CHAPTER 2

EXPERIMENTAL SECTION
CHAPTER - 2

2.1. INTRODUCTION

This chapter describes the purification of solvents and reagents, preparation of supporting electrolytes, synthesis of porphyrins and metalloporphyrins. Brief descriptions of the EPR and CV instrumentation are also presented.

2.2. PURIFICATION SOLVENTS AND REAGENTS

2.2.1. Dichloromethane: Dichloromethane was refluxed with potassium carbonate (anhydrous) for 2hrs and allowed to stand overnight. It was distilled and stored over molecular sieves (Linde-4A).

2.2.2. Chloroform: Chloroform was purified by passing through a column of basic alumina and then the eluate was used directly.

2.2.3. Benzaldehyde: Benzaldehyde was washed thoroughly with NaOH solution to remove benzoic acid and then it was distilled.

2.2.4. Pyrrole: Pyrrole was purified by distillation under reduced pressure from KOH pellets and stored in a dark sealed vessel.

2.2.5. N-Bromosuccinimide: The commercial NBS was purified by recrystallisation from hot water and dried.

2.2.6. Methanol: Methanol was distilled and used.

2.2.7. The reagent grade, analytical grade such as NiCl₂(BDH), vanadyl sulphate (CDH), Sodium acetate (S.Ds), pyridine (S.Ds), acetic acid (MERCK) etc. were used as received.
2.3. PREPARATION OF SUPPORTING ELECTROLYTE

2.3.1. Preparation of tetrabutylammonium perchlorate (TBAP):
TBAP was prepared according to the procedure as described\(^1\) and thrice recrystallised from methanol.

2.3.2. Preparation of tetrabutylammonium hexafluorophosphate [TBA( Pf\(_6\))] :
It was purchased from Fluka and thrice recrystallised from ethanol.

2.4. SYNTHESIS OF PORPHYRINS AND METALLOPORPHYRINS

2.4.1. TPP: TPP was prepared by the method of Adler et al.\(^2\) by the reaction of pyrrole and benzaldehyde in refluxing propionic acid. It was purified by the method of Badger et al.\(^3\) and thrice recrystallised from benzene. The purity of the product was checked by TLC and UV-visible spectra.
\[ \lambda_{\text{max}} \text{(nm)} \text{ (in chloroform): } 449, 483, 514, 549, 590, 648. \]

2.4.2. Bromination of TPP: TPP was brominated by the method of Samuels et al.\(^4\) or Callot\(^5\) by refluxing the reaction mixture of meso-TPP and NBS in chloroform.

2.4.3. (T(o-CI)PP): It was prepared according to the Adler et al.\(^2\) or Lindsey and Wagner\(^6\). It was also prepared by refluxing 2ml of freshly distilled pyrrole and 3.4ml of o-chloro benzaldehyde for 30minutes in 250ml of reagent grade propionic acid. The reaction mixture was cooled to room temperature and kept standing for 24hrs. The dark solid powder was collected by filtration on a buckner funnel and dried in a desiccator. The powdery solid was washed thoroughly with methanol till the greenish colour disappeared completely followed by hot water and air dried. The crude product was twice chromatographed on silica gel using chloroform as eluent. The product was
thrice recrystallised from chloroform - methanol (1:3) mixture and the purity was checked by TLC and UV-visible spectra.

\[ \lambda_{\text{max}} \text{ (nm) (dichloromethane): } 422, 480, 513, 545, 587, 644. \]

2.4.4. (T(m-Cl)PP) : The compound was prepared and purified according to the literature\(^7\). Also, we obtained a good product by the method of Adler et al.\(^2\) as follows - the reaction mixture consisting of 1.1ml of freshly distilled pyrrole and 2.137g of \( \text{m-} \) chloro benzaldehyde was refluxed for 30 minutes in 150ml of propionic acid. The reaction mixture was cooled to room temperature, filtered in a buchner funnel and dried in the vacuum pump. The solid material was washed with methanol till the filtrate was colourless and followed by hot water and air dried.

The product was chromatographed using chloroform as eluent. The product was rechromatographed using benzene as eluent. The eluate was evaporated to dryness and thrice recrystallised from chloroform - methanol (1:3). The purity of the product was checked by TLC and UV-visible spectra.

\[ \lambda_{\text{max}} \text{ (nm) (dichloromethane): } 422, 483, 513, 547, 588, 646. \]

2.4.5. (T(p-Cl)PP) : The compound was prepared as described above for T(m-Cl)PP.

\[ \lambda_{\text{max}} \text{ (nm) (dichloromethane): } 423, 484, 514, 549, 591, 648. \]

2.4.6. (T(o-CH\(_3\))PP) : The compound was prepared by the method of Lindsey and Wagner\(^6\). It was modified by refluxing the reaction mixture containing 3ml of freshly distilled pyrrole and 5.02ml of \( \text{o-} \) methyl benzaldehyde in 250ml of reagent grade
propionic acid for 30 minutes. The reaction mixture was cooled to room temperature and kept standing for 6 days. The solid material was collected by filtration on a buchner funnel and dried in a vacuum pump. The powdery solid was washed thoroughly with methanol till the greenish colour disappeared followed by hot water and air dried. The crude product was twice chromatographed in dry silica gel eluting in benzene and then recrystallised from chloroform – methanol (1:3). The purity of the product was checked by TLC and UV - visible spectra.

\[ \lambda_{\text{max}} \text{(nm) (dichloromethane): } 418, 484, 514, 549, 588, 645 \]

2.4.7. (T(m-CH₃)PP) : The compound was prepared according to the procedure as described above for T(o-CH₃)PP.

\[ \lambda_{\text{max}} \text{(nm) (dichloromethane): } 419, 486, 515, 551, 590, 647 \]

2.4.8. (T(p-CH₃)PP) : The compound was prepared according to the procedure as described in the literature\(^7\)\(^9\).

\[ \lambda_{\text{max}} \text{(nm) (dichloromethane): } 420, 486, 516, 552, 591, 649 \]

2.4.9. (T(m-NO₂)PP) : The compound was prepared according to the procedure of Bettelheim et al.\(^10\) and also a good product was obtained by refluxing 1.7ml of freshly distilled pyrrole, 3.775g of \textit{m}-nitro benzaldehyde (sigma chemical) and 300 ml of reagent grade propionic acid for 30 minutes. The reaction mixture was cooled to room temperature and kept standing for 18 hrs. The reaction mixture was filtered on a Buchner funnel and dried in the vacuum pump to remove the propionic acid. The solid material was dissolved in chloroform and kept in the dark for 36 days. The chloroform
was recovered, evaporated to dryness and washed with methanol followed by hot water till the filtrate was colourless. The product was purified by column chromatography using a mixture of benzene and chloroform. The purity of the product was checked by TLC and UV-visible spectra.

\[ \lambda_{\text{max}} \text{ (nm)} \text{ (dichloromethane): 423, 484, 515, 549, 590, 648.} \]

2.4.10. (T(m-F)PP): It was prepared according to the procedure described by Adler et al\(^2\). The reacting materials were 1.3ml of freshly distilled pyrrole, 2ml of \( m \)-fluoro benzaldehyde and 150ml of propionic acid. The compound was chromatographed by using benzene as eluent. The product was rechromatographed from chloroform. It was thrice recrystallised in chloroform-methanol (1:3). The purity of the product was checked by TLC and UV-visible spectra.

\[ \lambda_{\text{max}} \text{ (nm)} \text{ (dichloromethane): 419, 484, 515, 549, 589, 644} \]

2.4.11. (T(m-OCH\(_3\))PP): It was prepared according to the standard procedure\(^7\).

\[ \lambda_{\text{max}} \text{ (nm)} \text{ (dichloromethane): 423, 484, 515, 550, 589, 644} \]

2.4.12. (T(p-OCH\(_3\))PP): It was prepared according to the literature\(^7\).

\[ \lambda_{\text{max}} \text{ (nm)} \text{ (dichloromethane): 424, 488, 518, 556, 593, 651} \]

2.4.13. (T(o-Br)PP): It was prepared and purified as described above for T(o-Cl)PP.

\[ \lambda_{\text{max}} \text{ (nm)} \text{ (dichloromethane): 422, 482, 514, 544, 588, 655} \]

2.4.14. (T(m-Br)PP): It was prepared and purified as described above for T(o-Cl)PP.
$\lambda_{\text{max}}$ (nm) (dichloromethane): 422, 483, 514, 544, 589, 651.

2.4.15. (T(p-Br)PP) : The reaction mixture consisting of 0.51ml of freshly distilled pyrrole, 1.3852g of $p$-bromo benzaldehyde was added to 150ml of reagent grade propionic acid and refluxed for 30 minutes. The reaction mixture was cooled to room temperature, filtered on a buchner funnel and dried in the vacuum pump. The solid material was washed thoroughly with methanol till the greenish colour disappeared followed by hot water and air dried.

**Purification** : The crude product was dissolved in chloroform and chromatographed on silica gel. The second fraction yielded bright purple colour crystal. Using a mixture of benzene and chloroform rechromatographed the first fraction. The purity of the product was checked by TLC and UV - visible spectra. The final product was twice recrystallised from chloroform - methanol(1:3).

$\lambda_{\text{max}}$(nm) (dichloromethane): 423, 484, 515, 550, 590, 646.

2.4.16. VOTPP(Br) : The complex was prepared as described in the literature$^{9,11}$ by refluxing 20ml of glacial acetic acid, 10ml of pyridine, 350ml of vanadyl sulphate and 200mg of TPP(Br) for 8hrs. The reaction mixture was extracted with chloroform and washed with water till the greenish colour disappeared. It was dried over anhydrous sodium sulphate, filtered and evaporated to dryness. The crude product was purified by column chromatography on silica gel with chloroform elution. The product was thrice recrystallised from chloroform – methanol (1:3) and the purity was checked by TLC and UV-visible spectra.
Similarly, VOTPP(Br)_2, VOTPP(Br)_3, and VOTPP(Br)_4 were prepared by the above procedure.

- **VOTPP(Br)_2**: \( \lambda_{\text{max}} \text{ (nm) (in dichloromethane)}: 425, 549 \)
- **VOTPP(Br)_3**: \( \lambda_{\text{max}} \text{ (nm) (in dichloromethane)}: 427, 558 \)
- **VOTPP(Br)_4**: \( \lambda_{\text{max}} \text{ (nm) (in dichloromethane)}: 430, 591 \)

### 2.4.17

The phenyl substituted vanadyl porphyrins were synthesised according to the procedure as described above VOTPP(Br)_2.

- **VO(T(o-Cl)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 421, 546} \)
- **VO(T(m-Cl)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 422, 548} \)
- **VO(T(p-Cl)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 422, 546} \)
- **VO(T(o-CH_3)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 422, 546} \)
- **VO(T(m-CH_3)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 422, 547} \)
- **VO(T(p-CH_3)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 423, 548} \)
- **VO(T(m-NO_2)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 423, 546} \)
- **VO(T(m-F)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 421, 545} \)
- **VO(T(m-OCH_3)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 423, 547} \)
- **VO(T(p-OCH_3)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 428, 550} \)
- **VO(T(o-Br)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 423, 548} \)
- **VO(T(p-Br)PP)**: \( \lambda_{\text{max}} \text{ (nm) (dichloromethane): 423, 547} \)
2.4.18. **NiTPP(Br):** The complex was prepared by refluxing 250mg of TPP(Br) with 60ml of glacial acetic acid, 30ml of pyridine, 490mg of sodium acetate, 400mg of NiCl₂ till the reaction was completed. The reaction mixture was extracted with chloroform and washed with water till the greenish colour disappeared. The reaction mixture was dried over anhydrous sodium sulphate, filtered and evaporated to dryness. The crude product was purified by column chromatography on silica gel with chloroform elution. The product was thrice recrystallised from chloroform – methanol (1:3) and the purity was checked by TLC and UV-visible spectra. Similarly, NiTPP(Br)₂, NiTPP(Br)₃ and NiTPP(Br)₄ were prepared.

\[
\begin{align*}
\text{NiTPP(Br)} & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 416, 527 \\
\text{NiTPP(Br)}₂ & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 419, 527 \\
\text{NiTPP(Br)}₃ & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 420, 532 \\
\text{NiTPP(Br)}₄ & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 426, 541
\end{align*}
\]

2.4.19. The phenyl substituted Nickel porphyrins were prepared by the same procedure described above NiTPP(Br)

\[
\begin{align*}
\text{Ni(T}(m-\text{NO}_2)\text{PP}) & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 413, 526 \\
\text{Ni(T}(\alpha-\text{CH}_3)\text{PP}) & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 412, 525 \\
\text{Ni(T}(m-\text{CH}_3)\text{PP}) & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 413, 526 \\
\text{Ni(T}(p-\text{CH}_3)\text{PP}) & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 414, 528 \\
\text{Ni(T}(m-\text{OCH}_3)\text{PP}) & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 412, 526 \\
\text{Ni(T}(p-\text{OCH}_3)\text{PP}) & : \quad \lambda_{max} \text{ (nm) (dichloromethane): } 418, 530
\end{align*}
\]
2.4.20. **CoTPP(Br)**: The complex was synthesised by the method of Adler et al.\textsuperscript{12} It was chromatographed on silica gel by using benzene as eluent. The purity of the product was checked by TLC and UV-visible spectra. \( \lambda_{\text{max}} \) (nm) (dichloromethane): 411, 529

Similarly, CoTPP(Br)\textsubscript{2}, CoTPP(Br)\textsubscript{3} and CoTPP(Br)\textsubscript{4} were synthesised by the same procedure as described above.

- **CoTPP(Br)\textsubscript{2}**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 413, 531
- **CoTPP(Br)\textsubscript{3}**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 415, 547
- **CoTPP(Br)\textsubscript{4}**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 420, 557

2.4.21. The phenyl substituted cobalt complexes were prepared by the same procedure as described above. The purity of the complexes were checked by TLC and UV-visible spectra.

- **Co(T(o-Cl)PP)**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 409, 527
- **Co(T(m-Cl)PP)**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 409, 527
- **Co(T(p-Cl)PP)**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 416, 529
- **Co(T(o-CH\textsubscript{3})PP)**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 409, 528
- **Co(T(m-CH\textsubscript{3})PP)**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 410, 527
- **Co(T(p-CH\textsubscript{3})PP)**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 412, 527
- **Co(T(o-Br)PP)**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 410, 530
- **Co(T(m-Br)PP)**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 411, 528
- **Co(T(p-Br)PP)**: \( \lambda_{\text{max}} \) (nm) (dichloromethane): 412, 527
Co(T(m-NO$_2$)PP) : $\lambda_{max}$ (nm) (dichloromethane): 410, 527

Co(T(m-F)PP) : $\lambda_{max}$ (nm) (dichloromethane): 409, 526

Co(T(m-OCH$_3$)PP) : $\lambda_{max}$ (nm) (dichloromethane): 409, 528

Co(T(p-OCH$_3$)PP) : $\lambda_{max}$ (nm) (dichloromethane): 413, 530

2.5. INSTRUMENTATION:

2.5.1 CYCLIC VOLTAMMETRIC MEASUREMENTS:

Cyclic voltammograms were obtained with a three electrode system using a PAR model 174 polarographic analyser and a universal programmer model 175 coupled with a digigraphic recorder. The working electrode was a Beckman platinum rod and a platinum strip served as the auxiliary electrode. A commercial saturated Calomel Electrode (SCE) was used as the reference electrode and was separated from the bulk of the solution by a fritted glass septum. Deaeration was accomplished by bubbling N$_2$ gas through the solution for about 8–10 minutes prior to the recording. Nitrogen blanketed the solution during the recordings.

2.5.2. EPR MEASUREMENTS:

EPR spectra were obtained at room temperature as well as at liquid nitrogen temperature with E109(Varian) X-band spectrometer at 100 KHz modulation. For liquid nitrogen measurements a Cold Finger Dewar has been employed. Oxidation were carried out in EPR tube by dropping SbCl$_5$. All measurements were done after deaerating by bubbling N$_2$ gas through the solution in the tube. The g values were determined by using DPPH as reference (g = 2.0036).
REFERENCES


