

Synthesis and characterization of new *meso*-substituted unsymmetrical metalloporphyrins

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Abstract. The synthesis and characterization of new *meso*-substituted unsymmetrical metalloporphyrins has been described. A new modified Adler method was used for the synthesis of two unsymmetrical porphyrins. Reactions of these unsymmetrical porphyrins with metal acetates afforded the corresponding metalloporphyrins in high yields with excellent purity. These porphyrins and their metal derivatives were characterized by spectroscopic methods. However, the copper complexes were further studied by ESR spectra and zinc complex by fluorescence spectrum.

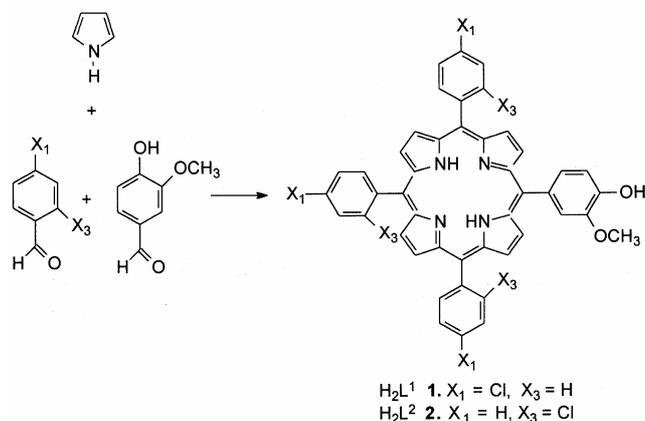
Keywords. *meso*-functionalization; unsymmetrical metalloporphyrins; EPR; fluorescence; metal–ligand interaction.

1. Introduction

Porphyrins are unique class of compounds with potential applications in all disciplines of science, including medicine.¹ The electronic properties of porphyrins can be changed by introducing suitable substituents at the *meso*-position or β -position. Porphyrins and metalloporphyrins are essential to the life of bacteria, fungi, plants and animals and have received considerable attention from many investigators in various fields. Synthetic porphyrins, especially *meso*-tetraphenylporphyrin derivatives substituted in the *para*-positions with soluble acidic, basic and neural groups are of potential interest in medicinal chemistry because they can form chelates either with some toxic heavy metals or with a gamma-ray emitting radioisotopes.^{2–4}

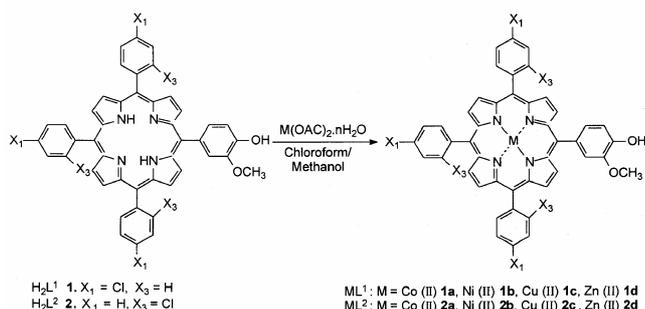
Synthesis and functionalization of porphyrins have received much attention. This has been mainly due to the use of these compounds in catalysis,⁵ photodynamic therapy of cancer cells,⁶ as materials with novel electrical properties⁷ and as biomimetic model systems of primary processes of natural photosynthesis.⁸ Cationic water soluble porphyrins and their metal complexes have been a subject of interest due to their strong affinities for DNA and potential nuclease activity.⁹

Metal complexes of tetrapyrrolic macrocycles play a key role with respect to life on earth because of their implications in a variety of enzymatic systems.¹⁰ Their ability to carry out the reactions rather unusual in organic chemistry has been the object of intensive investigations aiming to utilize them as a model compounds for biological systems and as catalysts.¹¹ Therefore, the synthesis of well defined *meso*-substituted unsymmetrical porphyrin derivatives (A_3B) is of great interest for development of new molecular structures. Two unsymmetrical porphyrins (A_3B , **1** and **2**) were synthesized using modified Adler method¹² (scheme 1).



Scheme 1. Synthesis of porphyrin (**1** and **2**).

*For correspondence



Scheme 2. Synthesis of metalloporphyrin (**1a–1d** and **2a–2d**).

We report here convenient synthesis of some metalloporphyrins (**1a–1d** and **2a–2d**) using *meso*-substituted unsymmetrical porphyrins (A_3B -type) (scheme 2).

2. Experimental

The pyrrole and propanoic acid were distilled before use. The IR spectra were recorded on Shimadzu infrared spectrophotometer (FT-IR-8400). The Far-IR spectra were recorded on Megna IR spectrometer (550 Nicolet). The NMR spectra were recorded on Varian (mercury YH-300) of 300 MHz using tetramethylsilane as internal standard. UV-Visible spectra were obtained on Shimadzu UV-spectrometer (UV-1601) using chloroform. Fluorescence spectra were recorded on Shimadzu spectrofluorophotometer (RF-5301 PC) in chloroform. Mass spectra were obtained on micromass (Q-TOF micro YA-105) using chloroform. Elemental analysis was carried out on Perkin Elmer (240c) elemental analyzer. ESR spectra were recorded on Bruker EMX EPR spectrometer (ER 041 XG-microwave bridge X-band and EPR spectrometer (Varian) with solid polycrystalline sample at room temperature and under liquid nitrogen (LNT). Silica gel (60–120 mesh) was used for column chromatography.

2.1 Synthesis of macrocycles and their complexes

5-[(4-Hydroxy-3-methoxy)phenyl]-10, 15, 20-tris(4-chlorophenyl)porphyrin (H_2L^1 , **1**) and 5-[(4-hydroxy-3-methoxy)phenyl]-10, 15, 20-tris(2-chlorophenyl)porphyrin (H_2L^2 , **2**) were prepared using modified Adler method.¹²

2.1a Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20-tris(4-chlorophenyl)porphyrinato] cobalt

(II) complex (CoL^1) (**1a**): A mixture of porphyrin (H_2L^1) 83.63 mg, 0.1 mmol) in CHCl_3 (10 ml) and $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$ (49.8 mg, 0.2 mmol) in methanol (10 ml) was stirred at 60°C for 30 min. After completion of reaction as indicated by TLC, the reaction mixture was cooled at room temperature. The solvent was evaporated under vacuum to afford crude product, which was purified by column chromatography (silica gel, CHCl_3 :pet ether = 6:4). A second moving band was collected and after evaporation of solvent furnished radish pink as a title compound (**1a**); Yield: 71.5 mg, 80%.

UV-Visible (λ_{max}): 408, 529 nm; IR (KBr): 630.7, 717.5, 802.3, 933.8, 1004.8, 1170, 1263.3, 1348.1, 1392.5, 1452.3, 1492.8, 1596.3, 2931.6, 3057.0, 3533.3 cm^{-1} ; Mass (TOF – MSES + 590) m/z (%): 821.185.

Anal calcd. for $\text{C}_{45}\text{H}_{27}\text{N}_4\text{O}_2\text{Cl}_3\text{Co} \cdot 4\text{H}_2\text{O}$ (%): C, 60.51; H, 3.94; N, 6.27.

Found (%): C, 60.42; H, 3.90; N, 6.17.

2.1b Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20-tris(4-chlorophenyl)porphyrinato] nickel (II) complex (NiL^1) (**1b**): A mixture of porphyrin (H_2L^1) (83.631 mg, 0.1 mmol) in CHCl_3 (10 ml) and $\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O}$ (49.76 mg, 0.2 mmol) in methanol (10 ml) was stirred at 50°C for 3 h. After completion of reaction as indicated by TLC, the solvent was removed under reduced pressure. Then crude product was purified by column chromatography (silica gel, CHCl_3 ; per ether = 8:2) to yield title compound (**1b**) as a purple solid; Yield: 71.44, 80%.

UV-Visible (λ_{max}): 416, 479, 528.0 nm; IR (KBr): 713.6, 804.3, 1089.7, 1203.5, 1261.4, 1350.1, 1454.2, 1502.4, 1558.4, 1652.9, 1845.7, 2374.2, 2983.7, 3180.4, 3649.1 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.25–1.55 (*br s*, 3H, OCH_3), 3.95 (*s*, 3H, OCH_3), 5.95 (*m*, 1H, Ar-OH), 7.15–7.65 (*m*, 12H, Ar-H), 7.95 (*m*, 3H, Ar-H), 8.7–8.85 (*m*, 8H, pyrrole-H); Mass (TOF – MSES + 350) m/z (%): 820.89.

Anal calcd. for $\text{C}_{45}\text{H}_{27}\text{N}_4\text{O}_2\text{Cl}_3\text{Ni} \cdot 4\text{H}_2\text{O}$ (%): C, 60.52; H, 3.95; N, 27.

Found (%): C, 60.40; H, 3.62; N, 6.19.

2.1c Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20-tris(4-chlorophenyl)porphyrinato] copper (II) complex (CuL^1) (**1c**): A mixture of porphyrin (H_2L^1) (100.35 mg, 0.12 mmol) in chloroform (10 ml) and $\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}$ (39.92 mg, 0.2 mmol) in methanol (5 ml) was stirred for 2 h. After completion of reaction as indicated by TLC, the solvent was

removed. The residue was washed with water and extracted with chloroform. The organic layer dried over anhydrous Na_2SO_4 , concentrated *in vacuo* to afford pink solid as a title compound (**1c**); Yield: 96.92 mg, 90%.

UV-Visible (λ_{max}): 413.0, 539 nm; IR (KBr): 717.5, 802.3, 929.3, 1002.9, 1168.8, 1203.5, 1344.3, 1492.8, 1577.7, 3045.4, 3527.6 cm^{-1} ; Far IR: 151.9, 255.4, 337.1, 421.1, 505.1 cm^{-1} ; Mass (TOF – MSES + 2.07 e3) m/z (%): 826.2 (M^+).

Anal calcd. for $\text{C}_{45}\text{H}_{27}\text{N}_4\text{O}_2\text{Cl}_3\text{Cu}\cdot 4\text{H}_2\text{O}$ (%): C, 60.20; H, 3.92; N, 6.24.

Found (%): C, 60.00; H, 3.82, N, 6.19.

2.1d *Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20-tris(4-chlorophenyl)porphyrinato] zinc (II) complex (ZnL^1) (1d)*: A mixture of porphyrin (H_2L^1) (83.631 mg, 0.1 mmol) in chloroform (8 ml) and $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (39.51 mg, 0.18 mmol) in methanol (8 ml) was stirred at room temperature for 4 h. After removal of solvent under reduced pressure, the residue was washed with water to remove excess metal acetate. The residue was then extracted with chloroform, organic layer was dried over anhydrous Na_2SO_4 , and removal of solvent under reduced pressure afforded purple solid as a title compound (**1d**); Yield: 71.9 mg, 80%.

UV-Visible (λ_{max}): 428, 555, 596.0 nm; IR (KBr): 719.4, 852.5, 933.5, 1255.6, 1338.5, 1446.5, 1598.9, 1978.8, 2366.5, 2599.9, 3159.9, 3643.3 cm^{-1} ; Far IR: 144.1, 162.8, 180.7, 209.5, 295.8, 333.2 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.15–1.5 (*br s*, OH of H_2O), 3.95 (*s*, 3H, OCH_3), 5.95 (*s*, 1H, Ar-OH), 7.25–7.75 (*m*, 12H, Ar-H), 8.15 (*m*, 3H, Ar-H), 8.95 (*m*, 8H, pyrrole-H); Mass (TOF – MSES + 400) m/z (%): 830.4205 (M^+).

Anal calcd. for $\text{C}_{45}\text{H}_{27}\text{N}_4\text{O}_2\text{Cl}_3\text{Zn}\cdot 4\text{H}_2\text{O}$ (%): C, 60.07; H, 3.92; N, 6.22.

Found (%): C, 60.09; H, 3.70, N, 5.90.

2.1e *Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20-tris(2-chlorophenyl)porphyrinato] cobalt (II) complex (CoL^2) (2a)*: A mixture of porphyrin (H_2L^2) (83.631 mg, 0.1 mmol) in CHCl_3 (10 ml) and $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (49.8 mg, 0.2 mmol) in methanol (10 ml) was stirred at 60°C for 30 min. After completion of reaction as indicated by TLC, the reaction mixture was cooled at room temperature. The solvent was evaporated under vacuum to afford crude product, which was purified by column chromatography (silica gel, CHCl_3 : pet ether = 5 : 5). A second moving band was collected and after evaporation of

solvent yielded pink solid as a title compound (**2a**); Yield: 80.4 mg, 90%.

UV-Visible (λ_{max}): 410.5, 529.50, 652.50 nm; IR (KBr): 715.5, 754.1, 873.7, 939.3, 1004.8, 1126.4, 1163.0, 1265.5, 1348.1, 1434.9, 1512.1, 1562.2, 2939.3, 3375.2, 3516.0 cm^{-1} ; Far IR: 69.4, 92.0, 145.7, 193.1, 273.3, 285.7 cm^{-1} ; Mass (TOF – MSES + 599) m/z (%): 821.33 (M^+).

Anal calcd. for $\text{C}_{45}\text{H}_{27}\text{N}_4\text{O}_2\text{Cl}_3\text{Co}\cdot 4\text{H}_2\text{O}$ (%): C, 60.51; H, 3.94; N, 6.27.

Found (%): C, 60.48; H, 3.91, N, 6.26.

2.1f *Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20-tris(2-chlorophenyl)porphyrinato] nickel (II) complex (NiL^2) (2b)*: A mixture of porphyrin (H_2L^2) (83.631 mg, 0.1 mmol) in CHCl_3 (10 ml) and $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (49.76 mg, 0.2 mmol) in CH_3OH (15 ml) was stirred at 60°C for 4 h. After evaporation to dryness under vacuum, the residue was purified by column chromatography (silica gel, CHCl_3 : pet ether = 5 : 5). The second pink band was collected and after evaporation of solvent afforded pink solid as a title compound (**2b**); Yield: 77.44 mg, 80%.

UV-Visible (λ_{max}): 420.0, 544, 583 nm; IR (KBr): 451.3, 640.3, 715.5, 752.2, 796.5, 1068.5, 1120.6, 1163.0, 1261.4, 1336.6, 1429.2, 1467.7, 1510.2, 1595.0, 2366.5, 3689.6 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.15–1.55 (*br s*, OH of H_2O), 3.95 (*s*, 3H, OCH_3), 5.95 (*s*, 1H, Ar-OH), 7.25–7.65 (*m*, 12H, Ar-H), 8.15 (*m*, 3H, Ar-H), 8.85–9.0 (*m*, 8H, pyrrole-H); Mass (TOF – MSES + 360) m/z (%): 820.62.

Anal calcd. for $\text{C}_{45}\text{H}_{27}\text{N}_4\text{O}_2\text{Cl}_3\text{Ni}\cdot 4\text{H}_2\text{O}$ (%): C, 60.52; H, 3.95; N, 6.27.

Found (%): C, 60.43; H, 3.82, N, 6.20.

2.1g *Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20-tris(2-chlorophenyl)porphyrinato] copper (II) complex (CuL^2) (2c)*: A mixture of porphyrin (H_2L^2) (83.63 mg, 0.1 mmol) in chloroform (8 ml) and $\text{Cu}(\text{OAc})_2\cdot \text{H}_2\text{O}$ (39.93 mg, 0.2 mmol) in methanol (5 ml) was stirred at room temperature for 2 h. After completion of metalation as indicated by TLC, the solvent was removed under reduced pressure. The residue was washed with water and extracted with chloroform. The organic layer dried over anhydrous Na_2SO_4 , concentrated *in vacuo* to afford reddish pink solid as a title compound (**2c**). Yield: 71.44 mg, 80%.

UV-Visible (λ_{max}): 415.50, 540, 619 nm; IR (KBr): 715.5, 754.1, 798.5, 933.5, 1001.0, 1122.5,

Table 1. UV-visible spectroscopic data of free base porphyrins (H_2L^1 , **1**) and metalloporphyrins (**1a–1d**).

Porphyrin/metalloporphyrins	Compound no.	UV-visible parameter (λ_{max}/nm)	
		Soret	Q bands
H_2L^1	1	423	517, 552, 591, 648
CoL^1	1a	408	529
NiL^1	1b	416	479, 528
CuL^1	1c	413	539
ZnL^1	1d	428	555, 596

1163.0, 1203.5, 1263.3, 1342.4, 1433.0, 1512.1, 1598.9, 2356.9, 3444.6 cm^{-1} ; Far IR: 164.4, 191.6, 218.0, 263.9, 296.9, 316.2, 330.8, 365.8, 405.5, 429.6, 579.8 cm^{-1} ; Mass (TOF – MSES + 1.99 e3) m/z (%): 826.2612 (M^+).

Anal calcd. for $C_{45}H_{27}N_4O_2Cl_3Cu \cdot 4H_2O$ (%): C, 60.20; H, 3.92; N, 6.24.

Found (%): C, 60.00; H, 3.72, N, 6.0.

2.1h *Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20-tris(2-chlorophenyl)porphyrinato] zinc (II) complex (ZnL^2) (**2d**):* A mixture of porphyrin (H_2L^2) (81.61 mg, 0.1 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (54.75 mg, 0.25 mmol) in (chloroform : methanol = 5 : 5 ml) was stirred for 3 h. After completion of metalation as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was extracted with chloroform and dried over anhydrous Na_2SO_4 , after evaporation of solvent under reduced pressure furnished purple solid as a title compound (**2d**); Yield: 76.4 mg, 85%.

UV-Visible (λ_{max}): 425, 593, 693 nm; IR (KBr): 715.5, 754.1, 796.5, 933.5, 999.1, 1068.5, 1120.6, 1163.0, 1261.4, 1336.6, 1512.1, 1568.9, 3058.9, 3525.6 cm^{-1} ; 1H -NMR (300 MHz, $CDCl_3$): 1.25–1.55 (*br s*, OH of H_2O), 4.0 (*s*, 3H, OCH₃), 6.0 (*s*, 1H, Ar-OH), 7.25–7.65 (*m*, 12H, Ar-H), 8.15 (*m*, 3H, Ar-H), 8.65–8.95 (*m*, 8H, pyrrole-H); Mass (TOF – MSES + 400) m/z (%): 829.52.

Anal calcd. for $C_{45}H_{27}N_4O_2Zn \cdot 4H_2O$ (%): C, 60.07; H, 3.92; N, 6.22.

Found (%): C, 60.12; H, 3.50, N, 6.0.

3. Results and discussion

The *meso*-substituted unsymmetrical porphyrins (H_2L^1 and H_2L^2) in chloroform and different metal acetates (in methanol) were allowed to react resulting in the formation of the corresponding metal complex (scheme 2).

3.1 UV-visible spectra

In free base porphyrins (**1**) and (**2**) showed one Soret band near to 400 nm and four Q bands in visible region. On metallation, the porphyrin ring deprotonates forming dianionic ligand. The metal ions behaved as Lewis acids accepting lone pairs of electrons form dianionic porphyrin ligand. Unlike most transition metal complexes, their colour is due to absorption(s) within the porphyrin ligands involving the excitation of electrons from π to π^* porphyrin ring orbital.¹³ The observation in all complexes indicates that the change in spectrum (fewer peaks) on metalation is due to increased symmetry relative to the free base porphyrins (H_2L^1 and H_2L^2). Comparative electronic data for free base porphyrins (**1**) and (**2**) and metalloporphyrins (**1a–1d**, **2a–2d**) are listed in tables 1–2 and figures 1–6.

The two hydrogens on the nitrogen atoms in free base porphyrin reduce the ring symmetry from square (for metalloporphyrins) to rectangular that is from D_{4h} to D_{2h} . In general, more symmetrical molecule gives simpler spectrum.

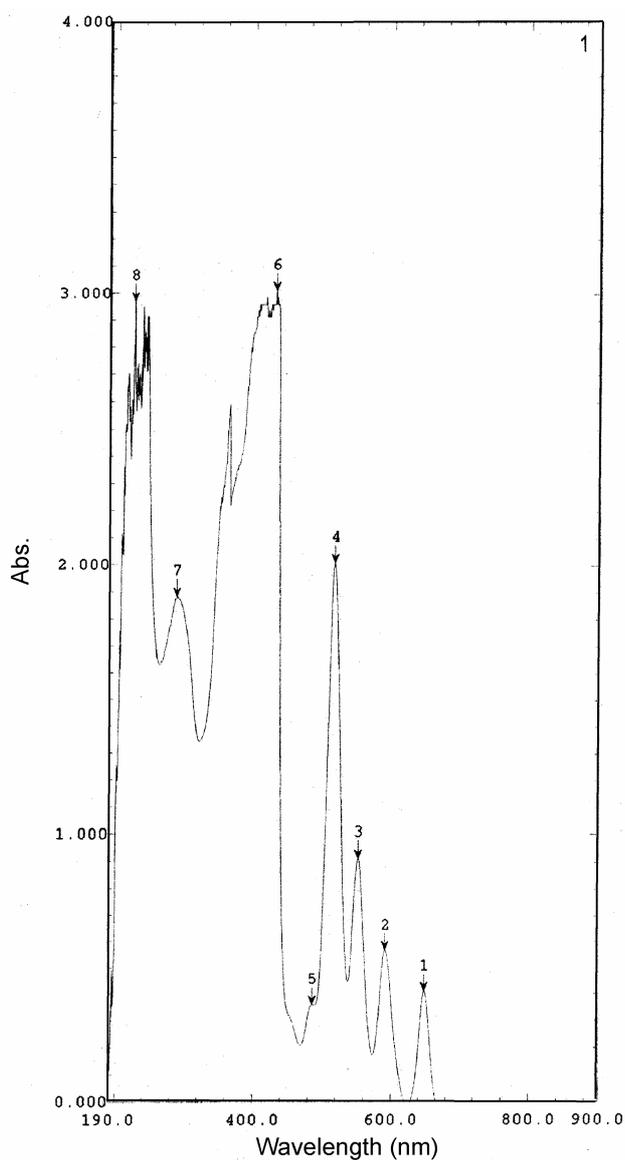
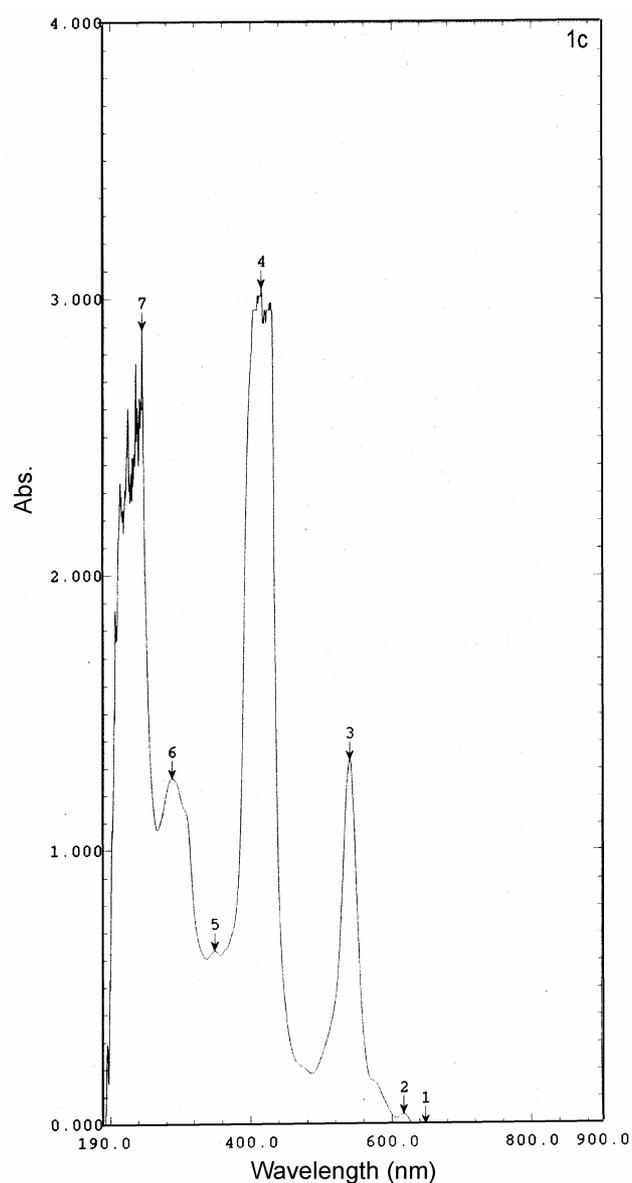
It is observed from tables 1 and 2 that when Zn binds to porphyrin compound (**1**) and (**2**), the absorption spectrum changes owing to the symmetry effect but the π to π^* energy gap is little affected and the regular metalloporphyrins are resulted. In contrast to the other metals (e.g. Ni, Co and Cu) peaks are shifted to the shorter wavelength due to metal $d\pi$ (dxz and dyz) to porphyrin π^* back bonding. The electronic spectra of free base ligand **1** and **2** with corresponding complex (**1c** and **2a**) and also comparative spectra are presented in figures 1–6.

3.2 IR spectra

The IR spectral data of porphyrins and metalloporphyrins ascertain some functional groups to exist. The ν_{N-H} absorption band of free base porphyrin is

Table 2. UV-visible spectroscopic data of free base porphyrin (H_2L^2 , **2**) and metalloporphyrins (**2a–2d**).

Porphyrin/metalloporphyrins	Compound no.	UV-visible parameter (λ_{max}/nm)	
		Soret	Q bands
H_2L^2	2	415	514.5, 548, 589, 650
CoL^2	2a	410.50	529.50, 652.50
NiL^2	2b	420	544, 583
CuL^2	2c	415.50	540, 619
ZnL^2	2d	425.0	593.0, 693.0

**Figure 1.** UV-visible spectrum of **1**.**Figure 2.** UV-visible spectrum of **1c**.

at about 3320 cm^{-1} , δ_{N-H} (in planarity) and δ_{N-H} (out of planarity) absorption band of porphyrin band is about 967 cm^{-1} and 728 cm^{-1} . The ν_{C-H} absorption

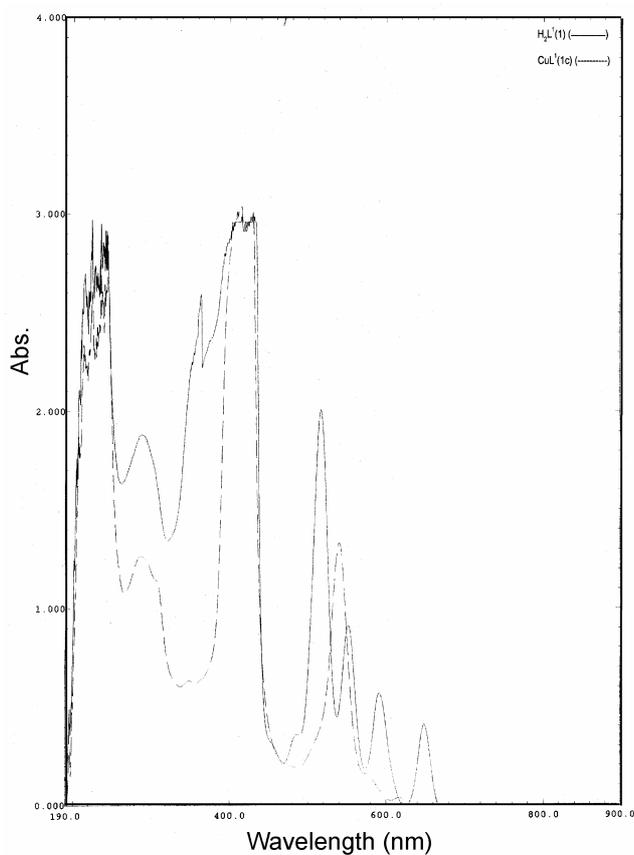
band of porphyrin is about 2920 cm^{-1} . Some peaks that appear in the range of 980 to 710 cm^{-1} are related to skeletal ring vibrations of free base por-

Table 3. ESR data for compounds (**1c** and **2c**) at room temperature.

Metalloporphyrins	Compound no.	g_{\parallel} (G)	g_{\perp} (G)	A_{\parallel} (G)
CuL ¹	1c	2.183	2.057	200.6
CuL ²	2c	2.106	2.060	204.8

Table 4. ESR data for compounds (**1c** and **2c**) at LNT.

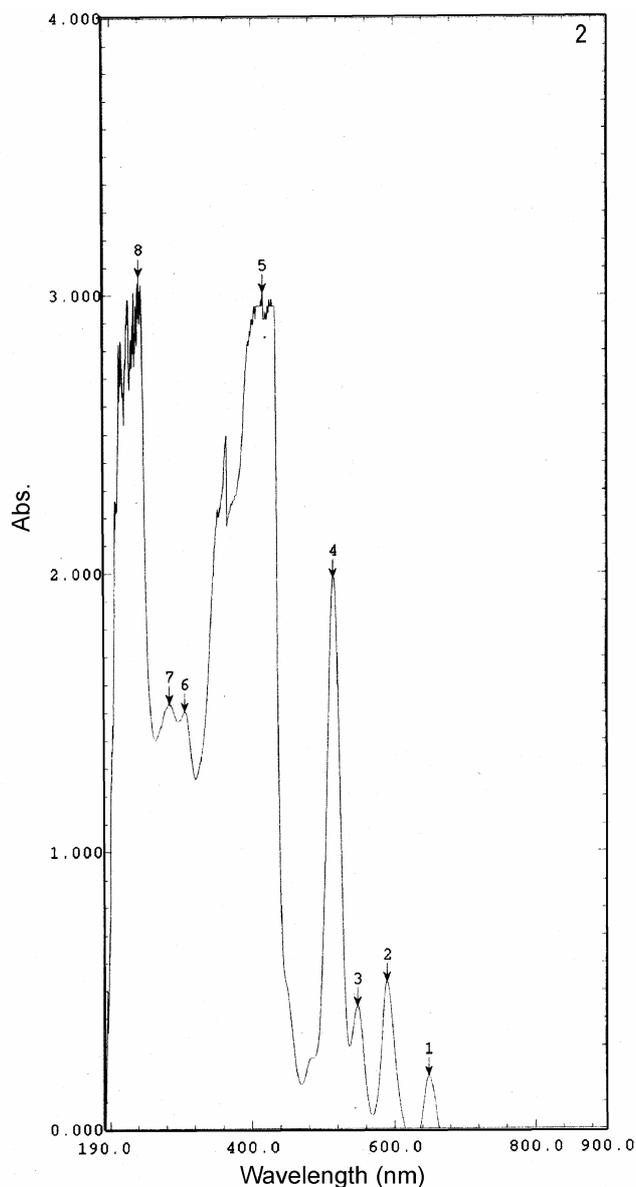
Metalloporphyrins	Compound no.	g_1	g_2	g_3	g_4
CuL ¹	1c	2.41	2.19	2.05	1.98
CuL ²	2c	2.106	2.06	—	—

All $G > 4$ **Figure 3.** Comparison of UV-visible spectrum of ligand H₂L¹(**1**) and CuL¹(**1c**).

phyrins. These bands disappear in the all synthesized metalloporphyrins after the metal insertion reactions and strong band near 1000 cm⁻¹ corresponds to skeletal ring vibration of metal porphyrin agree with the result of literature.¹⁴⁻¹⁶

3.3 NMR spectra

The ¹H-NMR data of free base porphyrins (**1**) and (**2**) in comparison with metalloporphyrins (**1a-d** and

**Figure 4.** UV-visible spectrum of **2**.

2a-d) showed that highly shielded peak at around -2.9 ppm is the N-H at the center of porphyrin ligand

and this peak disappeared after complexation of porphyrin with metal because the two H atom are replaced by metal ion.¹⁵ This is a great movement to high field on the basis of strong shield effect of porphyrin ring.

3.4 ESR spectra

Electron spin resonance study of complexes (1c) and (2c) was carried out at room temperature and under liquid nitrogen temperature. A large number of investigators working on porphyrins and related systems have utilized this method in probing into struc-

tural and dynamic aspects of porphyrins as well as their role in biological system.¹⁷ In case of paramagnetic systems one or more unpaired electrons may reside either on the π -ligand system or in the central metal atom or in both.

The values of g-tensor are in tables 3 and 4. For complexes (1c) and (2c), the anisotropy in the $g_{\parallel} = 2.203$ and $g_{\perp} = 2.05$ leads to D_{4h} symmetry of compound (square planar) around the Cu(II) ion. The splitting of spectra into four lines at LNT gives hyperfine constant $a = 178\text{G}$ which confirms the ground state of Cu(II) ion is as $S = 1/2$. The unpaired electron of the metal ion interact with Cu(II) nucleus with the nuclear spin $I = 3/2$ resulting in splitting of spectrum into four lines. This confirms the copper is in +2 state oxidation state, with $S = 1/2$ as a spin state resulting in a single line main EPR spectra.

Moreover, the value of G calculated as $g_{\parallel} - 2/g_{\perp} - 2$ comes out to be >4 for both the compounds which leads to packing of molecular planes one above the other. This confirms the planar arrangement of porphyrin ring in the three-dimensional space.

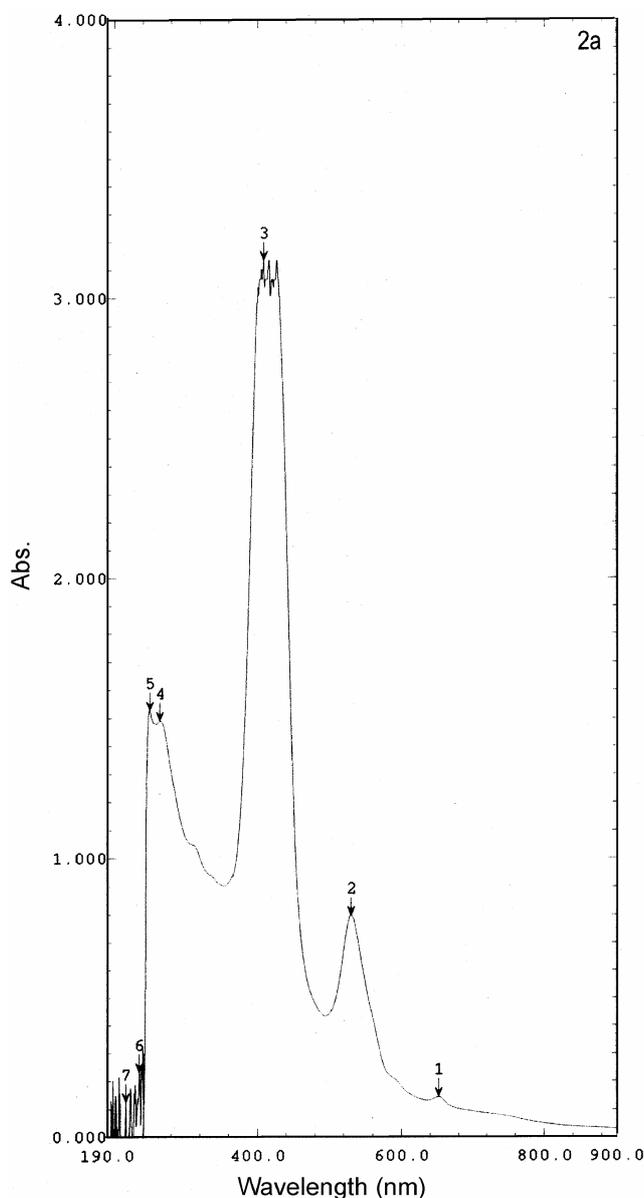


Figure 5. UV-visible spectrum of 2a.

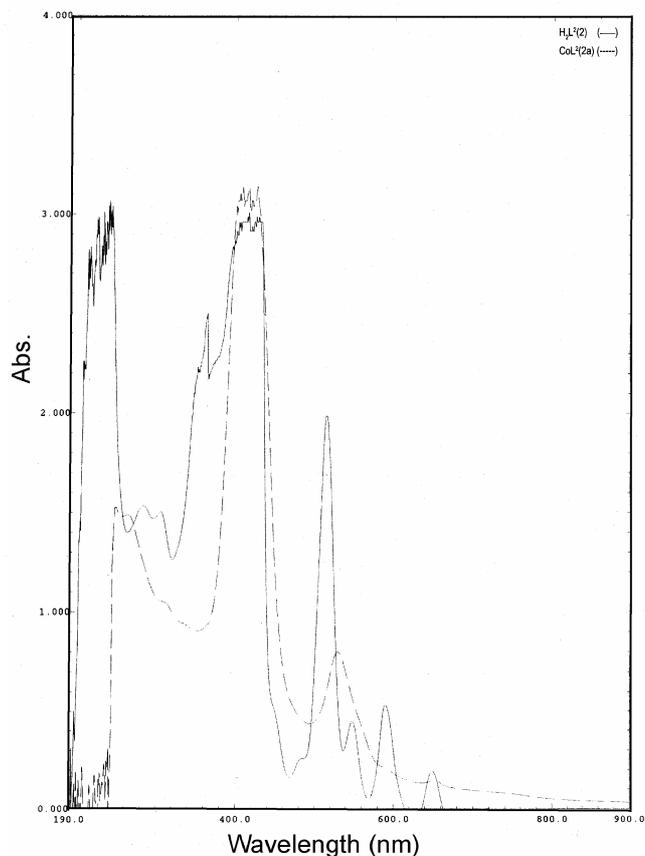


Figure 6. Comparison of UV-visible spectrum of ligand H_2L^2 (2) and CoL^1 (2a).

Table 5. Excitation and emission spectral data for compound (**2d**, ZnL²).

Emission spectra (in CHCl ₃)	Excitation spectra (in CHCl ₃)
$\lambda_{\text{ex}} = 555.0 \text{ nm}$	$\lambda_{\text{ex}} = 603.0 \text{ nm}$
$\lambda_{\text{em}} = 604.0 \text{ nm}$	$\lambda_{\text{em}} = 604.0 \text{ nm}$

Microwave frequency: 9.762770 GHz

Microwave power: 4 mW

Modulation frequency: 100 kHz

Receives gain: 5.02×10^{-4}

3.5 Fluorescence spectra

Fluorescence spectrum of Zn complex was studied. The excitation spectrum of fluorescence is in agreement with absorption spectrum. This implies that the fluorescence does not originate from some impurities. The excitation was carried out in visible range. The complex shows fluorescence behaviour (table 5).

The emission spectra has three peaks at 604, 649 and 785 nm whereas excitation spectra have four peaks at 412, 434, 556 and 603.0 nm.

Acknowledgements

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