International Journal of Recent Trends in Science And Technology, P-ISSN 2277-2812 E-ISSN 2249-8109
Special Issue, ACAEE: 2018 pp 454-462

Research Article

Synthesis, characterization and photo physical studies of metalloporphyrins

Aakanksha Yadav[1*], Anita K[2]

[1]Department of Chemistry, SRK University {[2] Career College }Bhopal, Madhya Pradesh, INDIA.
Email: aakankshayadav20@gmail.com

Abstract

Porphyrins are the key components in biological processes such as photosynthesis of plants and bacteria and the oxygen transport in the cardiovascular systems of humans and animals and thus attracted great interest from researchers of different fields. Our present study involves synthesis of trans-A2B2 porphyrin[4], A3 porphyrin[5] and symmetrical A4 porphyrin[6] by acid catalyzed condensation reaction of dipyrromethane (DPM), 3,5-di-tert-butylphenyldipyrromethane with 3,5-di-tert-butyl-benzaldehyde in the presence of trifluoroacetic acid (TFA) as catalyst and p-chloronil as oxidant. Porphyrins4, 5 and 6 were metallated with Ni2+ and Cu2+. The photo-physical studies have been done via UV-Vis and fluorescence. In UV-Vis all the metalated porphyrins exhibit characteristic Soret band in the range of 400-420 nm and Q band in the range of 515-540 nm. In comparison to free base porphyrins, metalated porphyrins showed less number of Q-bands because of their higher symmetry. Soretband and Q band of all metallo-porphyrins were bathochromically shifted with respect to free base. In Fluorescence studies, only free base porphyrins gave fluorescence while the fluorescence of all metallated porphyrins were completely quenched because of heavy metal effect (spin-orbit coupling).

Key Word: porphyrins, metalloporphyrins, dipyrromethane, trifluoroacetic acid

***Address for Correspondence:**
Dr. Aakanksha Yadav, Department of Chemistry, SRK University, Bhopal, Madhya Pradesh, INDIA.
Email: aakankshayadav20@gmail.com

Access this article online	
Quick Response Code:	Website: www.statperson.com
	Accessed Date: 26 March 2018

INTRODUCTION

Porphyrin is a group of heterocyclic macromolecule organic compound, composed of four pyrrole subunits interconnected at carbon atoms via methene bridges (=CH-). The Porphyrin is an 18 πelectron system and hence exhibits aromaticity. The simplest porphyrin is known as porphine which is the H-analogue (R1-R12 = H), and substituted porphines are called porphyrins. These are one of the vital chemical units essential for several lifeprocesses on the earth. Many biological molecules function with prosthetic groups essentially made of these units. Chlorophylls of chloroplasts which drive photosynthesis, heme as a component of hemoglobin that transportsoxygen to animal tissues and as the central unit of myoglobin ensures the storage of oxygenall these have active sites essentially made of porphyrin core[1,3.] Due to their remarkable and quite flexible photo-physical properties, they have been extensively developed for various bio applications, like photodynamic cancer therapy[3,5]. However, related systems are also being developed for engineering applications for inorganic/organic hybrid materials[6] such as optical power limiting[7,8], photovoltaics[9] and chemical sensors[10,11]. In order to achieve more insight in the complicated natural porphyrins, it is therefore essential to create simpler, synthetic systems that can be studied easily. The biological and chemical importance of metalloporphyrins has made to focus on the nature of the metal ligand linkages in such complexes as well as all the physicochemical properties of the macrocycles.

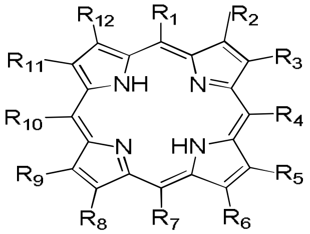


Figure 1: Structure of Porphyrin

The porphyrin ring provides a vacant site at its center, ideally suited of metallation. The NH proton inside the porphyrin ring possess acidic character and hence can get deprotonated and porphyrin ring become porphyrinato ions. These di-anion species with their electronically sensitive planar π framework and central cavity with more or less rigid structure exhibit remarkably ligation characteristics with metal ions. Thus derivatives of porphyrin with almost all metal ions and semimetal ions have been synthesized. The decisive factor to form stable metalloporphyrins is the compatibility of porphyrin ring size with the ionic radii of the metal ion. Hence the metal complexes only result only when these two sizes match each other. The porphyrinatodianion is ideally suited as a tetradenate ligand with metalions. Thus the minimum coordination number of the metal ion possible in a metalloporphyrin is four. The geometry of free base porphyrin is Square planar but it varies with metal ions. Metalloporphyrin may have square planar, square planar bipyramidal and octahedral geometries. They have ability to exhibit variable oxidation states in metalloporphyrins is another impotant feature in this class of compounds.

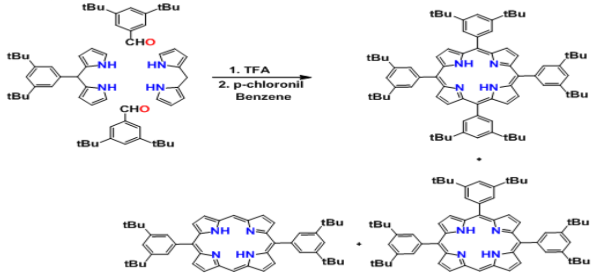
INSTRUMENTATION AND METHODS

Synthesis of 4, 5 and 6 (scheme1)

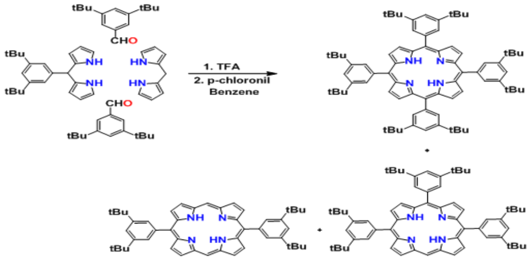
A mixture of 1.25 g of 3,5-di-tert-butylDPM, 0.546 g of *meso*-free DPM, 1.615 g of 3,5-di-tert-butylbenzaldehyde and 584 ml of $CHCl_3$ have been taken in 1000 ml RB and degassed with Ar, set the reaction mixture for half an hour on stirrer. Add 0.850 ml of TFA and again keep for 2 hrs. Add 3.36 g of p-chloronil and set the reaction mixture for 1 hr. and Ar was removed. After 2 hrs, pass the reaction mixture to the basic alumina column and evaporate the solvent under reduced pressure, followed by silica gel column by $CHCl_3$ in hexane. Then separate ^{4,5} and ^{6} with gel permeation chromatography. Molecular masses of **4** ($C_{48}H_{54}N_4$) = 686.43, **5** ($C_{62}H_{74}N_4$) = 875.2778, **6**($C_{76}H_{94}N_4$) =1063.61 Data for **4**^{1}H-NMR (500 MHz, $CDCl_3$) δ; 10.30 (s, 1H), 9.39 (d, J = 4.6 Hz, 2H), 9.13 (d, J = 4.6 Hz, 2H), 8.15 (d, J = 1.7 Hz, 1H), 7.84 (t, J = 1.6 Hz, 1H), 1.58 (s, 18H). Data for **5**^{1}H-NMR (500 MHz, $CDCl_3$) δ; 10.11 (s, 1H), 8.98 (d, J = 4.6 Hz, 4H), 8.88 (d, J = 4.7 Hz, 4H), 8.84 (d, J = 4.7 Hz, 4H), 8.04 (d, J = 1.8 Hz, 2H), 7.99 (d, J = 1.8 Hz, 2H), 7.73 (t, J = 1.8 Hz, 3H), 7.71 (t, J = 1.8 Hz, 3H), 1.47 (s, 36H). Data for **6**^{1}H- R (500 MHz, $CDCl_3$) δ; 8.82 (s, 4H), 8.01 (d, J = 1.8 Hz, 4H), 7.71 (d, J=1.8 Hz, 2H), 7.29(t, J=1.8 Hz, 1H), 1.4 (s, 38H).

Synthesis of 4A, 5A and 6A (scheme 2)

A mixture of **4**, **5** and **6** have been taken separately in different RB, 12.424 g of Nickel(II)acetate tertahydrate saturated with 13.8 ml of methanol in 69.3 ml of $CHCl_3$ was heated at reflux for 20 hrs. at 60°C. The solution was washed with $NaHCO_3$ and NaCl solution, dried over Na_2SO_4 and filter, the solvent was completely evaporated. Then the residue was passed through short plug of silica gel using $CHCl_3$ in hexane. Molecular masses of **4A** ($C_{48}H_{52}N_4Ni$)=742.355, **5A** ($C_{62}H_{72}N_4Ni$) = 874.591, **6A** ($C_{76}H_{92}N_4Ni$) = 1118.67 Data for **4A**^{1}H-NMR (500 MHz, $CDCl_3$) δ; 9.94 (s, 1H), 9.18 (d, J = 4.7 Hz, 2H), 8.99 (d, J = 4.7 Hz, 2H), 7.94 (d, J = 1.7 Hz, 2H), 7.77 (t, J = 1.7 Hz, 2H), 1.51 (s, 17H). Data for **5A**^{1}H-NMR (500 MHz, $CDCl_3$) δ; 9.75 (s, 1H), 9.06 (d, J = 4.7 Hz, 2H), 8.86 (d, J = 4.7 Hz, 2H), 8.76 (d, J = 4.7 Hz, 2H), 7.83 (d, J = 1.8 Hz, 2H), 7.80 (d, J = 1.8 Hz, 2H), 7.66 (t, J = 1.8 Hz, 2H), 7.64 (t, J = 1.8 Hz, 2H), 1.42 (s, 36H). Data for **6A**^{1}H-NMR (500 MHz, $CDCl_3$) δ; 8.71 (s, 2H), 7.80 (d, J = 1.8 Hz, 2H), 7.63 (t, J = 1.8 Hz, 1H), 1.39 (s, 17H).

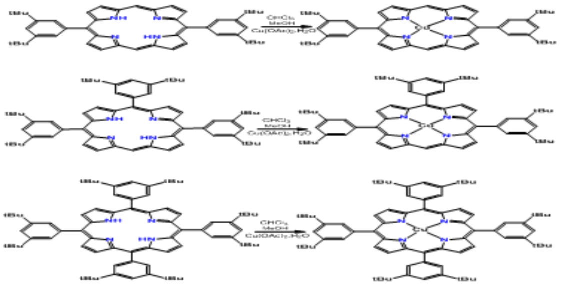


Scheme1: Synthetic scheme of 4, 5 and 6



Scheme2: Synthetic scheme of 4A, 5A and 6A Synthesis of 4B, 5B and 6B (scheme 3)

A mixture of ^{4,5} and ^{6} have been taken separately in different RB and dissolve each compound in 5-10 ml of $CHCl_3$ and add copper acetate salt in each RB, set the reaction mixture at room temperature for 3 Hrs. Molecular masses of **4B** ($C_{48}H_{52}N_4Cu$) = 747.35, **5B** ($C_{62}H_{72}N_4Cu$) = 935.51, **6B** ($C_{76}H_{92}N_4Cu$) = 1123.66



Scheme 3: Synthetic scheme of 4B, 5B and 6B

RESULTS AND DISCUSSION

trans-A2B2 porphyrin ^{4}, A3 porphyrin ^{5} and symmetrical A4 porphyrin ^{6} have been synthesized by acid catalyzed condensation reaction of dipyrromethane (DPM), 3,5-di-tert-butylphenyl DPM with 3,5-di-tert-butyl-benzaldehyde in the presence of Trifluoro acetic acid (TFA) as a catalyst and *p*-chloronil as an oxidant (Scheme 1). All three porphyrins have been successfully separated by employing size exclusion column chromatography. The molecular masses of $^{4, 5}$ and ^{6} have been confirmed by matrix assisted laser desorption ionization (MALDI) technique. Molecular mass of **4**:$(M+H)^+$ = 686.429, calcd for $C_{48}H_{54}N_4$=686.435 (Figure2). Molecular mass of **5**:$(M+H)^+$=874.591, calcd for $C_{62}H_{74}N_4$ =874.591(Figure3). Molecular mass of **6**:$(M+H)^+$ = 1062.767, calcd for $C_{76}H_{94}N_4$ = 1062.748(Figure 4).

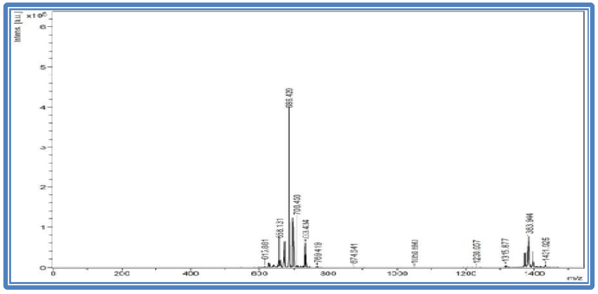


Figure 1: MALDI TOF mass spectrum of 4

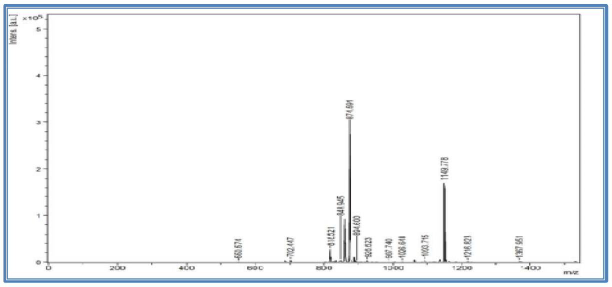


Figure 2: MALDI TOF mass spectrum of 5

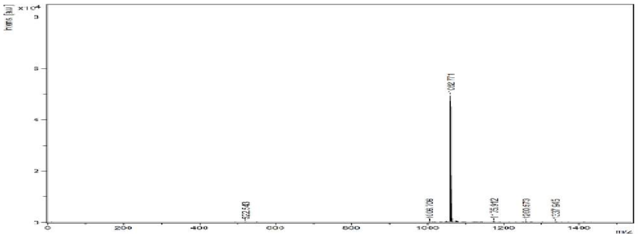


Figure 3: MALDI TOF mass spectrum of 6

The solution state structure of **4** was deduced from its neat ^{1}H-NMR spectrum. Figure 4 shows the partial ^{1}H-NMR spectrum of **4.** Because of its high symmetry, less number of signals was observed as we expected. Two *meso*-free protons resonate as singlet at 10.3 ppm. The β-pyrrolic protons resonate as a set of doublets at 9.3 and 9.1 ppm. *ortho*- and *para*- protons of phenyl group resonate as a doublet and a triplet at 8.15 and 7.84 ppm respectively. The resonance of 3,5-di-tert-butyl group was noticed as a singlet with high intensity at 1.58 ppm. The inner NH-protons of **4** resonate as a broad signal at -3 ppm. This could be ascribed to the diamagnetic anisotropy of porphyrin ring.

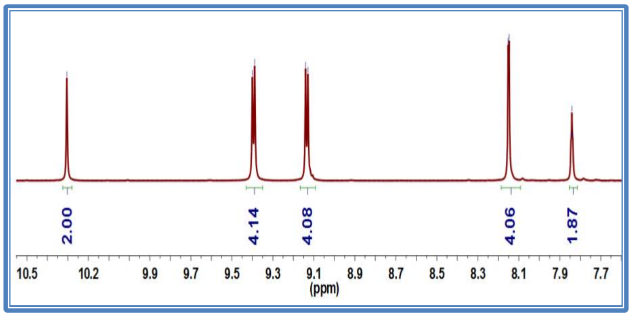


Figure 4: Partial ^{1}H-NMR spectrum of 4

The solution state structure of **5** was confirmed from its remarkable ^{1}H-NMR spectrum. Figure 5 shows the partial ^{1}H-NMR spectrum of **5**. The spectrum of **5** has more number of signals compare to **4** because of its less symmetry. Here, *meso*-protons resonante as a singlet at 10.11 ppm. The *β*-pyrrolic protons resonate as two sets of doublets at 8.98 and 8.88 and 8.84 and 8.04 ppm respectively. *ortho*- and *para*- protons of phenyl group resonate as a set of doublets and a set of triplets at 8.04 and 7.99 and 7.73 and 7.71 ppm respectively. The resonance of 3,5-di-tert-butyl group was noticed as a singlet at 1.47 ppm. The inner NH-protons of **5** resonate as a broad signal at **-**2.97 ppm. This could be attributed to the diamagnetic anisotropy of porphyrin ring.

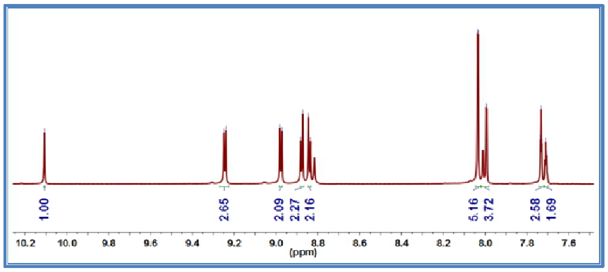


Figure 5: Partial 1H-NMR spectrum of 5

The structure of **6** was confirmed from its neat ^{1}H-NMR spectrum. Figure 6 shows the partial ^{1}H-NMR spectrum of **6**. Compound **6** is so symmetric that the ^{1}H-NMR spectrum gives the least number of signals in comparison to **4** and **5**. The *β*-pyrrolic protons resonate as a singlet at 8.82 ppm. *ortho*-protons of phenyl group resonate as a doublet at 7.71 ppm whereas *para*-protons resonate as a triplet at 7.29 ppm. The resonance of 3,5-di-tert-butyl group was noticed as a singlet with high intensity at 1.4 ppm. The inner NH-protons of **6** resonate as a broad signal at **-**2.66 ppm.

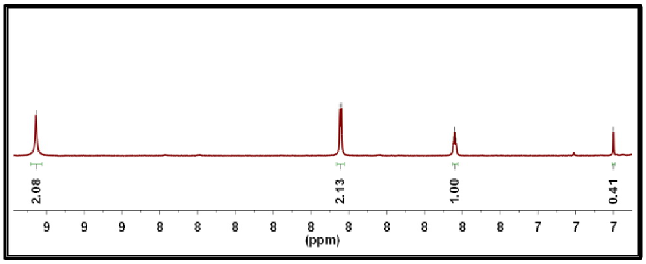


Figure 6: Partial ^{1}H-NMR spectrum of 6

Metallation of$^{\mathbf{4,5}}$ and $^{\mathbf{6}}$ have been achieved by treating chloroform solution of free bases with metal acetates ($M(OAc)_2.xH_2O$) in methanol at room temperature. Molecular masses of nickel (**4A**, **5A** and **6A)** and copper (**4B**, **5B** and **6B**) porphyrin analogues have been confirmed by MALDI TOF mass spectrometry. Molecular mass of **4A**: $(M+H)^+$= 742.345, calcd for $C_{48}H_{52}N_4Ni$= 742.355 (Figure 7). Molecular mass of **5A**: $(M+H)^+$ = 930.495, calcd for $C_{62}H_{72}N_4Ni$ =930.511 (Figure8). Molecular mass of **6A**: $(M+H)^+$ = 1118.825, calcd for $C_{76}H_{92}N_4Ni$= 1118.67 (Figure 9).

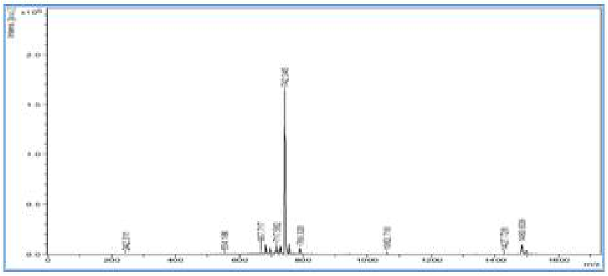


Figure 7: MALDI TOF spectrum of 4A

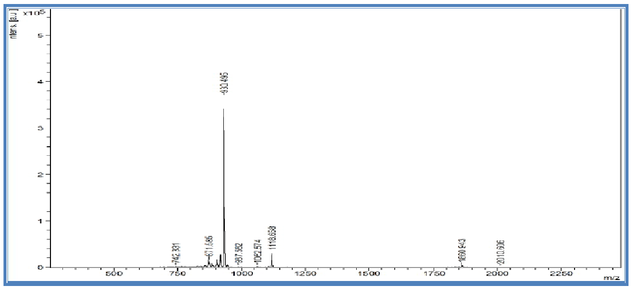


Figure 8: MALDI TOF spectrum of 5A

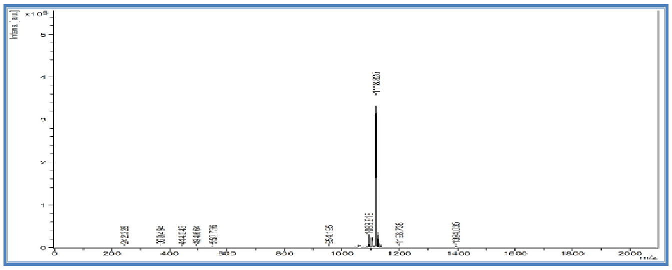


Figure 9: MALDI spectrum of 6A

The solution state structure of **4A** was confirmed from its neat ^{1}H-NMR spectrum. Figure 10 shows the partial ^{1}H-NMR spectrum of **4A.** Because of its high symmetry, less number of signals were observed. Two *meso*-free protons resonate as singlet at 9.94 ppm. The β-pyrrolic protons resonate as a set of doublets at 9.18 and 8.99 ppm. *ortho*- and *para*- protons of phenyl group resonate as a doublet and a triplet at 7.94 and 7.77 ppm respectively. The resonance of 3,5-di-tert-butyl group was noticed as a singlet with high intensity at 1.51 ppm.

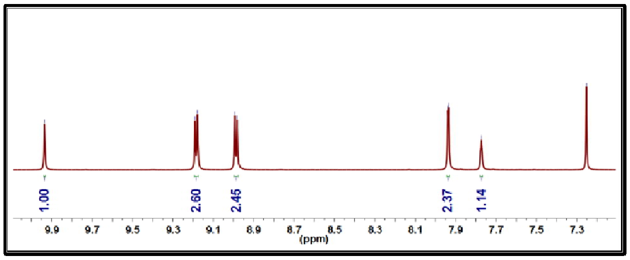


Figure 10: Partial ^{1}H-NMR spectrum of 4A

The solution state structure of **5A** was confirmed from its neat ^{1}H-NMR spectrum. Figure 11 shows the partial ^{1}H-NMR spectrum of **5A. 5A** shows more number of signals because of its less symmetry than **4A**. Here, *meso*-protons resonante as a singlet at 9.75 ppm. The β-pyrrolic protons resonate as two sets of doublets at 9.06 and 8.86 and 8.76 and 7.83 ppm respectively. *ortho*- and *para*- protons of phenyl group resonate as a set of doublets and a set of triplets at 7.83 and 7.80 and 7.66 and 7.64 ppm respectively. The resonance of 3, 5-di-tert-butyl group was noticed as a singlet at 1.42 ppm.

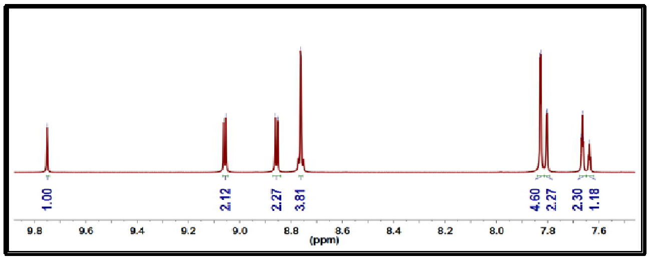


Figure 11: Partial ^{1}H-HMR spectrum of 5A

The structure of **6A** was confirmed from its neat ^{1}H-NMR spectrum. Figure 12 shows the partial ^{1}H-NMR spectrum of **6A**. Compound **6A** is so symmetric that the ^{1}H-NMR spectrum gives the least number of signals in comparison to **4A** and **5A**. The β-pyrrolic protons resonate as a singlet at 8.71 ppm. *ortho*-protons of phenyl group resonate as a doublet at 7.80 ppm whereas *para*-protons resonate as a triplet at 7.64 ppm. The resonance of 3, 5-di-tert-butyl group was noticed as a singlet with high intensity at 1.39 ppm.

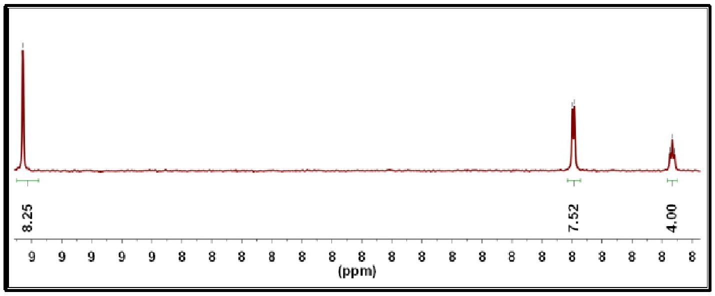


Figure 12: Partial ^{1}H-NMR spectrum of 6A

Molecular mass of 4B: $(M+H)^+$= 747.357, calcd for $C_{48}H_{52}N_4Ni$= 747.35 (Figure 13). Molecular mass of 5A: $(M+H)^+$ = 935.494, calcd for $C_{62}H_{72}N_4Ni$ =935.51 (Figure14). Molecular mass of 6A: $(M+H)^+$ = 1123.623, calcd for $C_{76}H_{92}N_4Ni$= 1123.66 (Figure 15).

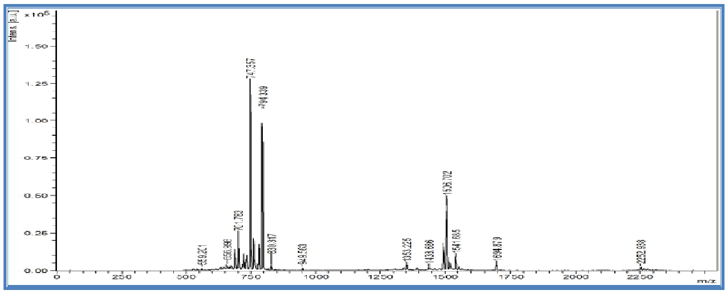


Figure 13: MALDI TOF spectrum of 4B

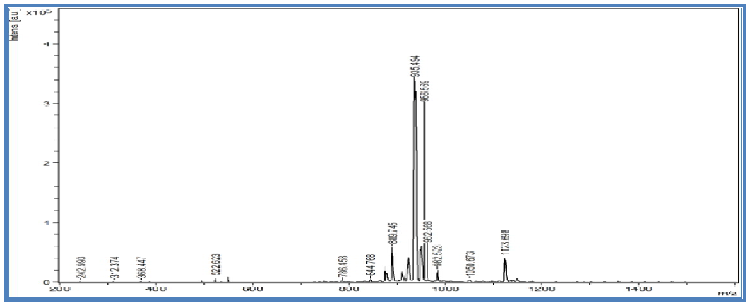


Figure 14: MALDI TOF spectrum of 5B

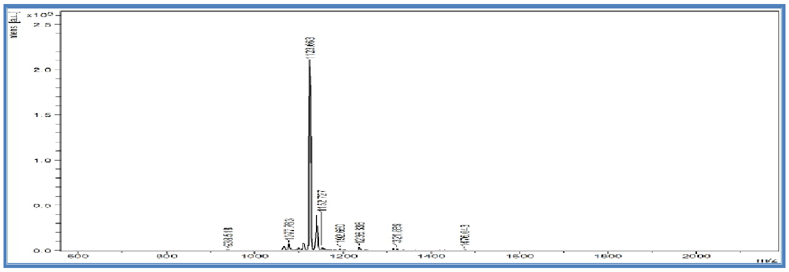


Figure 15: MALDI TOF spectrum of 6B

Photo-physical properties

UV-Visible spectra were recorded for **4A**, **5A**, **6A**, **4B**, **5B** and **6B** in dichloromethane (~10^{-7}M). The molar extinction coefficients have been calculated and listed in table given below.

S. No	Compound	B_{max}□ (nm) □□($M^{-1}cm^{-1}$)	Q_{max}□ (nm) □ ($M^{-1}cm^{-1}$)
1.	**4A**	402 (3.72)	514 (0.29)
2.	**5A**	410 (2.76)	521 (0.26)
3.	**6A**	417 (2.18)	528 (0.21)
4.	**4B**	406 (2.43)	529 (0.11)
5.	**5B**	411 (4.28)	531 (0.16)
6.	**6B**	417 (6.60)	538 (0.36)

All metallated porphyrins exhibit characteristic Soret band in the range of 400-420 nm and Q band in the range of 515-540 nm. In comparison to free base porphyrins (figure3.18), metallatedporphyrins showed less number of Q-bands because of their higher symmetry.

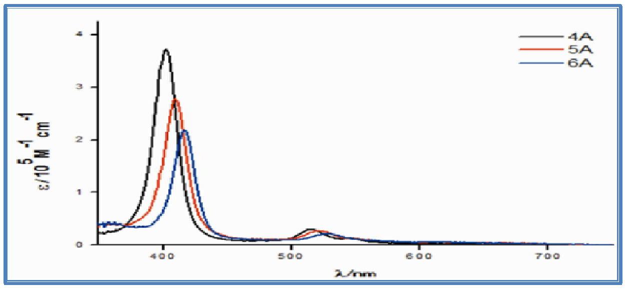


Figure 16: Electronic absorption spectra of 4A, 5A and 6A

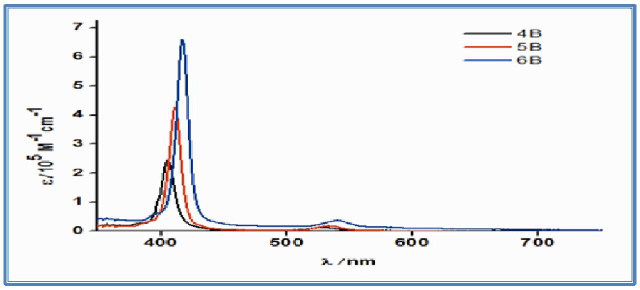


Figure 17: Electronic absorption spectra of 4B, 5B and 6B

Soret or □□band and Q band of all metallo-porphyrins were bathochromically shifted. The shift of 8 nm has been observed for each 3, 5-di-tert-butylphenyl group in Soret and Q bands. The molar extinction coefficients of Ni (II) porphyrins decrease with increasing number of 3, 5-di-tert-butylphenly groups. In contrast, the molar extinction coefficient of Cu (II) porphyrins has been linearly increased with number of 3, 5-di-tert-butylphenly groups.

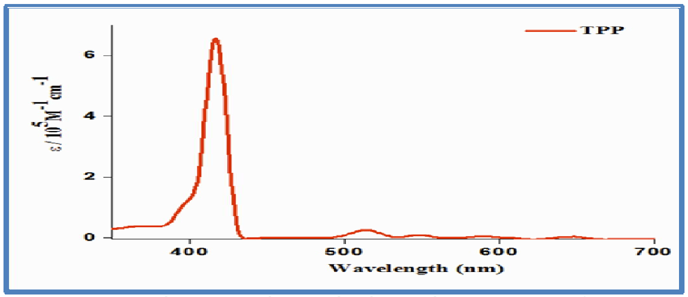


Figure 18: Electronic absorption spectrum of TPP

Fluorescence studies

Fluorescence studies have been carried out for **4**, **5** and **6** in CH_2Cl_2 with the concentration of 10^{-7}M. All the samples were excited at λ_{max} of Soret band (figure 19). The fluorescence emission in free bases is carried out because of first excited state i.e., from LUMO to HOMO. When substitution of t-butyl group increased, the HOMO level will be lifted, as result in there is decrease in energy gap between HOMO and LUMO, due to this red shift is observed i.e., Bathochromic shift.

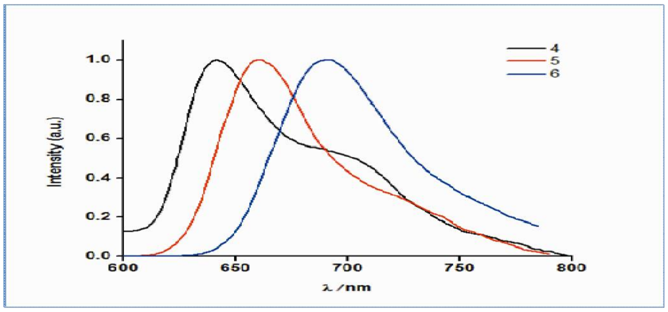


Figure19: Fluorescence emission spectra of 4, 5 and 6

CONCLUSION

The free base porphyrins and metallo-porphyrins have been designed and synthesized. All the synthesized compounds have been well characterized by MALDI-TOF mass spectrometry and NMR spectroscopy. The Photo-physical properties including UV-Vis and fluorescence exhibit characteristics Soret band in range of 400-420 nm and Q-band in the range of 515-540 nm, metalledporphyrins show less number of Q-bands because of their higher symmetry. The Soret bands of all metalledporphyrins are Bathochromically shifted. In fluorescence, metalledporphyrins were completely quenched because of heavy metal effect (spin-orbit coupling).

REFERENCES

1. J.W. Buchler, "The Porphyrins", D. Dolphin (Ed.), Academic, New York,Vol. 1, Part A, Structure and Synthesis (1978).
2. D. Ostfeld, Tsutsui, Acc. Chem. Res., 7, 52 (1974).
3. O.A. Golubchikov and B.D. Berezin, Russ. Chem. Rev., 55(8), 1361, (1986).
4. Rogers, J.; Nguyen, K.; Hufnagle, D.C.; McLean, D.G.; Su, W.; Gossett, K.M.; Burke, A.R.; Vinogradov, S.A.; Pachter, R.; Fleitz, P.A. Observation and interpretation of annulated porphyrins: studies on the photophysical properties of meso-tetraphenylmetalloporphyrins, J. Phys. Chem. A. 2003, 107, 11331–11339.
5. Krasnovskii, A.A.; Bashtanov, M.E.; Drozdova, N.N.; Yuzhakova, O.A.; Luk'yanets, E.A. Laser induced singlet-oxygen-sensitised delayed fluorescence of dyes in aqueous solutions. Quantum Electron. 2002, 32, 83–86.
6. Henderson, B.W.; Dougherty, T.J. How does photodynamic therapy work? Photochem. Photobiol.1992, 55, 145–157.
7. Takagi, S.; Eguchi, M.; Tryk, D.A.; Inoue, H. Porphyrin photochemistry in inorganic/organic hybrid materials: Clays, layered semiconductors, nanotubes, and mesoporous materials. Photochem. Rev. 2006, 7, 104–126.
8. Calvete, M.; Yang, G.Y.; Hanack, M. Porphyrins and phthalocyanines as materials for optical limiting. Synth. Met. 2004, 141, 231–243.
9. Zhao, Z.; Poon, C.-T.; Wong, W.-K.; Wong, W.-Y.; Tam, H.-L.; Cheah, K.-W.; Xie, T.; Wang, D.Synthesis, photophysical characterization, and surface photovoltage spectra of windmill-shaped phthalocyanine–porphyrin heterodimers and heteropentamers. Eur. J. Inorg. Chem. 2008,119–128.
10. Li, L.; Kang, S.W.; Hardena, J.; Sunc, Q.; Zhoua, X.; Daic, L.; Jaklia, A.; Kumarb, S.; Li, Q. Nature-inspired

light-harvesting liquid crystalline porphyrins for organic photovoltaics. Liq. Cryst. 2008, 35, 233–239.
11. Mitra, S.; Foster, T.H. Photochemical oxygen consumption sensitized by a porphyrin phosphorescent probe in two model systems. Biophys. J. 2000, 78, 2597–2605.
12. Biesaga, M.; Pyrzynska, K.; Trojanowicz, M. Porphyrins in analytical chemistry a review. Talanta 2000, 51, 209–224.

Source of Support: None Declared
Conflict of Interest: None Declared