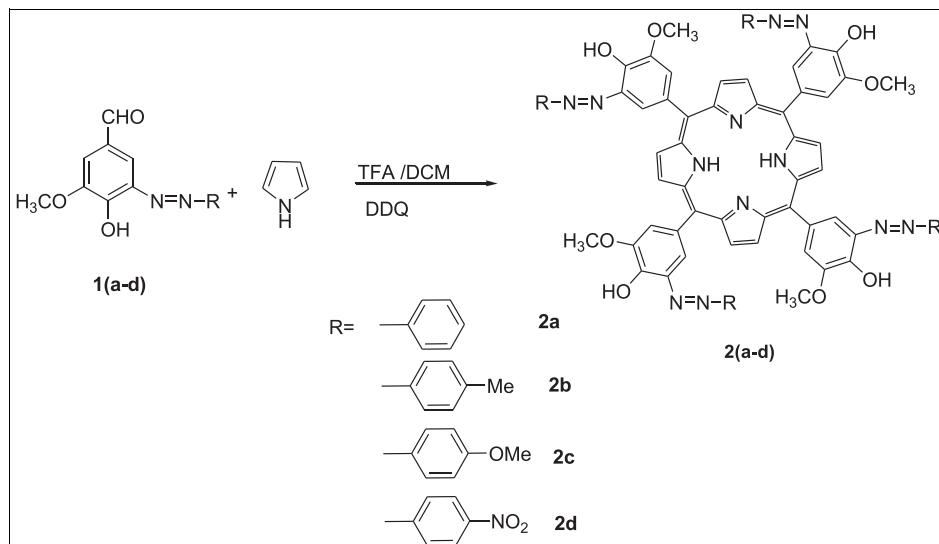


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A new series of novel covalently connected *meso*-tetrakis(3-azophenyl-4-hydroxy-5-methoxyphenyl)porphyrins were synthesized by linking azobenzene unit at the *meta*-position of the *meso*-phenyl group. These are characterized by UV-vis, IR, ¹H-NMR, CHN, and FABMS spectroscopic techniques. All the porphyrin compounds showed a typical high energy Soret band at around 435 nm and azobenzene absorption at around 350 nm in UV-vis spectra. Fluorescence intensity of *meso*-tetrakis(3-(4-methoxyazophenyl)-4-hydroxy-5-methoxyphenyl)porphyrin (**2c**) has been observed to be maximum compared with other azobenzene porphyrins.

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INTRODUCTION

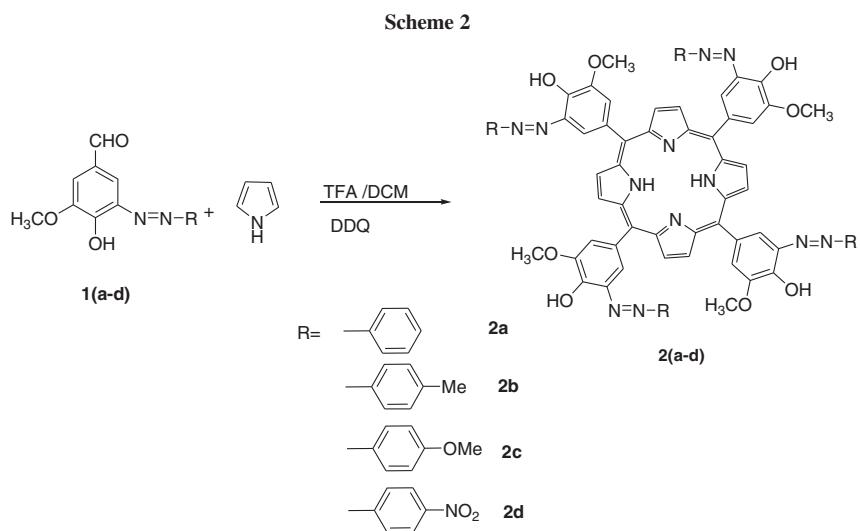
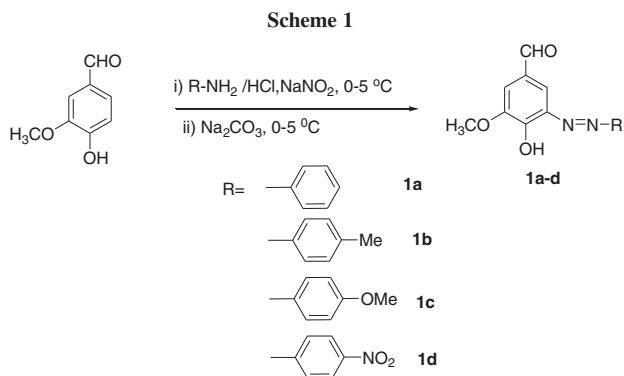
Porphyrins and their derivatives have become the current focus of research because of their outstanding physicochemical properties and applications in diverse fields [1]. The elegant porphyrin derivatives can act as models for natural photosynthesis [2], sensitizers in dye-sensitized solar cells [3], nonlinear optical materials [4], and photoswitches in the fabrication of molecular electronic/optical devices [5]. In these fields, the investigation of photoinduced electron transfer and *cis*–*trans* isomerization reactions is essential in understanding the mechanism and processes of these molecular scale photochromic compounds. Azobenzene and some azobenzene derivatives could perform *cis*–*trans* isomerization under photochemical reactions and might undergo energy transfer [6]. A number of molecular assemblies, which can potentially exhibit modulation of their fluorescence/redox properties that is induced by *cis*–*trans* isomerization of the appended azobenzene units, are being developed by many researchers [7]. Porphyrin-based systems are useful in the design of devices involving long-wavelength

excitation because of the favorable spectral and luminescence properties of these extensively π -conjugated macrocyclic systems. However, many attempts were made to build functionally active porphyrin-based photoswitches with switching action being effected by the azobenzene moiety [8]. Feng and coworkers reported a novel class of covalently connected azonaphthalene porphyrin derivatives, and they studied tautomerism in these novel classes of compounds [9]. Most of the azobenzene containing porphyrins carry azobenzene group unit either in the *para*-position of the *meso*-phenyl group [10], via a flexible linker [11], or by axial coordination [12]. Recently, Peters *et al.* reported azobenzene-confined porphyrins containing two azobenzene units on two *ortho*-positions of one *meso*-phenyl group to limit the number of possible switching gates [13]. However, the incorporation of azobenzene unit at the *meta*-position of the *meso*-phenyl group in *meso*-tetraphenylporphyrins has not been reported in the literature. In this manuscript, the synthesis of *meso*-tetrakis(3-azophenyl-4-hydroxy-5-methoxyphenyl)porphyrins (**2a–b**) was reported, and azobenzene units were incorporated in the *meta*-position of the *meso*-phenyl group of these porphyrins.

RESULTS AND DISCUSSIONS

The synthesis of azobenzene aldehydes and azobenzene–porphyrins is outlined in Schemes 1 and 2. To the best of our knowledge, this is the first reported synthesis of azobenzene–porphyrins where the azobenzene units are incorporated in the *meta*-position of the *meso*-phenyl group in *meso*-tetraphenylporphyrins. *meso*-Tetrakis(3-azophenyl-4-hydroxy-5-methoxyphenyl)porphyrins (**2a–b**) were prepared by treating substituted 3-azophenyl-4-hydroxy-5-methoxybenzaldehydes (**1a–d**) with pyrrole by adopting the Lindsey method. Substituted 3-azophenyl-4-hydroxy-5-methoxybenzaldehydes (**1a–d**) had been synthesized by treating 3-methoxy-4-hydroxybenzaldehyde with diazonium salts which were obtained by diazotization of corresponding *p*-substituted anilines (Scheme 1). The substituted azobenzene aldehydes (**1a–c**) were obtained in around 35% yield and 3-(4-nitroazophenyl)-4-hydroxy-5-methoxybenzaldehyde (**1d**) in 56% yield.

The azobenzene-substituted aldehydes (**1a–d**) were treated with pyrrole in the presence of trifluoroacetic acid and dichloromethane solvent at room temperature as



shown in Scheme 2. Further, the reaction mixture was oxidized with DDQ. The solvent was removed, and the residue was subjected to flash silica gel column chromatography to give the corresponding porphyrins (**2a–c**) up to 22% yield. The yield was only 10% in the case of the nitro-substituted porphyrin (**2d**). The decrease in yield may be due to the electron withdrawing nature of the nitro group.

Ultraviolet–visible spectra of all the porphyrin compounds show a Soret band at around 435 nm and four low intense Q bands between 500 and 660 nm. In addition to these bands, each porphyrin also shows typical azobenzene absorption at around 350 nm. The absorption peak at 350 nm indicates that the azo unit in these porphyrins exists in *trans* form. The fluorescence spectra of these azobenzene-substituted porphyrins in *trans* form were recorded in dichloromethane solvent. Fluorescence emission spectra of these porphyrins **2a–d** in dichloromethane solvent

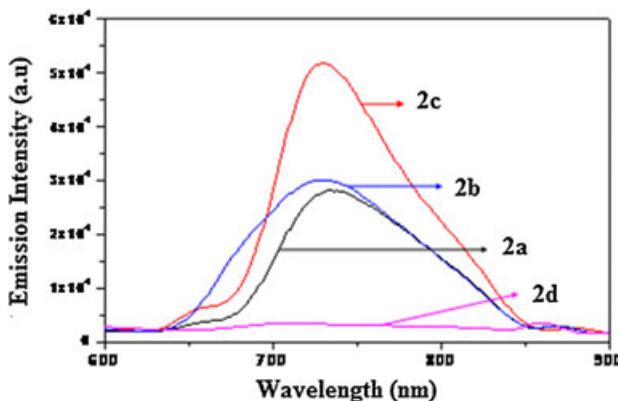


Figure 1. Fluorescence emission spectra were recorded for all the porphyrins (**2a–d**) at the concentration of 5×10^{-6} mol/L and $\lambda_{\text{ex}} 550$ nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

excited at 550 nm are shown in Figure 1. Emission intensity of 5.2×10^4 au has been observed for **2c** and 3×10^4 and 2.8×10^4 au for **2b** and **2a**, respectively, at around 730 nm. The emission maxima of **2d** were quenched in comparison with other azobenzene-substituted porphyrins. The quenching may be due to the intramolecular electron transfer from porphyrin to nitro units in the case of **2d**, and emission intensity is increased because of intramolecular transfer of electrons from the methoxy group to porphyrin in the case of **2b**. The detailed cis-trans isomerism and electrochemical and emission studies are in progress.

EXPERIMENTAL

Ultraviolet-visible spectra were recorded on a SHIMADZU UV 160 A UV-vis-NIR spectrophotometer (Kyoto, Japan), using chloroform as solvent. IR spectra were recorded as KBr pellets using a SHIMADZU 8010 FTIR spectrophotometer. ^1H -NMR spectra were recorded on Varian FT 400 MHz instrument (USA) using CDCl_3 as solvent and TMS as internal reference. FAB mass spectra were recorded on a VG Micromass 7070H (F or CI) auto spectrometer (USA). The C, H, and N analyses of the compounds were performed on a Carlo Erba Model EA 1108 CHNS-O elemental analyzer (Milan, Italy). Porphyrins were purified by flash column chromatography (Aldrich) using 230–400 mesh silica gel. Fluorescence spectra were obtained using Fluoromax-P spectrometer (Kyoto, Japan).

Synthesis of 3-azophenyl-4-hydroxy-5-methoxybenzaldehyde (1a). A mixture of aniline (2.5 g, 27 mmol), conc. HCl (8 mL), and water (8 mL) was taken in a conical flask and cooled to 0°C. To this, a cold sodium nitrite solution (2 g in 10 mL of water) was added slowly below 5°C while stirring. Meanwhile, 3-methoxy-4-hydroxybenzaldehyde (3.8 g, 25 mmol) was dissolved in 30 mL of 10% sodium carbonate solution and cooled in freezing mixture. This diazonium solution was added to the cold aldehyde solution in a period of 30 min without raising the temperature above 5°C. After the complete addition, the reaction mixture was left at room temperature for 1 h and filtered yielding a dark red colored product. The crude product was passed through column chromatography using the mixture of chloroform:hexane (60:40) as eluent to give **1a**. Yield 37.5% (2.4 g); mp: 129–130°C; IR (potassium bromide): 3425 (b, O-H stretch), 1688 (s, -CHO stretch), 1596, 1483, 1434, 1402 (m, aromatic C=C, N=N stretch) cm^{-1} ; ^1H -NMR (deuteriochloroform): δ 14.25 (s, 1H, OH), 9.90 (s, 1H, CHO), 8.15 (s, 1H, ArC₂-H), 7.91 (d, 2H, C₂ and C₆-H of azophenyl), 7.50 (m, 4H, ArC₆-H and azophenyl-H), 4.06 (s, 3H, O-CH₃); MS: m/z 257 ($\text{M}+\text{H}$)⁺ requires 256. *Anal.* Calcd for C₁₄H₁₂N₂O₃: C, 65.62; H, 4.68; N, 10.93. Found: C, 65.58; H, 4.72; N, 10.96%.

3-(4-Methylazophenyl)-4-hydroxy-5-methoxybenzaldehyde (1b). Yield 32.6% (2.2 g); mp: 138°C; IR (potassium bromide): 3426 (b, O-H stretch), 1686 (s, -CHO stretch), 1598, 1482, 1436, 1408 (m, aromatic C=C, N=N stretch) cm^{-1} ; ^1H -NMR (deuteriochloroform): δ 14.25 (s, 1H, OH), 9.94 (s, 1H, CHO), 8.06 (s, 1H, ArC₂-H), 7.8 (d, 2H, C₂ and C₆-H of azophenyl), 7.47 (s, 1H, ArC₆-H), 7.35 (d, 2H, C₃ and C₅-H of azophenyl), 4.00 (s, 3H, O-CH₃), 2.45 (s, 3H, CH₃); MS: m/z 271 ($\text{M}+\text{H}$)⁺ requires 270. *Anal.* Calcd for C₁₅H₁₄N₂O₃: C, 66.66; H, 5.18; N, 10.37. Found: C, 65.58; H, 5.07; N, 10.51%.

3-(4-Methoxyazophenyl)-4-hydroxy-5-methoxybenzaldehyde (1c). Yield 34.96% (2.5 g); mp 148°C; IR (potassium bromide): 3428 (b, O-H stretch), 1688 (s, -CHO stretch), 1600, 1484, 1438, 1418 (m, aromatic C=C, N=N stretch) cm^{-1} ; ^1H -NMR (deuteriochloroform): δ 14.21 (s, 1H, OH), 9.95 (s, 1H, CHO), 8.05 (s, 1H, ArC₂-H), 7.90 (d, 2H, C₂ and C₆-H of azophenyl), 7.51 (s, 1H, ArC₆-H), 7.06 (d, 2H, C₃ and C₅-H of azophenyl), 4.02 (s, 3H, O-CH₃), 3.95 (s, 3H, O-CH₃); MS: m/z 287 ($\text{M}+\text{H}$)⁺ requires 286. *Anal.* Calcd for C₁₅H₁₄N₂O₄: C, 62.93; H, 4.89; N, 9.79. Found: C, 63.08; H, 4.72; N, 9.61%.

3-(4-Nitroazophenyl)-4-hydroxy-5-methoxybenzaldehyde (1d). Yield 55.8% (4.2 g); mp 142–143°C; IR (potassium bromide): 3428 (b, O-H stretch), 1686 (s, -CHO stretch), 1600, 1486, 1438, 1416 (m, aromatic C=C, N=N stretch) cm^{-1} ; ^1H -NMR (deuteriochloroform): δ 13.81 (s, 1H, OH), 9.95 (s, 1H, CHO), 8.52 (d, 2H, C₃ and C₅-H of azophenyl), 8.2 (m, 3H, ArC₂-H and C₂ and C₆-H of azophenyl), 7.52 (s, 1H, ArC₆-H), 4.02 (s, 3H, O-CH₃); MS: m/z 302 ($\text{M}+\text{H}$)⁺ requires 301. *Anal.* Calcd for C₁₄H₁₁N₃O₅: C, 55.81; H, 3.65; N, 13.95. Found: C, 55.68; H, 3.73; N, 13.81%.

General procedure. Synthesis of meso-tetrakis(3-azophenyl-4-hydroxy-5-methoxyphenyl)porphyrin (2a). A mixture of 3-azophenyl-4-hydroxy-5-methoxybenzaldehyde **1a** (0.512 g, 2 mmol) and pyrrole (0.134 g, 2 mmol) was dissolved in 150 mL of dichloromethane under nitrogen atmosphere in the dark. To this, trifluoroacetic acid (2 mmol) was added while stirring at room temperature. The reaction mixture was stirred at room temperature for 2 h under nitrogen atmosphere. Then, DDQ (2 mmol) was added and refluxed for 2 h to oxidize the porphyrinogen to the corresponding porphyrin. The dichloromethane was removed under reduced pressure, and the obtained solid material was subjected flash silica gel column chromatography using chloroform:methanol (99:1) as eluent to give a purple color solid **2a** (150 mg, 25%); mp > 300°C; UV-vis: λ_{max} nm (deuteriochloroform) (log ξ): 345 (5.25), 435 (5.82), 525 (4.69), 560 (4.41), 600 (4.3), 655 (4.08); IR (potassium bromide): 3443 (broad, N-H and O-H str of porphyrin), 1599, 1503, 1462 (C=C, C=N in plane bend), 981, 926 (porphyrin macrocyclic bend), 835, 796 (s, aromatic C=C-H out-of-plane bend) cm^{-1} ; ^1H -NMR (deuteriochloroform): δ 13.7 (s, 4H, 4× OH), 9.06 (s, 8H, pyrrole C-H), 8.48 (s, 4H, C₂-H), 7.98–7.96 (d, 8H, C₂ and C₆ azophenyl-H), 7.91 (s, 4H, C₆-H), 7.51–7.56 (m, 12H, azophenyl-H), 4.08 (s, 12H, 4× O-CH₃), 2.61 (s, 2H, porphyrin N-H); FABMS: m/z 1216 ($\text{M}^{+}+2$) requires 1214. *Anal.* Calcd for C₇₂H₅₄O₈N₁₂: C, 71.17; H, 4.44; N, 13.83. Found: C, 71.26; H, 4.36; N, 13.74%.

meso-Tetrakis(3-(4-methylazophenyl)-4-hydroxy-5-methoxyphenyl)porphyrin (2b). Yield 22%; mp > 300°C; UV-vis: λ_{max} nm (deuteriochloroform) (log ξ): 350 (5.53), 435 (5.89), 525 (4.90), 560 (4.68), 600 (4.41), 655 (4.58); IR (potassium bromide): 3443 (broad, N-H and O-H str of porphyrin), 1600, 1472 (C=C, C=N in plane bend), 978, 922 (porphyrin macrocyclic bend), 822.6, 795 (s, aromatic C=C-H out-of-plane bend) cm^{-1} ; ^1H -NMR (deuteriochloroform): δ 13.73 (s, 4H, 4× OH), 9.06 (s, 8H, pyrrole C-H), 8.46 (s, 4H, C₂-H), 7.90 (s, 4H, C₆-H), 7.86–7.84 (d, 8H, C₂ and C₆ azophenyl-H), 7.33–7.31 (d, 8H, C₃ and C₅ azophenyl-H), 4.08 (s, 12H, 4× O-CH₃), 2.43 (s, 12H, 4× CH₃), 2.61 (s, 2H, porphyrin N-H). FABMS: m/z 1272 ($\text{M}^{+}+2$) requires 1270. *Anal.* Calcd for C₇₆H₆₂O₈N₁₂: C, 71.81; H, 4.88; N, 13.23. Found: C, 71.69; H, 4.81; N, 13.28%.

meso-Tetrakis(3-(4-methoxyazophenyl)-4-hydroxy-5-methoxyphenyl)porphyrin (2c). Yield 22.5%; mp > 300°C; UV-vis:

λ_{\max} nm (deuteriochloroform) ($\log \xi$): 370 (5.47), 440 (5.84), 520 (4.77), 555 (4.68), 600 (4.31), 655 (4.73); IR (potassium bromide): 3437 (broad, N-H and O-H str of porphyrin), 1579, 1452, 1413 (C=C, C=N in plane bend), 979, 922 (porphyrin macrocyclic bend), 822, 796 (s, aromatic C=C-H out-of-plane bend) cm^{-1} ; $^1\text{H-NMR}$ (deuteriochloroform): δ 13.76 (s, 4H, 4 \times OH), 9.04 (s, 8H, pyrrole C-H), 8.42 (s, 4H, C₂-H), 7.92 (s, 4H, C₆-H), 7.87–7.85 (d, 8H, C₂ and C₆ azophenyl-H), 7.53–7.51 (d, 8H, C₃ and C₅ azophenyl-H), 4.08, (s, 12H, 4 \times O-CH₃), 3.91 (s, 12H, 4 \times O-CH₃), 2.65 (s, 2H, porphyrin N-H); FABMS: *m/z* 1336 (M⁺+2) requires 1334. *Anal.* Calcd for C₇₆H₆₂O₁₂N₁₂: C, 68.36; H, 4.64; N, 12.59. Found: C, 68.12; H, 4.51; N, 12.48%.

meso-Tetrakis{3-(4-nitroazophenyl)-4-hydroxy-5-methoxy-phenyl}porphyrin (2d). Yield 10.6%; mp > 300°C; UV-vis: λ_{\max} nm (deuteriochloroform) ($\log \xi$): 360 (5.52), 430 (5.80), 525 (4.97), 560 (4.69), 595 (4.61), 660 (4.50); IR (potassium bromide): 3422 (broad, N-H and O-H str of porphyrin), 1592, 1423, 1493, 1402 (C=C, C=N in plane bend), 970, 924 (porphyrin macrocyclic bend), 855, 798 (s, aromatic C=C-H out-of-plane bend) cm^{-1} ; $^1\text{H-NMR}$ (deuteriochloroform): δ 13.72 (s, 4H, 4 \times OH), 9.06 (s, 8H, pyrrole C-H), 8.54–8.52 (d, 8H, C₃ and C₅-H of azophenyl), 8.44 (s, 4H, C₂-H), 7.90 (s, 4H, C₆-H), 7.86–7.84 (d, 8H, C₂ and C₆ azophenyl-H), 4.06 (s, 12H, 4 \times O-CH₃), 2.62 (s, 2H, porphyrin N-H). FABMS: *m/z* 1396 (M⁺+2) requires 1394. *Anal.* Calcd for C₇₂H₅₀O₁₆N₁₆: C, 61.98; H, 3.58; N, 16.06. Found: C, 61.82; H, 3.51; N, 15.92%.

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