter II

EPR spectra of powdered Cutmpyp at 120K

Fig. 2.7.19

EPR spectra of powdered Cutmpyp at 120K

Fig. 2.7.20
Chapter II

EPR spectra of powdered Cutmpyp in KBr at 120K

Fig. 2.7.21

EPR spectra of powdered Cutmpyp in KBr at 120K

Fig. 2.7.22
Chapter II

EPR spectra of Cutmpyp solution in DMF at 120K

Fig. 2.7.23

EPR spectra of Cutmpyp solution in DMF at 120K

Fig. 2.7.24
Chapter II

Fig. 2.7.25

EPR spectra of powder CoTPPS at room temp.

Fig. 2.7.26

EPR spectra of powder CoTPPS at room temp.
Fig. 2.7.27

EPR spectra of Colmpyp at 120K

Fig. 2.7.28
Chapter II

EPR spectra of Colpps powdered in KBr at room temp.

Fig.2.7.29

EPR spectra of Colpps powdered in KBr at room temp.

Fig.2.7.30
Chapter II

Fig. 2.7.31

EPR spectra of powder Cotppsume at room temp.

Fig. 2.7.32

EPR spectra of powder Cotppsume at room temp.
Fig. 2.7.33

Fig. 2.7.34
EPR spectra of powered Cotppsm in KBr at 120K

Fig. 2.7.35

EPR spectra of powered Cotppsm in KBr at 120K

Fig. 2.7.36
Chapter II

Fig. 2.7.37

EPR spectra of Cotmpyp at room temp.

Fig. 2.7.38

EPR spectra of Cotmpyp at room temp.
Chapter II

EPR spectra of CoTMPyP at 120K

Fig. 2.7.39

EPR spectra of CoTMPyP at 120K

Fig. 2.7.40
Chapter II

Fig. 2.7.41

EPR spectra of powdered Cotmpyp in KBr at 120K

Fig. 2.7.42

EPR spectra of powdered Cotmpyp in KBr at 120K
2.8 **MASS SPECTROMETRY:**

The electrospray mass spectrum was recorded on MICROMASS QUATTRO II triple quadrupole mass spectrometer. The sample was discovered in water and was introduced into the ESI source through a syringe pump at the rate of 5µ/min. the ESI capillary was set at 3.5 KV and the cone voltage was 40V. The spectra were collected at 6 scans and the final output was averaged spectra of 6-8 scans.
Chapter II

Fig. 2.8.1: Mass spectrum of NiTPPS
Chapter II

Fig. 2.8.2: Mass spectrum of CuTPPS
