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NEW *MESO*-SUBSTITUTED UNSYMMETRICAL PORPHYRINS: SYNTHESIS AND SPECTRAL STUDIES

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ABSTRACT

Three new unsymmetrical porphyrins bearing *meso*-functionlization have been synthesized and characterized. The structural assignment of these porphyrins was based on UV-visible, IR, ^{1}H NMR, mass, spectra and elemental analysis. The Present communication deals with new methodology for the synthesis of porphyrins, which is different from the general synthetic procedure developed by Adler.

Key words: General synthesis, Unsymmetrical structure, Aldehydes, Pyrrole, Spectral study.

INTRODUCTION

Considerable interest has already been devoted to study of multisite receptors[1]of cation/anion binding[2] and of the mechanism of single and multimetallic enzymes[3]. Synthetic porphyrins, especially *meso*-tetraphenylporphyrin derivatives substituted in the para-positions with soluble acidic, basic and neutral groups are of potential interest in medicinal chemistry, because they can form chelates either with some toxic heavy metals or with gamma-ray emitting radioisotopes[4-6]. Since the porphyrin units in symmetrical arrays are identical, it is difficult to achieve selective excitation of the porphyrin unit upon irradiation to study electron transfer or energy transfer. Selective excitation of the porphyrin can be achieved easily if the porphyrin units in the array are not identical (unsymmetrical). *Meso*-substituted porphyrins bearing specific patterns of functional groups are valuable components in the synthesis of porphyrin-based biomemetic systems and molecular materials[7-8].

An attractive routes for the synthesis of these valuable compounds are reported previously[8,9]. However, poor yields, drastic conditions and long reaction times are the limitations associated with these reported methods. Even Adler method[10] is also unsatisfactory due to the formation of high level tar, which creates problem of purification.

This problem is sometimes overcomed by using modified Adler method[11], which involves the use of absolute ethanol to minimize purification problem. However, this method was applied for synthesis of *meso*-substituted porphyrins and it is more convenient as the reaction temperature is controlled between 124-126^{0}C, which minimizes tar formation and ultimately resulted in slightly higher yields of desired products without use of excess pyrrole. Keeping this in mind, we have promoted to synthesize the

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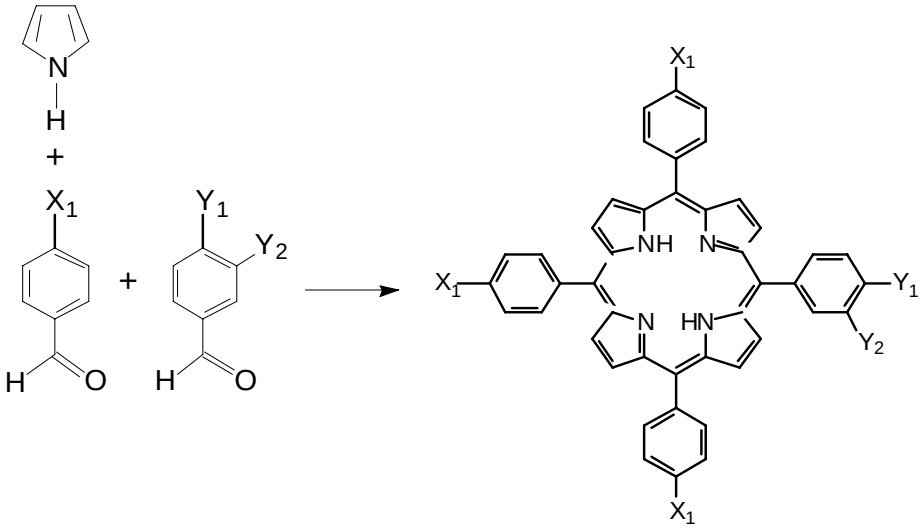
porphyrins having different *meso*-functionalization. Presently, we have prepared a new unsymmetrical substituted pophyrins **(A_3B) (1-3) (Scheme 1)**.



1. X_1 = H, Y_1 = $N(CH_3)_2$, Y_2 = H

2. X_1 = Cl, Y_1 = $NHCOCH_3$, Y_2 = H

3. X_1 = H, Y_1 = OH, Y_2 = OCH_3

Scheme 1: Synthesis of porphyrins (1-3)

RESULTS AND DISCUSSION

Compound **1, 2** and **3** were characterized by UV-Visible IR, ^{1}H NMR and mass spectra. The data of UV-Visible spectra were recorded in $CHCl_3$ (Table 1). Results in Table 1 indicates that according to Scott rule, aromatic derivatives, which are substituted in para positions display a stronger red shift of soret absorption band was observed in compound No. 2 from spectral data.

Table 1: UV-Visible spectral data (nm) of the porphyrins (1-3) in chloroform

Compd. No.	Soret band	Q bands			
		Qy (1-0)	Qy (0-0)	Qx (1-0)	Qx (0,0)
1	415	519.50	558.0	651.50	-
2	416	516.0	-	-	-
3	413	516.50	552.0	591.0	648.0

Infrared spectroscopy data confirmed presence of some functional groups. For example, IR bands (out of planarity) at 705.9, 731.9 cm^{-1} and IR peaks (in planarity) at 968.2, 966.3, 970.1 cm^{-1} indicates presence of NH in all three compounds and it was also confirmed by IR bands at 3315.4, 3317.3 cm^{-1}. IR band at 3504.4 in compound **3** indicates presence of –OH. IR value at 2925.8 indicates presence of C-H. The presence of C=C and C=N are confirmed due to IR bands at 1473.5, 1485.1, 1469.7, 1519.8, 1593.1, 1595.0 cm^{-1}. Structures of new compounds are also confirmed by ^{1}H NMR spectra. Chemical shifts are reported with reference to internal tetramethylsilane. The negative chemical shift of these compounds between 2.65 to 2.82 indicates presence of highly shielded NH at the center of porphyrin ligand because of conjugative effect displayed by the porphyrin ring. Highly shielded NH signal (-2.82) of compound **2** is due

to all meso-phenyl carbon substituted at para positions. The peaks at 1.22 to 1.6 δ is due to the OH of water and the peak at 3.22 is due to two CH_3 groups in compound 1. Similarly peaks at 2.29 and 7.84 are due to CH_3 and NH group respectively in compound **2**. In compound **3**, the peaks at 4.1 and 6.0 are due to OCH_3 and –OH respectively. M^+ values from mass spectra are in agreement with the molecular weight of these three synthesized compounds. However, yields of the title compounds are very low (8-9%) because reaction prefers the formation of symmetrical *meso*-substituted porphyrins in major amount.

In conclusion, UV-Vis, IR, ^{1}H NMR, mass spectra and elemental analysis agreed with the structures of these unsymmetrical porphyrins.

EXPERIMENTAL

All reagent grade chemicals were obtained either from Aldrich (USA) or S. D. Fine Chemicals, Mumbai (India). The pyrrole, benzaldehyde and propionic acid were freshly distilled before use. Other chemicals were used as received. For TLC Silica gel (60-120 mesh) was used.

The electronic absorption spectra were recorded on a Shimadzu (UV-1601) spectrophotometer. IR and ^{1}H NMR spectra were recorded on Shimadzu (FT-IR-8400) and Varian (Mercury-YH-300) on 300 MHz respectively. Elemental analysis was carried out on Perkin Elmer (240C) elemental analyzer and mass spectra were recorded on a (Q-TOF YA 105) Micromass Spectrometer.

Synthesis of 5-[(4-N,N-dimethylamino)phenyl)10,15,20 tris(phenyl) porphyrin (1)

To a mixture of benzaldehyde (8.024 g, 0.076 mol) and 4-N, N-dimethylaminobenzaldehyde (3.754 g, 0.025 mol) in propoionic acid (300 mL) was heated at 124-126^{o}C and at this temperature pyrrole (6.789 g, 0.101 mol) was added slowly and reaction mixture was further heated at this temperature for 45 min. Propionic acid (200 mL) was distilled off from the reaction mixture under vaccum (10 mm Hg). After cooling the reaction mixture at room temperature, absolute ethanol (100 mL) was added to a reaction mixture, which was then stored overneight in a freezer at 5^{o}C. The purple coloured precipitate was filtered off and washed with methanol (2 x 10 mL) and further purified by column chromatography. On a column of silica gel (60-120 mesh) using chloroform as a eluent. The first band was pink, which contained symmetrical 5, 10, 15, 20 (tetraphenyl) porphyrin as a major amount. A third band, which moved very slowly contained multi-hydroxyporphyrin. The second band containing target molecule was collected and taken to dryness under vacuum on a rotary evaporator. The unsymmetrical meso-substituted porphyrin was further purified by repeating column chromatography to furnish title compound **1** (1.47 g, 8%).

UV-Visible (λ_{max}): 259.50, 415, 519.50, 558, 592.50, 651.50 nm; IR (KBr): ν = 705.9,740.6, 800.4, 875.6, 968.2, 1161.1, 1190, 1353.9, 1473.5, 1519.8, 1604.7, 3315.4 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = - 2.65 (br, s, 2H, NH), 1.22-1.57 (br, s,-OH of H_2O), 3.22 (s,6H, 2 X CH_3), 7.22-7.78 (m, 15H, Ar-H), 8.2 (m, 4H, Ar-H), 8.92 (m, 8H, pyrrole-H); Mass (Q-TOF MSES 2.45e3) m/z: 658 (M^+)

Anal calcd for $C_{46}H_{35}N_5.4H_2O$: C, 75.69%; H, 5.93%; N, 9.59%; Found: C, 75.01%; H, 5.80%, N, 9.40%.

Synthesis of 5-[(4-acetamido) phenyl- 10, 15, 20 tris (4-chlorophenyl) porphyrin (2)

To a mixture of 4-chlorobenzaldehyde (10.63 g, 0.076 mol) and 4-acetamidobenzaldehyde (4.10 g, 0.025 mol) in propionic acid (300 mL) was heated at 124-126^{0}C and at this temparature pyrrole (6.78 g, 0.101 mol) was added slowly and reaction mixture was further heated at this temperature for 45 minutes. The remaining experimental procedure was in a manner similar to describe for compound **1**. In this case also

second purple band was collected, taken to dryness under vacuum and further purified by repeated column chromatography to afford title compound **2** (1.70 g, 8%).

UV-Visible (λ_{max}): 234.0, 373.50, 416, 516 nm; IR (KBr): ν = 731.9, 798.3, 846.7, 966.3, 1091.6, 1396.4, 1485.1, 1593.1, 1691.5, 2374.3, 3568.1 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = - 2.82 (br, s, 2H, NH), 1.24-1.6 (br, s,-OH of H_2O), 2.29 (s,3H, CH_3), 7.24-7.7 (s, 12H, Ar-H), 7.84 (m, 1H, NH, 8.1-8.24 (m, 4H, Ar-H), 8.59-8.82 (m, 8H, pyrrole-H), Mass (Q-TOF MSES 1.58e3) m/z: 776.3270 (M^+); Anal calcd for $C_{46}H_{30}N_5Cl_3O.4H_2O$: C, 65.2%; H, 4.50%; N, 8.26%; Found : C, 65.0%; H, 4.40 %, N, 8.10%.

Synthesis of 5-[(4-hydroxy-3-methoxy) phenyl]–10,15,20 tris-(phenyl) porphyrin (3)

To a mixture of benzaldehyde (8.0242 g, 0.076 mol) and vanillin (3.81 g, 0.025 mol) in 300 ml of propionic acid was heated at 124-126^{o}C and at this temperature pyrrole (6.78 g, 0.101 mol) was added slowly and the reaction mixture was further heated at this temperature for 45 min. The remaining experimental procedure was in a manner similar to described for compound **1**. The second purple band containing the target compound **3** was collected, taken to dryness under vacuum and further purified by repeated column chromatography to furnish title compound **3** (1.66 g, 9%).

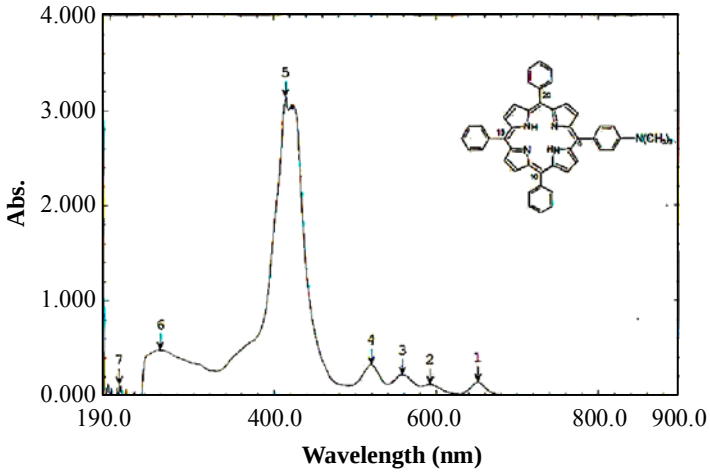


Fig. UV-visible spectra of Compound 1

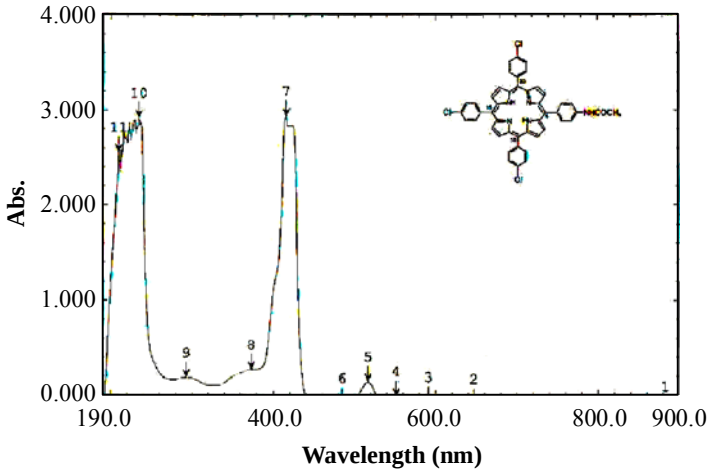


Fig. UV-visible spectra of Compound 2

UV-Visible (λ_{max}): 413.0, 516.50, 552.0, 591.0, 648.0 nm; IR (KBr): ν = 705.9, 798.5, 928.8, 970.1, 1035.7, 1120.6, 1166.9, 1199.6, 1267.7, 1350.1, 1411.8, 1469.7, 1512.1, 1595.0, 2925.8, 3317.3, 3504.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = - 2.74 (br s, 2H-NH), 1.24-1.6 (br s, -OH of H_2O), 4.1 (s, 3H, OCH_3), 6.0 (s,1H, Ar-OH), 7.25-7.90 (m, 15H, Ar-H), 8.22 (m, 3H, Ar-H), 8.95 (m, 8H, Pyrrole-H); Mass (Q-TOF MSES 2.45e3) m/z: 660 (M^+); Anal calcd for $C_{45}H_{32}N_4O_2.4H_2O$: C, 73.75%, H, 5.50%, N, 7.64%; Found: C, 73.70%; H, 5.10 %; N, 7.60%.

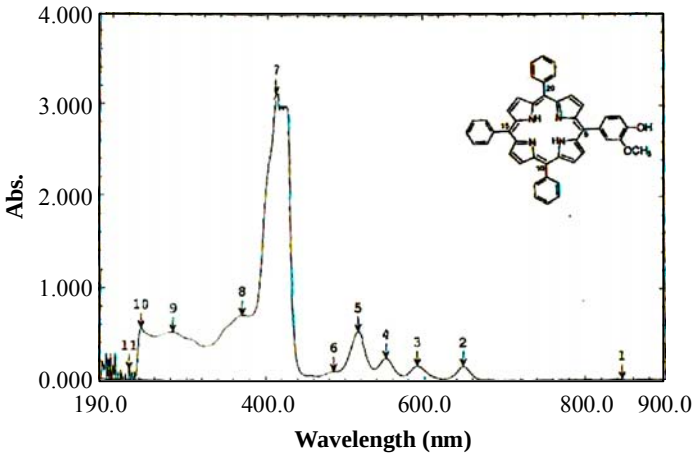


Fig. UV-visible spectra of Compound 3

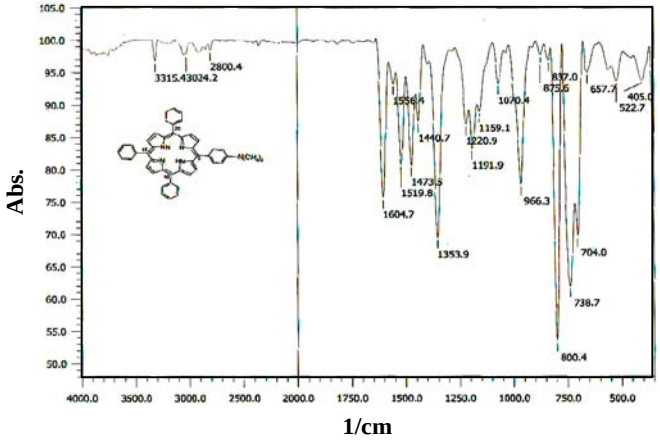


Fig. IR spectra of Compound 1

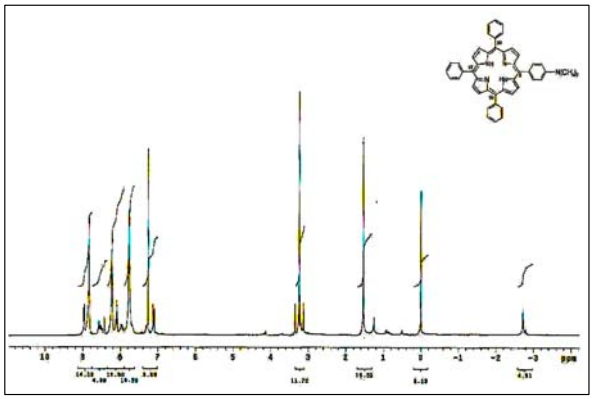


Fig. NMR spectra of Compound 1

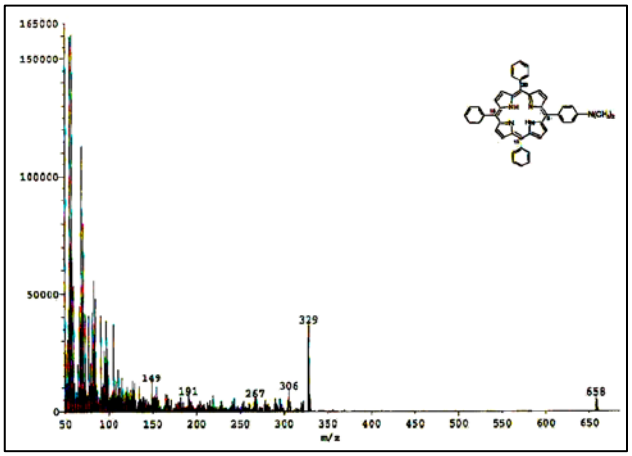


Fig. Mass spectra of Compound 1

IR Spectral data (cm^{-1}) of three porphyrins

1	2	3	Assignment
740.6	731.9	705	δ (N-H) Out of planarity
968.2	966.3	970.1	δ (N-H) In Planarity
1473.5	1485.1	1469.7	ν (C= N ,C=C)
		1120.6	δ (C-O-C)
3115.4		3317.3	ν (N-H)

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