Synthesis and Spectral Characterization of meso-Tetrakis-(o-Substituted phenyl) Porphyrin

T. Dhanasekaran, and V. Narayanan*
Department of Inorganic Chemistry, University of Madras, Guindy Campus, Tamilnadu, India.
* vnnara@yahoo.co.in

Abstract

Synthesis of 5, 10, 15, 20 – meso - tetrakis-(o-substituted phenyl) porphyrin was carried out by taking 2-nitrobenzaldehyde and pyyrole in propionic acid. The synthesized nitro substituted porphyrin was further reduced to its corresponding substituted amine using $SnCl_2$-HCl as the reducing agent. Porphyrin synthons that have functional groups at the o-positions are usually employed since they locate near the central metal and thereby they enhance selectivity and turn over number especially in the porphyrin-catalyzed reactions. FT-IR, UV-Vis and NMR were used to characterize the synthesized nitro and amino porphyrin. UV-Vis spectrum clearly confirms the formation of porphyrin. The Soret and Q band peaks were observed at 422 nm and 517, 550, 594, 652 nm respectively. Further fluorescence studies were also carried out.

Keywords Pyrrole, 2-nitrobenaldehyde, Porphyrin

INTRODUCTION

Porphyrins are unique class of compounds with potential applications in all disciplines of science and even in medicine. Synthesis and functionalization of porphyrins have received much attention. This has been mainly due to the use of these compounds in catalysis [1]. The application and importance of porphyrins and metalloporphyrins in the field of biomedicine have increased significantly. They can be used as photosensitizing drugs in photodynamic therapy [2, 3]. Mesoporous molecular sieves are found to be promising hosts for encapsulating metalloporphyrin; they act as efficient catalysts for the alkene epoxidations [4]. When coupled to the unprotected peptide, DNA [5], some metalloporphyrins are used as therapeutic drugs to correct the disorder of heme metabolism and suppress tumors [6].The ortho-substituted tetraphenyl porphyrins have been the subject of considerable recent investigation, particularly the ortho-amino substituted picket-fence porphyrins [7] in which long chain or bulky ortho substituents prevent rotation about the porphyrin-phenyl bond at room temperature

. The stability of the porphyrin macrocycle has been supported by the argument that is an 18 π-electrons system, which exhibits aromaticity. Indeed and as expected, it could be also explained because the reaction of pyrroles with aldehydes, which is one of the most accessible synthetic procedures to synthesize porphyrins [8], is thermo-dynamically favoured, since after condensation the number of particles decreases, rotational freedom degrees are restricted and the bond energies become stronger.

Generally in porphyrin, o-position was sensitive. Because substituted groups in o-position make steric hindrance. And also restrict a free rotation. The ortho-nitro groups are important, since they remove electron density from the porphyrin ring and provide steric hindrance improving the stability of the metalloporphyrin catalysts in oxidation reactions[9]. The nitro group can improve the ability of porphyrin systems to act as radiosensitizers [10].The most frequently employed building blocks of these models are the atropoisomers of tetra(o-aminophenyl) porphyrins[11] first prepared and separated by Collman et al. Nishino et al. described elegant studies of the thermal atropisomerism of tetrakis(2-nitrophenyl)porphyrin.

In this paper, we report synthesis of meso-tetrakis (o-nitro) group and nitro groups are converted to amines using $SnCl_2$.con.HCl. These porphyrins serve as precursors for preparation of bis-deep-pocket porphyrins analogous to the picket-fence porphyrins. Structurally H_2TNPP and reduced H_2TAPP are characterized by using UV-visible absorption spectrum. Soret band obtained at 421nm and Q bands at 517, 550, 595, 650nm respectively. The FT-IR spectrum clearly shows that the porphyrin has phenyl and NO_2 substituents and amines groups also observed clearly 1345, 1525, 3385cm^{-1} respectively. The ^{1}H NMR of the nitro and amine groups resonance in the fixed region and finally Fluorescence spectrum of H_2TNPP and reduced H_2TAPP was studied. The excitation spectrum of fluorescence is in agreement with absorption spectrum, the peaks are observed at 435, 650nm.

Materials and Method

Experimental

The pyrrole and proponic acid were distilled before use. The NMR spectra were recorded on Varian (mercury YH-500) of 500 MHz using tetramethylsilane as internal standard. TLC analysis was performed on aluminum foil plates pre-coated with silica gel (60 F-254, Merck AG). UV-Visible spectra were obtained on Perkin-Elmer UV-spectrometer (UV-1601) using Chloroform. The IR spectra were recorded on Shimadzu infrared spectrophotometer (FT–IR-8400). Fluorescence spectra were recorded using Perkin-Elmer on spectrofluorimeter (RF-5301 PC) in chloroform.

Synthesis of 5,10,15,20 meso-Tetrakis(2-nitro phenyl) Porphyrin

The method used to synthesize of H_2TNPP is based on the strategy described by Lindsey. The nitro groups are substituted at the 2-position taking 2-nitrobenzaldehyde (6.05g) (Aldrich) and 125ml of propionic acid (Aldrich) were heated to boiling in a 3-necked flask. The reaction was carried out in an oil bath with stirring using a mechanical stirrer. 2.8 ml of freshly distilled pyrrole was added to this solution dropwise for 30 minutes and the mixture was refluxed for 1h.100 ml of $CHCl_3$ at 80^o C was added to the reaction mixture. When the solution was allowed to cool, preventing the separation of tarry by-products. The resulting mixture was then cooled to room temperature. The purple crystalline was isolated by using suction filtration and washed with $CHCl_3$ (three 50 ml portion) until the washings were essentially colourless. The crude product was dried under vacuum. (Yield - 1.2 g, 19.8%) The absorbtion maxima in chloroform was observed at 652, 595, 552, 420 nm.

Synthesis of 5,10,15,20 meso-Tetrakis (2-amino phenyl) Porphyrin

The H_2TNPP (0.5 g) was dissolved in 15 ml of Con HCl and $SnCl_2$.$2H_2O$ (3.5 g) was added to this and heated to 80 °C. The solution was refluxed for 1.0 h and titrated in an ice bath with concentrated liquor ammonia until strongly basic. The warm solution was extracted with five 200-mL portions of $CHCl_3$.The combined organic fraction was dried over $MgSO_4$ and rotoevaporated to dryness. The impure 5, 10, 15, 20-tetrakis (2-aminophenyl) porphyrin was washed by $CHCl_3$ on a 5 X 20 cm silica gel column to remove less polar impurities. The top band was removed with acetone, dried over $MgSO_4$, and recrystallized from chloroform/methanol. (Yield - 0.3g, 60%).

Result and Discussion

^{1}H NMR spectroscopy

The sample was analysed using ^{1}H NMR. The chemical shifts of β-pyrrole hydrogens (8 H) were appear at 5-6.5 ppm (close to the nitrophenyl groups) [12]. Then the inner N-H proton (2 H) gives the signals at -2.69ppm, because due to the shielding experienced by N-H proton in the centre of the porphyrin are also affected by the nitrophenyl groups, increasing the nitro groups leads to the expected high frequency shift of the N-H signal.The chemical shifts of phenyl hydrogens (16H) in the spectrum in the downfield appear at 7-8.5ppm. As shown in below figure1,

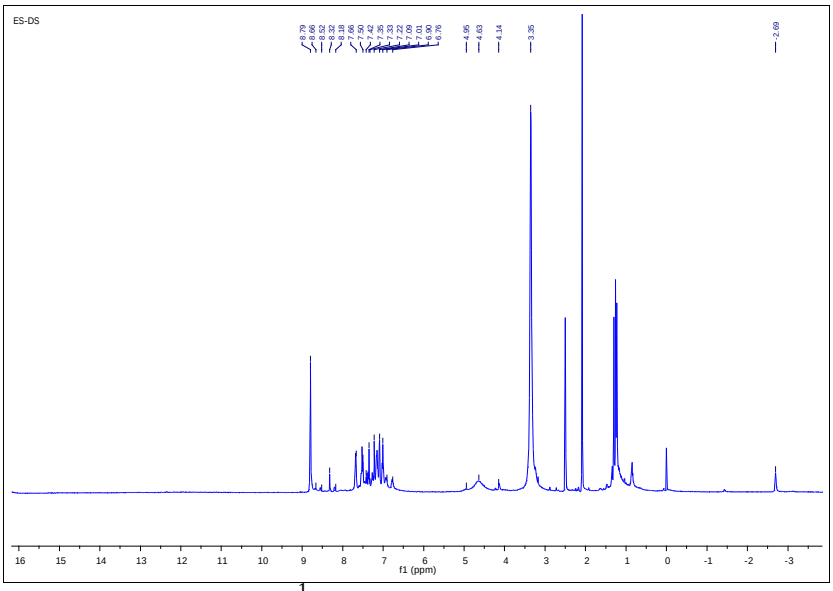

Figure1. ^{1}H-NMR Spectrum of H_2TNPP

UV-Visible Absorption Spectroscopy

The absorption spectra of porphyrin are dominated by the strong bands corresponding with the π-π* transitions in the porphyrin ligand [13]. The two kinds of bands are recognized in the absorption spectra of porphyrin Soret(S) band and Q band. Generally ultraviolet and visible spectrum (410 -440 nm), called S bands; while the latter named Q band (450- 700 nm).The absorbance of H_2TNPP were observe at 418 nm(S band) and 552 nm, 595 nm, 652 nm (Q band) and the reduced H_2TAPP were appear at 421 nm(S band) and 556 nm, 597 nm (Q band). The figure2 is shown in below,

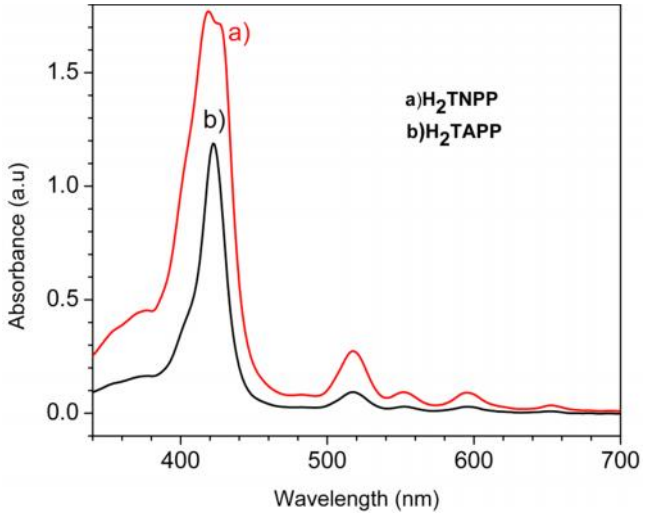

Figure2. UV-Vis Spectra of a) H_2TNPP and b) H_2TAPP

Infrared spectroscopy

The ν N–H absorption band of free base porphyrin is at about 3320 cm^{-1}.The ν C–H absorption band of porphyrin is about 2920 cm^{-1}. Some peaks that appear in the range of 980 to 710 cm^{-1} are related to skeletal ring vibrations of free base porphyrin [14]. The exact position of these bands depends on the substitutions and unsaturation within the NO_2 group. 1345-1525 cm^{-1} and 1352-1525 cm^{-1} absorption ranges to the asymmetrical and symmetrical vibrations, respectively. The N-H pyrrole was observed at 3318 cm^{-1} [15]. For the NH_2 groups in 5,10,15,20-tetrakis (o-amino phenyl)porphyrin), reported these absorptions at 3400 and 1330 cm^{-1}, The (figure 3) shows the amine and N-H peaks at 3386 and 3217 cm^{-1} respectively.1495 and 1619 cm^{-1} peaks appears for bent.

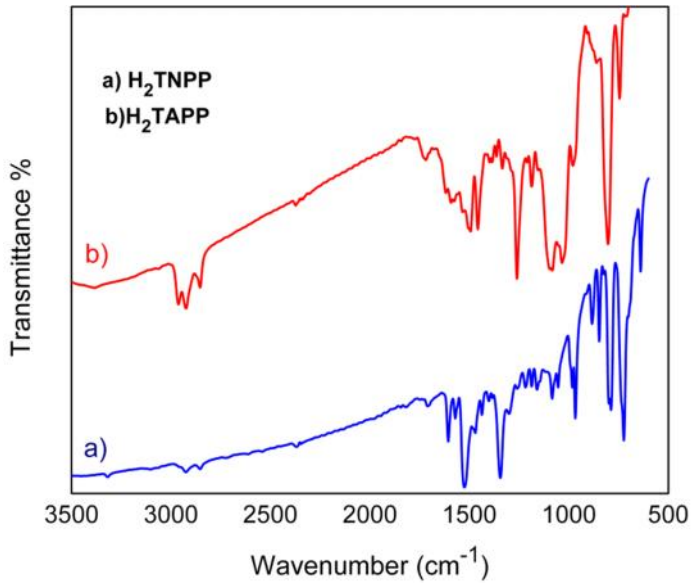

Figure3. FT-IR Spectra of a) H_2TNPP b) H_2TAPP

Fluorescence spectroscopy

The excitation spectrum of fluorescence is in agreement with absorption spectrum. The excitation was carried out in visible range. The complex shows fluorescence behaviour. [16].The emission spectra of H_2TNPP at 638 nm, 696 nm whereas excitation peak at 421 nm and the emission spectrum of H_2TAPP appears at 658 nm ,710 nm respectively to the response excitation at 425 nm as shown in figure 4.

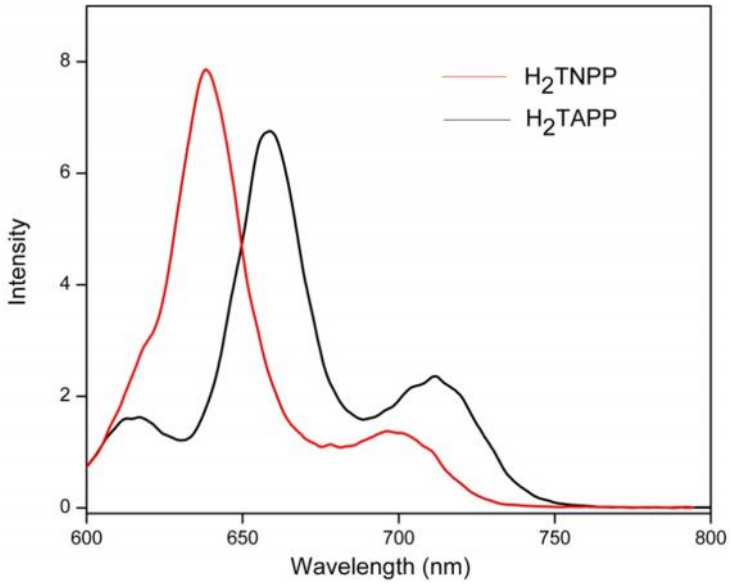

Figure4. Fluorescence spectra of H2TNPP

Conclusion

We have synthesized and characterized by UV-visible absorption, ^{1}H NMR, FTIR, and Fluorescence spectroscopy. These porphyrin forms to which bulky groups can be attached at the ortho positions, to form bis-deep pocket porphyrins. These porphyrins will possess small pockets adjacent to the central core on both faces of the macrocycle. These porphyrins are important as possible of the self-assembly type and they are potentially good catalysts due to the versatility of the nitro and amine groups which can be used to support them in different materials.

Acknowledgement

The authors wish to thank the university authorities for providing the laboratory facilities.

References:

1. B. Meunier, “Metalloporphyrins as versatile catalysts for oxidation reactions and oxidative DNA cleavage,” Chem. Rev., vol. 92, 1992, pp.1411-1456.
2. R. Bonnett, “Photosensitizers of the Porphyrin and phthalocyanine series for photodynamic therapy,” Chem. Soc. Rev., vol. 24, 1995, pp.19-32.
3. V.Narayanan and P. Natarajan. “Photochemistry of macromolecular metal complexes (III) synthesis, spectral and electrochemical properties of macromolecular bound protoporphyrin in aqueous solution,” J. Polym. Sci. A Polym. Chem., Vol. 30, 1992, pp. 2475-2488.
4. A. Kalilur Rahiman, K. Rajesh, K. Shanmuga Bharathi, S. Sreedaran, V. Narayanan, “Manganese (III) porphyrinen capsulated Ti, Si-mesoporous molecular sieves as heterogeneous catalysts for the epoxidation of alkenes,” Appl. Catal., A,” vol. 314, 2006, pp. 216-225.

5. R. K. Jain, D. A. Sarracino, C. Richert. “A tetraphenylporphyrin peptide hybrid with high affinity for single-stranded DNA,” Chem. Commun., vol.3, 1998, pp.423-424.
6. R. Haug, H. Griesser, T. Sabirov, C. Richert, “DNA-Porphyrin hybrids as reaction centers for photosensitized ene reactions with singlet oxygen,” J. Porphyrins Phthalocyanines, vol. 16, 2012, pp. 488-498.
7. K. Rajesh, A. Kalilur Rahiman, K. Shanmuga Bharathi, S. Sreedaran, V. Gangadevi, V. Narayanan, “Synthesis, characterization and bioactive evaluation of copper(II) 5,10,15,20-tetrakis[α,α,α,α-2-(2,6-bis(4-methylpiperazine-1yl-methyl)-4-iminomethylphenol)phenyl]porphyrin: A picket-fence porphyrin,” Spectrochim. Acta, Part A, vol.77, 2010, pp.652-660.
8. B. R James, G. G Meng, K. A Skov, ”Porphyrin chemistry pertaining to the design of anti-cancer drugs; part 1, the synthesis of porphyrins containing *meso* -pyridyl and *meso* -substituted phenyl functional groups,” Can. J. Chem, Vol.72, 1994, pp.1894-1909.
9. M. R. Detty, S. L. Gibson, S. J. Wagner, “Current clinical and preclinical photosensitizers for use in photodynamic therapy,” J. Med. Chem., Vol. 47, 2004, pp. 3897-3915.
10. M.D. Simon, C. Richert, “Synthesis and selection of aminoacyl- and dipeptidyl-tetraphenylporphyrins: toward target-specific nucleic-acid ligands,” Nucleus, vol. 5, 1999, pp. 23-28.
11. J.P. Collman , R.R. Gagne , T.R. Halbert , J.C. Marchon , C.A. Reed, “Reversible oxygen adduct formation in ferrous complexes derived from a picket fence porphyrin model for oxymyoglobin,” J. Am. Chem. Soc, vol.95, 1973, pp.7868–7870.
12. N.D. Gupta, T.J. Bardos, “Synthesis porphyrins. I. synthesis and spectra of some para-substituted meso-tetraphenylporphines (I),” J.Am. Chem. Soc., vol.3, 1966, pp. 495-502
13. V. Sol, J. C. Blais, V. Carre, R. Granet, M. Guilloton, M. Spiro, P. Krausz, “Synthesis, spectroscopy, and photocytotoxicity of glycosylatedamino acid porphyrin derivatives as promising molecules for cancer phototherapy,” J. Org. Chem., vol. 64, 1999, pp. 4431-4444.
14. K. Berlin, R.K. Jain, M.D. Simon, C. Richert,”A porphyrin embedded in DNA,” J. Org. Chem., vol. 63, 1998, pp. 1527-1535.
15. C. Quintana, A. Roger, A. J. Shelnutt, “Synthesis and spectroscopic characterization of bis-pocket porphyrins:tetrakis(2,6-dinitrophenyl)porphyrin and catalytic activity of a manganese(II1) Chloride derivative in alkane oxidation,” Inorg. Chem., vol. 28, 1989, pp 3421–3425.
16. W.T. Chena, X.G. Yia, Z.G. Luo, H.R Fub, J. Liu, “Synthesis, crystal structure, and photoluminescence of a zinc metalloporphyrin,” Russ. J. Phys. Chem. A, vol. 88, 2014, pp. 1228–1231.