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# Synthesis, Charaterisation of Tetra Phenyl Porphyrin Iron Chloride Metal Complexes and its Recent Advances in the Field of Medical Science

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**Abstract**

A novel series of clathrochelates of tetra phenyl porphyrin iron chloride complexes type of [RTPPFe (III)Cl] where R = $NO_2$, Cl, H, $CH_3$,$OCH_3$. TPP= Tetra phenyl porphyrin,were synthesized by universal mixed solvent method. Porphyrins are tetra pyretic macrocyclic with fascinating and variegated complexes.They have essential significance and leading technologies. Porphyrin metal complexes established synthetic path with advantageous, photophysical characteristic and high sensitivity selectivity response. RTPPFe(III) Cl were obtained in the mixed solvent propionic acid, glacial acetic acid and m-nitrotoluene under reflux for 2h. X ray measurements suggests that the central nitrogen atom are somewhat out of the plane of the molecule, facilitating attachment of a smaller angle between the phenyl group and the porphin plane tetra porphyrin. The structure of clathrochelates tetra phenyl porphyrin complexes has been elucidated on the basis of infrared electronic spectral data and magnetic susceptibility measurement.

**Key Words :**Porphyrinclathrochelates mixed solvent,Tetra phenyl, Dioxygen

**1. Introduction :**Over past years, application of substituted porphyrin base complexes and their derivatives have been investigated extensively for the treatment of cancer by phototherapeutic. In current time substituted porphyrin base complexes have been studied of biomimetic chemistry (1, 2) enterology, analytical chemistry. In resent time, complexes of iron porphyrin are widely used as metal compound to stimulate the catalytic behavior of cytochrome $P_{450}$ enzymes in life processes. These complexes also can be widely used as catalyzed the selective oxidation of saturated hydro carbons, aromatic hydro carbons chains with dioxygen. The tetra aryl porphyrins were first obtained by Rothemud. Till now these are two easy and practical method adopted of synthesizing porphyrin complexes. A famous chemical scientist alder and Longo converted aromatic aldehyde and pyrrole to corresponding porphyrin complexes in a single refluxing carboxylic acid with air oxidation. Another scientist Lindey's group developed another synthetic process to obtain substituted tetra phenyl porphyrin compounds in $CH_2$ $CL_2$ solvent with $BF_3$ etherate as a catalyst and p-chloranil as oxidant. For larger scale, Lindey's synthetic method was used to obtain substituted tetra phenyl porphyrin complexes. But due to higher cost of synthesis and restricted their application, Lindey's method was not applied. In this work tetra phenyl porphyrin iron chloride complexes were synthesized with one pot method. Structure of porphyrin base complexes were characterized by Uv-vis, IR, and elemental analysis.

## 2. Results and Discussion

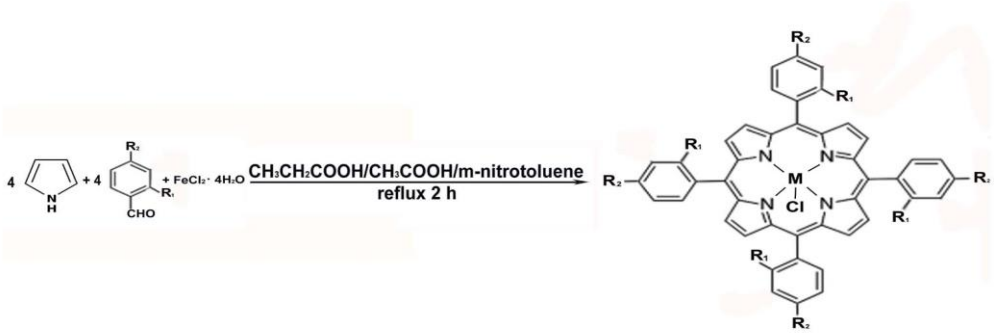
Material and method- all chemical were used of E. Merck quality.

**2.1 Synthesis of**RTPPFe (III) Cl – RTPPFe (III) Clwere synthesized by Adler two step method. They are synthesized by the direct condensation of pirrole with substituted benzaldehydes. The free base porphyrin were purified through $Al_2O_3$ and eluted with $CH_2Cl_2$. The solvent was kept under vacuum. The purified porphyrin complexes were obtained in yields of blow 20%.

**2.2 Synthesis of :**o- $NO_2$TPPFeCl – Glacial acid (10ml) m- nitrotoluene (10ml) and propionic acid (50ml) were added into a 250ml three- neck round bottom flask. It is equipped with stirrer, reflux condenser and dropping funnels. Mixer was reflux for 35 min. o- nitro benzaldehyde (1.5gm) dissolved in propionic acid (20ml) fresh distilled pyrrole (0.7ml) dissolved in m- nitrotoluene (12ml) were added into the flask through two droppingfullness in 20min. Now mixer was started to heat an after 15 min. heating was stopped and cooled 90-100$^0$c. Now $FeCl_2.4H_2O$ (2.5g.)was added into the solution and was again heated to reflux with magnetic string for about 50min. When thin layer of alumina indicated no free dis porphyrin at this point. Yield iron porphyrin was up to 28.9%. The free base porphyrins were purified by a column of $Al_2O_3$ and eluted with $CH_2Cl_2$. Other iron porphyrin complexes were prepared with the same procedure. The obtained Complexes was analyzed as-

| Element | Found % | Calculated % |
|---|---|---|
| Iron | 7.88 | 7.98 |
| Carbon | 6.75 | 62.45 |
| Hydrogen | 2.86 | 3.15 |
| Nitrogen | 6.67 | 7.02 |

**2.3 Substituted tetra phenyl porphyrin Iron chloride compound was prepared by using one pot mixed solvent method. –**




1. $R_1$= $NO_2$, Cl, $CH_3$, $OCH_3$, H; $R_2$ = H
2. $R_1$ = H; $R_2$ = $NO_2$, Cl, $CH_3$, $OCH_3$
3. M= Fe (III)

It was observed the absorption band in the UV-vis region of iron porphyrin compounds – $NO_2$ group located at -223nm which revealed the red shift compared with other iron porphyrin compounds. The strong electron withdrawing -$NO_2$ group decreased the electronic density of the porphyrin ring. The л- л* electron excitation of porphyrin ring required the light of smaller energy. According to the absorption band located in the long wavelength region. IR and FIR spectra data of porphyrin compounds were listed in the following table-1

| No. | Compounds | $\nu_{N-H}$ | ($\delta_{N-H}$) | $\nu_{=C-H}$ | $\nu_{C=C}$ | $\nu_{C=N}$ | $\gamma_{=C-H}$ | $\nu_{Fe-N}$ | $\nu_{Fe-Cl}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1. | o-$N_2$TPP | 3322 | 969 | 3062 | 1605 | 1348 | 723 | - | - |
| 2. | o-ClTPP | 3326 | 968 | 3055 | 1625 | 1347 | 752 | - | - |
| 3. | o-CH3TPP | 3316 | 966 | 3015 | 1600 | 1347 | 737 | - | - |
| 4. | o-$OCH_3$ TPP | 3321 | 967 | 3070 | 1580 | 1348 | 752 | - | - |
| 5. | TPP | 1309 | 965 | 3050 | 1593 | 1350 | 731 | - | - |
| 6. | p-$MO_2$ TPP | 3320 | 968 | 3054 | 1596 | 1346 | 795 | - | - |
| 7. | p-ClTPP | 3316 | 968 | 3025 | 1626 | 1350 | 795 | - | - |
| 8. | p-$CH_3$TPP | 3316 | 966 | 3025 | 1560 | 1350 | 799 | - | - |
| 9. | p-$OCH_3$TPP | 3322 | 966 | 2925 | 1597 | 1345 | 803 | - | - |
| 10. | o-$NO_2$TPPFeCl | - | - | 2925 | 1608 | 1344 | 742 | 990 | 368 |
| 11. | o-ClTPPFeCl | - | - | 2922 | 1674 | 1335 | 755 | 1000 | 371 |
| 12. | o-$CH_3$TPPFeCl | - | - | 3014 | 1599 | 1333 | 754 | 999 | 360 |
| 13. | o-$OCH_3$TPPFeCl | - | - | 2935 | 1597 | 1335 | 155 | 999 | 362 |
| 14. | TPPFeCl | - | - | 2924 | 1598 | 1342 | 752 | 990 | 380 |
| 15. | p-$NO_2$TPPFeCl | - | - | 2926 | 1596 | 1345 | 800 | 999 | 369 |
| 16. | p-ClTPPFeCl | - | - | 3132 | 1680 | 1339 | 807 | 998 | 360 |
| 17. | P-$CH_3$TPPFeCl | - | - | 3020 | 1495 | 1335 | 798 | 998 | 362 |
| 18. | p-$OCH_3$TPPFeCl | - | - | 2924 | 1608 | 1335 | 809 | 999 | 360 |

It was also observed that at absorption frequencies were different for free base porphyrin and iron porphyrin complexes with different functional groups. The N-H bond stretching and bonding frequencies of free base porphyrin located at -3300$cm^{-1}$ and -960$cm^{-1}$.

It when the iron ion was inserted into the porphyrin ring, the N-H bond vibration frequency of free base porphyrin disappeared. The band at 2924~3132$cm^{-1}$ were assigned to the C-H bond of the benzene ring and pyrrole ring. The band of 1495 ~ 1680$cm^{-1}$ and 1335 ~ 1352$cm^{-1}$ were assigned to the C=C stretching mode and the C=N stretching respectively.

**3. The recent advances of porphyrin based metal complexes in the field of medical science-** Chemistry involving metal based drugs, soon after the entry of cisplatin into the clinic wide range of related compounds were prepared and evaluated neutral Pt (II) complexes with square – planer geometry, including two cis coordinated leaving groups were defined as critical structure for anticancer activity. Gold (III) complexes have long been sought for anticancer treatment. Many gold complexes have displayed interesting anticancer potencies. But their medical application have always been hampered by their poor stability in solution. (7) che et al (9). Research showed that the [Au (TPP)] Cl. (Were $H_2$TPP=tetra phenyl porphyrin) complexes exhibited potent in vitro anticancer activities toward a panel of cancer cell lines many metal complexes have been synthesized and evaluated to overcome the problems of painful insulin injection and side effects for type- 1/ type- 2 diabetes mellitus all though chromium (II) manganese, copper, cobalt, zink, and vanadium and ions have been reported to exhibit insulin mimetic or enhancing properties in vitro and in vivo. Vanadium seems to be the most promising one especially, when coordinated to certain organic ligands. The insulin like effect of vanadium sell on cells and [1112] anddiabaticanimals has stimulated research

into the clinical use of vanadium compounds has insulin mimetic. Numerous other studies have been reported for metal complexes as medicinal agents. The use of Zn applied topically to promote the healing of wounds delay to around 500bc and silver is now commonly applied to prevent infection in bum patients. Zn is used to treat herpes, possibly by inhibiting viral DNA polymerase. Acrodermatitisenteropathy Cais and autosomal recessive metabolic disorder effecting the uptake of Zn for which patient depends of long on Zn supplement to survive.

Amongst the different generation of PS available today, current research seems to focus on the development or investigation into various porphyrin PS types. Porphyrin PSs and their derivatives are organic heterocyclic macrocycles with a high phototoxicity [17] and can be applied in multiple diagnostic and therapeutic functions. However porphyrin exhibit low water solubility and self-aggregation properties, which cause major challenges in PS subcellular localization and uptake , thus affecting the overall treatment outcomes in PDT and PTT cancer therapy [18]. Furthermore, these phototherapies allow porphyrin to combine with other therapeutic modalities in a highly adjuvant-dependent manner [19]. Therefore, many researches have shifted their focus into porphyrin-based nanomedicines [19,20], since nanomedicines can enhance the bioavailability of therapeutic agents and so assist then to accumulate passively in tumors via the enhanced permeability and retention (EPR) effect [21]. Lastly, the multifunctionality of nanomedicines is of great value in order to assist in alleviating unwanted cancer treatment side effects [2].

**4. Abbreviation:-**

PDT- Photodynamic Therapy

PEG- Polyethylene glycol

PET- Proteron Emission Tomography

PTT- Photochemical Therapy

SDT- Sonodynamic Therapy

TPP – Tetra Phenyl Porphyrin

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