Chapter-2

Experimental Section

2.1. Introduction

This chapter deals with the experimental techniques used and the synthesis of porphyrin and metalloporphyrins, purification of solvents and other reagents used in cyclic voltammetric and ESR studies.

2.2 Solvents

Common solvent and other reagents used at various stages of this work were purified according to the standard procedures described¹.

1) Chloroform: Drum samples were dried over CaCl₂ and distilled twice before being employed for synthesis, extraction and running column. For recrystallization and other physical measurements spectroscopic grade solvent was used.

2) Dichloromethane: Drum samples were refluxed over K₂CO₃ (anhydrous) for about 4 hours and distilled. This solvent has been used for synthesis, extraction and running column. For recrystallization and other physical measurements spectroscopic grade solvent was used.

3) Methanol: Drum samples were refluxed over CaO(anhydrous) for about 6 hours and distilled with iodine and Mg turnings twice.
This solvent has been used for synthesis, extraction and running column. For recrystallization and other physical measurements spectroscopic grade solvent was used.

4) Pyrrole: Pyrrole was purified by distillation under reduced pressure in the presence of KOH pellets and stored in a dark sealed bottle.

2.3. Oxidizing agent

Antimony pentachloride solution (1M solution in dichloromethane) was purchased from Aldrich Chemical Company and used directly.

2.4. Reagents and supporting electrolytes

This section describes the methods of preparation of tetra-n-butylammonium perchlorate (TBAP) and the complexes which were used during the course of our investigation. Some of the reagents were procured commercially.

i) Sodium perchlorate

Sodium perchlorate has been prepared by neutralization of sodium carbonate (AnalR) with hydrogen perchloric acid (Qualigen, AR). After complete neutralization, the volume of the reaction mixture was concentrated and allowed to cool and sodium perchlorate crystallizes out. It was then recrystallized from
distilled water, several times. The purity of the sample has been tested by running a cyclic voltammogram.

ii) Tetra-n-butylammonium perchlorate (TBAP)

A saturated solution of tetrabutylammonium iodide (Aldrich Chemical Company) has been prepared in distilled water. To this solution, sodium perchlorate was added, while tetrabutylammonium perchlorate precipitates out instantly. It has been stirred constantly till the formation of the precipitate and filtered fast. In order to avoid the liberation of iodine excess of sodium perchlorate was added. The precipitates have been suction filtered and dried by pressing between filter papers. After complete drying, tetrabutylammonium perchlorate was dissolved in methanol and reprecipitated out by adding distilled water. It was then filtered and dried as before, then recrystallized from methanol. Glassy crystals were formed. The purity of the sample has been tested by running a cyclic voltammogram.

2.5. Synthesis of Porphyrins

2.5.1. *meso-5,10,15,20-Tetrakis(2,5-methoxyphenyl)porphyrin*

*meso-5,10,15,20-Tetrakis(2,5-dimethoxyphenyl)porphyrin* was prepared according to the method as described in the literature. In a 500 mL round bottom flask fitted with nitrogen bubbler 2,5-dimethoxy benzaldehyde (0.4952 g, 2.98 mmol) and
pyrrol (210 μl, 2.98 mmol) were dissolved in 300 mL of dichloromethane. After purging nitrogen for 10 min, the condensation of 2, 5-dimethoxy benzaldehyde and pyrrole was initiated by adding catalytic amount of BF₃·OEt₂ (120 μl, of 2.5M stock solution). The reaction mixture was stirred at room temperature for 1 hour. The progress of the reaction was monitored by taking aliquots of the reaction mixture at regular intervals and oxidizing with p-chloranil and recording the absorption spectra which clearly confirmed the formation of porphyrin. After 1 hour p-chloranil (0.7327g, 2.98 mmol) was added and the reaction mixture was stirred in air for additional 1 hour. The solvent was removed under reduced pressure and the crude compound was purified by silica gel column chromatography using dichloromethane.

λ<sub>max</sub>: 419 nm(S), 513nm, 546nm, 587nm, 642nm

2.5.2. meso-5,10,15,20-Tetrakis(o-nitrophenyl)porphyrin

meso-5,10,15,20-Tetrakis(o-nitrophenyl)porphyrin was prepared according to the method as described in the literature<sup>4</sup>.

λ<sub>max</sub>: 421 nm(S), 516nm, 551nm, 593nm, 649nm

2.5.3. meso-5,10,15,20-Tetrakis(p-hydroxyphenyl)porphyrin

meso-5,10,15,20-Tetrakis(p-hydroxyphenyl)porphyrin was prepared according to the method as described in the literature<sup>5</sup>.
To a solution containing 18.3180g (150 mmol) of p-hydroxy benzaldehyde in 300 ml propionic acid 13.5 mL (106 mmol) of propionic anhydride were added. The resulting solution was allowed to reflux with stirring under the protection of bubbled nitrogen. Then 10.40 mL (150 mmol) of freshly distilled pyrrole in 10 mL of propionic acid was added drop wise. After the addition the reaction mixture was stirred for further 30 min, and then 300 mL of 90% ethanol was added under vigorous stirring. The mixture was cooled to room temperature and kept at 15°C overnight. The tarry mixture was filtered and the solid product was washed repeatedly with a mixture of ethanol and propionic acid (1:1 in volume), then with hot water until the rinsed solution were no longer dark. The filter cake was dried in air overnight, then at 150°C for 2 hour. The purple coloured crystalline meso-5, 10,15,20-Tetrakis(p-hydroxyphenyl)porphyrin were obtained.

\[ \lambda_{\text{max}} : 421 \text{ nm(S)}, 518\text{nm}, 555\text{nm}, 593\text{nm}, 649\text{nm} \]

2.5.4. meso-5,10,15,20-Tetrakis(pyridyl)porphyrin

meso-5,10,15,20-Tetrakis(pyridyl)porphyrin was purchased from Sigma-Aldrich chemical and was used directly.

2.6. Synthesis of metalloporphyrins

2.6.1. Vanadyl meso-5,10,15,20-Tetrakis(2,5-methoxyphenyl)porphyrin VO[T(2,5-(OCH₃)₂)PP]₆
The reaction was carried out with a mixture of 13.5 mL of glacial acetic acid, 6.5 mL of pyridine, 297 mg (1.37 mmol) of vanadyl sulphate and 358.21 mg (0.42 mmol) meso-5,10,15,20-Tetrakis(2,5-dimethoxyphenyl)porphyrin \([T(2,5-(OCH_3)_2)PP]\) were taken in a 100 mL round bottom flask and was refluxed until the reaction was essentially complete (usually 4 to 5 hour). The crude product was cooled and washed with water thrice and the crude compound was purified by running through a silica gel column using dichloromethane.

Vanadyl meso-5,10,15,20-Tetrakis(o-nitrophenyl)porphyrin \(\text{VO}[T(o-NO_2)PP]\), Vanadyl meso-5,10,15,20-Tetrakis(p-hydroxyphenyl)porphyrin \(\text{VO}[T(p-OH)PP]\) and Vanadyl meso-5,10,15,20-Tetrakis(pyridyl)porphyrin \(\text{VO}[TpyP]\) were prepared according to the above method given in the literature\(^6\).

\(\text{VO}[T(2,5-(OCH_3)_2)PP]\)

\(\lambda_{\text{max}}\) in dichloromethane: 425 nm, 546 nm

\(\text{VO}[T(o-NO_2)PP]\)

\(\lambda_{\text{max}}\) in dichloromethane: 426 nm, 551 nm

\(\text{VO}[T(p-OH)PP]\)

\(\lambda_{\text{max}}\) in dichloromethane: 428 nm, 550 nm

\(\text{VO}[TpyP]\)

\(\lambda_{\text{max}}\) in dichloromethane: 420 nm, 545 nm.
2.6.2. Manganese meso-5,10,15,20-Tetrakis (2,5-methoxy-phenyl) porphyrin \( \text{Mn}[T(2,5-(\text{OCH}_3)_2)\text{PP}]^6 \)

The reaction was carried out with a mixture of 335mg (1.37mmol) of manganese (II) acetate in methanol and 358.21 mg (0.42mmol) of meso-5,10,15,20-Tetrakis (2,5-dimethoxyphenyl) porphyrin \( \text{T}(2,5-(\text{OCH}_3)_2)\text{PP} \) in chloroform. The solution was taken in a 100 mL round bottom flask and refluxed until the reaction was essentially completed, usually around 5 hour. The Crude product was cooled and washed with water thrice, the crude compound was purified by running a silica gel column chromatography using dichloromethane.

Manganese meso-5,10,15,20-Tetrakis (o-nitrophenyl) porphyrin \( \text{Mn}[T(o-\text{NO}_2)\text{PP}] \), Manganese meso-5,10,15,20-Tetrakis (p-hydroxyphenyl) porphyrin \( \text{Mn}[T(p-\text{OH})\text{PP}] \) and Manganese meso-5,10,15,20-Tetrakis(pyridyl)porphyrin \( \text{Mn}[\text{TpyP}] \) were prepared according to the above method given in the literature\(^6\).

\( \text{Mn}[T(2,5-(\text{OCH}_3)_2)\text{PP}] \)
\( \lambda_{\text{max}} \) in dichloromethane: 411 nm, 480nm (Soret), 575 nm, 607 nm

\( \text{Mn}[T(o-\text{NO}_2)\text{PP}] \)
\( \lambda_{\text{max}} \) in dichloromethane: 414 nm, 480nm (Soret), 584 nm, 620 nm
λ_{max} in dichloromethane: 417 nm, 480 nm (Soret), 585 nm, 623 nm

Mn[TpyP]

λ_{max} in dichloromethane: 417 nm, 475 nm (Soret), 575 nm, 609 nm.

2.6.3. Cadmium and copper porphyrins

Cadmium meso-5,10,15,20-Tetrakis (2,5-methoxyphenyl) porphyrin Cd[T(2,5-(OCH₃)₂)PP]

The reaction was carried out with a mixture of 335 mg (1.37 mmol) of cadmium (II) acetate in methanol and 358.21 mg (0.42 mmol) of meso-5,10,15,20-Tetrakis(2,5-dimethoxyphenyl)porphyrin [T(2,5-(OCH₃)₂)PP] in chloroform. The solution was taken in a 100 mL round bottom flask and refluxed until the reaction was essentially completed, usually around 5 hours. The crude product was cooled and washed with water thrice, the crude compound was purified by running a silica gel column chromatography using dichloromethane.

Cadmium meso-5,10,15,20-Tetrakis (o-nitrophenyl) porphyrin Cd[T(o-NO₂)PP], Copper meso-5,10,15,20-Tetrakis (2,5-methoxyphenyl) porphyrin Cu[T(2,5-(OCH₃)₂)PP] and Copper meso-5,10,15,20-Tetrakis (o-nitrophenyl) porphyrin Cu[T(o-NO₂)PP] were prepared according to the above method given in the literature.
Cd[T(2,5-(OCH₃)₂)PP]
λ_max in dichloromethane: 427 nm, 549 nm

Cd[T(o-NO₂)PP]
λ_max in dichloromethane: 429 nm, 555 nm

Cu[T(2,5-(OCH₃)₂)PP]
λ_max in dichloromethane: 422 nm, 542 nm

Cu[T(o-NO₂)PP]
λ_max in dichloromethane: 424 nm, 556 nm

2.7. Instrumentation

2.7.1. Electron Paramagnetic Resonance (EPR)

EPR measurements were done using JEOL JES TE100 EPR spectrometer working at X band frequencies having 100 kHz field modulation at Pondicheery University, Pondicheery.

Oxidation was carried out in ESR tube by adding drops of 1M SbCl₅. All measurements were done after deaerating by bubbling nitrogen gas through the solution in the tube. The g values were determined by using solid DPPH as reference (g = 2.0036).

2.7.2. Cyclic voltammetric measurements

Redox potentials were determined using CHI 620B Electrochemical Analyzer, NEHU, Shillong, Meghalaya, India. The electrolytic cell is comprised of the following. A CHI(102) platinum electrode was used as a working electrode. An Ag/AgCl electrode
was employed as a reference electrode. A platinum wire was used as an auxiliary electrode. Dry dichloromethane was used as the solvent. The amount of 0.1M of tetra-n-butylammonium perchlorate (TBAP) was used as supporting electrolyte. The solvent in the electrolyte cell was deaerated with oxygen free dry nitrogen gas before any measurement had been done and nitrogen blanket above the solution has been maintained. Calibration of \( E_{1/2} \) values and diffusion current were made by using a known concentration of pure ZnTPP in dichloromethane/TBAP(0.1M) medium.

2.7.3. UV spectroscopy

Absorption spectroscopy was measured by BECKMAN 650DU Spectrophotometer, NEHU, Shillong, Meghalaya, India. Visible spectrums were measured in between the range 350-750 nm. Oxidations were carried out in quartz cuvette by adding drops of 1M SbCl₅.
References


4. (a) I. Gupta, and M. Ravikanth., *Tetraheron*, 59, 6131(2003),
(b) I. Gupta, and M. Ravikanth., *Tetr.Lett*, 43, 9453(2002),

5. Z. Jing, G. Yang, C. Shaokui, Z. Wennan, and W. Dongmai.,