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Synthesis of *meso*-furyl porphyrins with N_4, N_3S, N_2S_2 and N_3O porphyrin cores

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Abstract—A series of *meso*-furyl porphyrins with four different porphyrin cores (N_4, N_3S, N_2S_2 and N_3O) were synthesized and characterized. The comparison of NMR, optical and fluorescence properties of *meso*-furyl porphyrins with porphyrins with six-membered aryl groups indicates that electronic properties of porphyrins were changed drastically on the introduction of furyl groups at *meso* positions. The maximum shifts in spectral bands were observed for *meso*-furyl porphyrins with N_2S_2 core. On protonation, the absorption bands of *meso*-furyl porphyrins were further red shifted. All these changes were ascribed to the possibility of more planarity of the *meso*-furyl porphyrins due to the small size of the furyl groups which results in extending the π-delocalisation of the porphyrin ring in to the furyl groups.

1. Introduction

The porphyrins lie at the focal point formed from divergent fields of research including solar energy conversion, catalysis of orgnaic reactions and medicine.[1] Porphyrin macrocycles are synthetically very flexible and by introducing substituents selectively at the β- or *meso*-positions, the properties can be tuned at will for any application. *meso*-Tetraarylporphyrins offer attractive features in this context and have been used in a wide variety of model systems owing to their ease of synthesis and facile functionalization. However, the reports on porphyrins having *meso* substituents as five-membered heterocycles such as pyrrole, thiophene, furan etc are scarce. In recent times, there have been a few reports on *meso*-tetrathienylporphyrins.[2] Effenberger et al.[2a] synthesized anthryloligothienylporphyrins containing the anthracene donor, the porphyrin acceptor and a conjugated oligothiophene bridge. This system showed an efficient energy transfer from anthracene to porphyrin unit mediated by the oligothiophene π-bridge. The oligomeric thienyl porphyrins also showed film forming and efficient conductivity behaviour. The optical, redox and axial ligation studies of *meso*-thienyl porphyrins were also explored recently.[2d] Interestingly, to the best of our knowledge, there are no reports of porphyrins with furyl substituents at *meso*-positions.[3] In this paper we report a detailed account of the synthesis of the seven *meso*-furyl porphyrins with four different porphyrin cores such as N_4, N_3S, N_2S_2 and N_3O (Chart 1). The electronic properties of *meso*-furyl porphyrins were compared with *meso*-tetraarylporphyrins. The properties were siginificantly altered by substituting six-membered aryl rings with five-membered furyl rings and they have the potential to have wide applications in materials chemistry.

2. Results and discussion

2.1. *meso*-Furyl porphyrin with N_4 porphyrin core 1

Interestingly, there has been no report on the synthesis of tetrafurylporphyrin with N_4 core. Initially we synthesized 5,10,15,20-tetrakis(2-furyl)porphyrin **1** by condensing 1 equiv. of furan-2-aldehyde with 1 equiv. of pyrrole in CH_2Cl_2 at room temperature in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$. The crude compound showing a single spot on TLC was purified by silica gel column chromatography using CH_2Cl_2 as eluent to afford **1** in 12% yield. The porphyrin **1** was characterized by NMR, mass spectroscopy, C, H, N analysis, absorption and fluorescence spectroscopy. In ^1H NMR, the pyrrole was appeared as a sharp singlet and down field shifted by 0.44 ppm (Table 1) compared to 5,10,15,20-tetrakis(phenyl)porphyrin (H_2TPP).[4] The NH signal also appeared as a sharp singlet and was downfield shifted by 0.20 ppm compared to H_2TPP indicating that furyl groups at *meso* positions significantly alter the π-delocalisation of the porphyrin ring. The porphyrin **1** was further confirmed by elemental analysis and the presence of a strong *m/z* peak at 574.7 in mass spectrum. The absorption spectrum of **1** recorded in toluene showed three clear Q-bands and one soret band (Fig. 1) unlike H_2TPP which showed four clear Q-bands and one soret band. The absorption bands in **1** were red shifted by 15–25 nm with

Keywords: *meso*-furyl porphyrins; core-modified porphyrins; bathochromic shifts; porphyrin planarity.
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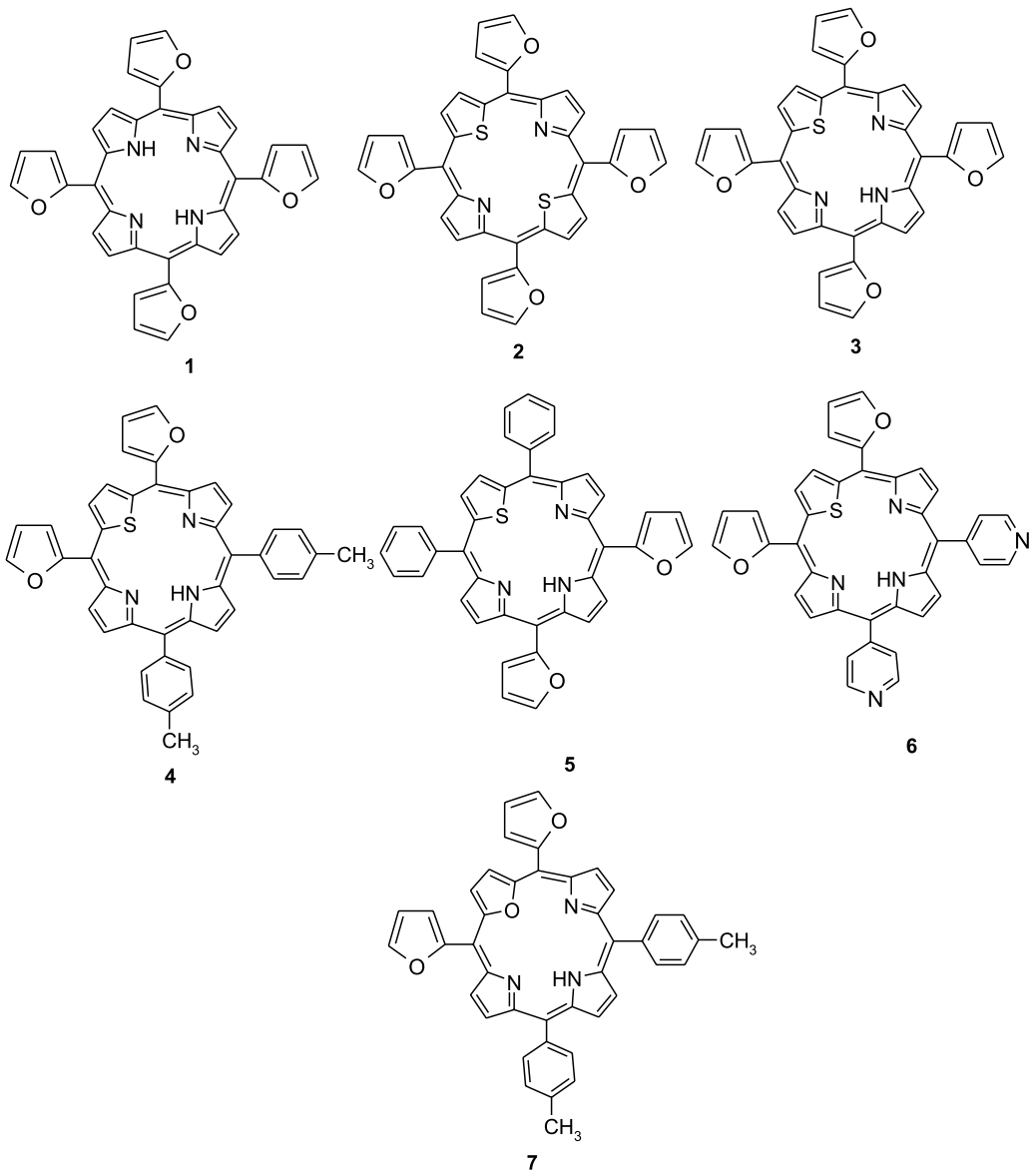


Chart 1.

Table 1. ^{1}H NMR chemical shifts (δ in ppm) of selected protons

Porphyrin	Thiophene/furan	Pyrrole	NH	Reference
H_2TPP	–	8.72 (s)	−2.79 (s)	4
H_2TTP	–	9.15 (s)	–	2(d)
1	–	9.16 (s)	−2.59 (s)	This work
S_2TPP	9.68 (s)	8.67 (s)	–	4
2	10.05 (s)	8.97 (s)	–	This work
STPPH	9.81 (s)	8.61 (d), 8.72 (d), 8.88 (s)	−2.66 (s)	8
3	10.21 (s)	8.85 (d), 9.01 (d), 9.22 (d)	−2.41 (s)	This work
4	10.19 (s)	8.60 (d), 8.86 (d), 8.97 (d)	−2.32 (s)	This work
5	9.75 (s)	8.73 (d), 8.88 (d), 9.30 (d)	−2.75 (s)	This work
6	10.26 (s)	8.54 (d), 8.84 (m), 9.05 (m)	−2.43 (s)	This work
OTPPH	9.16 (s)	8.52 (d), 8.62 (d), 8.89 (s)	−1.65 (s)	10
7	9.87 (s)	8.71 (bs), 8.94 (bs), 9.08 (bs)	–	This work

significant reduction of ε-values compared to H_2TPP.[4] Similar red shifts were observed with *meso*-thienyl porphyrins[2d] compared to H_2TPP but the magnitude of shifts were larger in **1** indicating that the furyl groups at *meso* positions alter the π-delocalisation of porphyrin ring more effectively than thienyl groups at *meso* positions (Table 2). The dications generated by the addition of two drops of trifluoroacetic acid simplified the three Q-banded spectrum to a single Q-band along with one soret band (Fig. 1 inset). The absorption bands of $\mathbf{1}H_2^{2+}$ were further red shifted compared to **1** (Table 3). A similar effect was observed for H_2TPP and its dication derivative. It was shown by Stone and Fleischer[5] that the red shift of the soret and Q-bands observed in the formation of dication of H_2TPP is due to greater resonance interaction with the phenyl groups with extension of conjugation in the dications. This was possible because of the reduced steric hindrance between the porphyrin plane and the phenyl rings in the dication, since the presence of two extra protons on nitrogens tilts the pyrroles rings out of the molecular

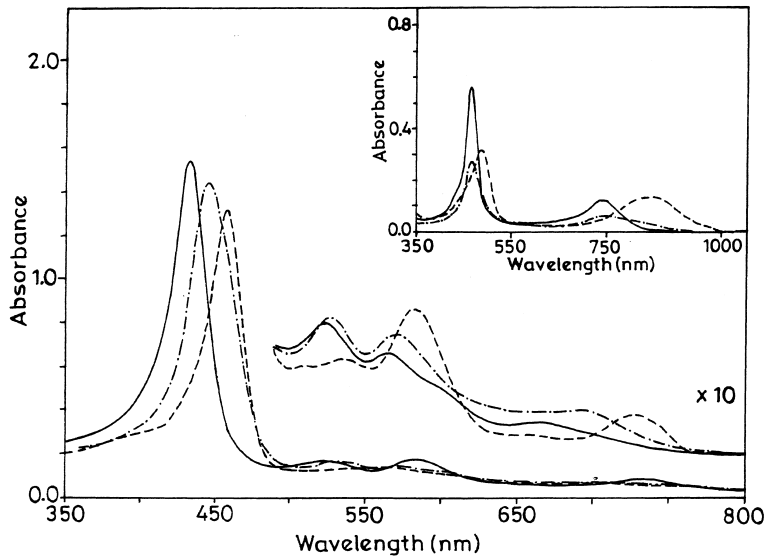


Figure 1. Comparison of the absorption spectra of *meso*-furyl porphyrins **1** (—), **2** (– – – –) and **3** (–•–•–•–) recorded in toluene. The inset shows the absorption spectra of dications of **1**, **2** and **3** in toluene. The dications were generated by the addition of a drop of trifluoroacetic acid to approximately 5×10^{-6} M.

Table 2. Absorption data of meso-furyl porphyrins **1**–**7** recorded in toluene

Porphyrin	Soret band $\lambda_{(nm)}$ ($\varepsilon\times10^{-4}$)	Absorption Q-bands, $\lambda_{(nm)}$ ($\varepsilon\times10^{-3}$)				Reference
		IV	III	II	I	
H_2TPP	417(52.5)	514(22.9)	548(10.7)	590(7.9)	647(7.2)	4
1	433(17.2)	526(7.6)	571(6.9)	605(sh)	670(1.6)	This work
H_2TTP	426(38.9)	523(19.9)	560(10.5)	597(7.6)	661(7.2)	2(d)
S_2TPP	435(25.0)	514(26.0)	547(7.0)	633(2.2)	696(4.5)	4
2	458(8.3)	536 (sh)	585(6.2)	–	740(1.4)	This work
STPPH	429(18.7)	513(17.1)	547(4.4)	618(1.9)	675(3.0)	8
3	448(9.9)	530(6.8)	575(7.5)	632(sh)	705(2.3)	This work
4	442(15.9)	524(12.5)	566(10.6)	618(sh)	691(3.7)	This work
5	435(16.1)	519(12.9)	558(6.8)	623(2.9)	687(2.8)	This work
6	441(4.0)	524(5.8)	564(4.6)	628(3.4)	691(3.9)	This work
OTPPH	419(21.9)	507(15.4)	539(3.0)	569(2.6)	671(2.8)	10
7	427(7.9)	513(9.9)	550(4.6)	612(2.7)	673(1.9)	This work

plane. In **1**, since the furyl groups are smaller than phenyl groups, the furyl groups were expected to be almost in plane with the porphyrin ring which reflected in the red shifts of **1** compared to H_2TPP. Upon dication formation, the resonance interaction between the porphyrin and *meso* furyl groups were further increased. The emission spectrum of **1** (Fig. 2) exhibited one band which was red shifted with reduction of qunatum yields compared to the emission bands of H_2TPP due to greater resonance interaction in **1** (Table 4). Unfortunately we did not get suitable crystals for X-ray structural studies to prove the presence of greater resonance interaction with *meso* furyl groups in **1**.

Table 3. Absorption data of dicationic porphyrins of **1**–**7** recorded in toluene

Porphyrin	Soret band, $\lambda_{(nm)}$ ($\varepsilon\times10^{-4}$)	Q-band(s), $\lambda_{(nm)}$ ($\varepsilon\times10^{-3}$)
$TPPH_4^{2+}$	448 (43.6)	608 (9.0), 659 (50.9)
$\mathbf{1}H_4^{2+}$	466 (16.2)	745 (34.6)
$S_2TPPH_2^{2+}$	463 (28.0)	697 (31.5), 735 (29.7)
$\mathbf{2}H_2^{2+}$	487 (9.9)	849 (42.1)
$STPPH_3^{2+}$	456 (19.0)	699 (24.0)
$\mathbf{3}H_3^{2+}$	468 (8.1)	752 (18.9)
$\mathbf{4}H_3^{2+}$	480 (4.2)	721 (11.9)
$\mathbf{5}H_3^{2+}$	472 (19.7)	759 (49.1)
$\mathbf{6}H_3^{2+}$	444 (0.55)	750 (0.97)
$OTPPH_3^{2+}$	434 (26.8)	621 (12.0), 656 (14.0)
$\mathbf{7}H_3^{2+}$	459 (6.5)	683 (9.9)

2.2. *meso*-Furyl porphyrin with N_2S_2 porphyrin core 2

To synthesize 5,10,15,20-tetrakis(2-furyl)-21,23-dithiaporphyrin **2**, the unknown diol 2,5-bis(2-furylhydroxymethyl)thiophene **8** was required. The diol **8** was prepared[6] by treating 1 equiv. of 2,5-dilithiothiophene with 2 equiv. of furan-2-aldehyde in THF as shown in Scheme 1. The formation of diol was confirmed by TLC which showed two major spots corresponding to mono-ol and diol. The mono-ol and -diol mixtures were separated by silica gel column chromatography using a petroleum ether/ethyl acetate mixture. The mono-ol moved as the first band in petroleum ether/15% ethyl acetate (25% yield) and the diol **8** was then collected as a second band in petroleum ether/20% ethyl acetate. The diol **8** was recrystallized twice

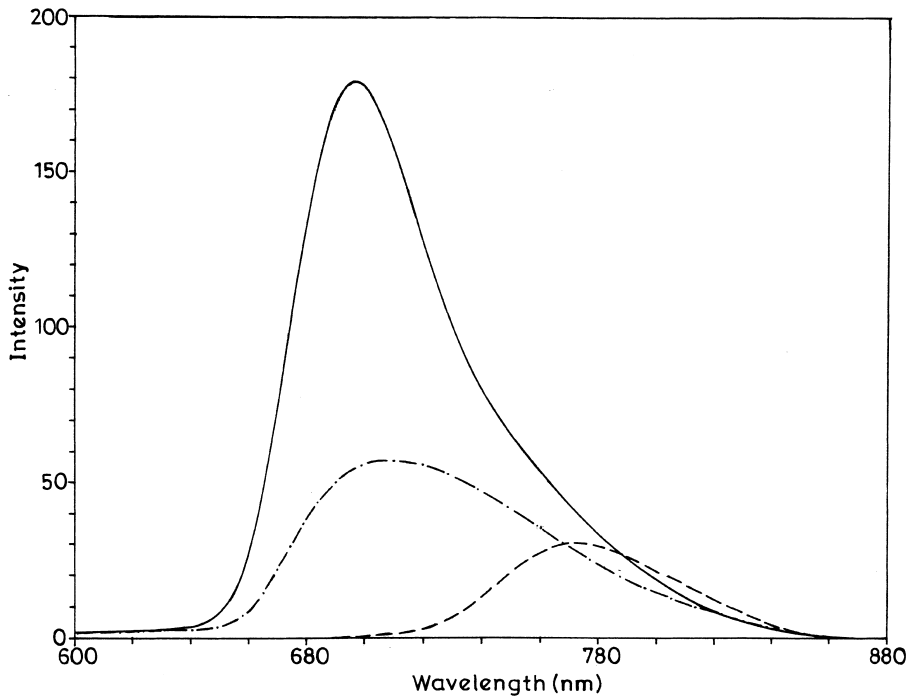


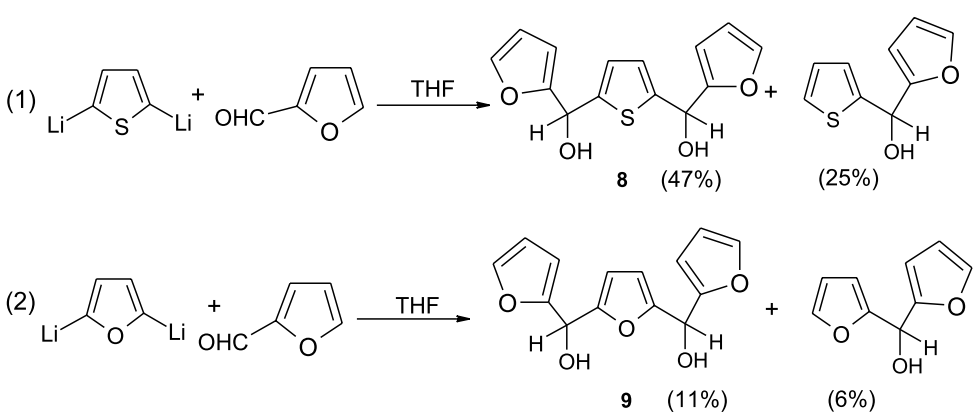
Figure 2. Fluorescence spectra of **1** (—), **2** (– – – –) and **3** (–•–•–•–) in toluene. The concentration used was approximately 5×10^{-6} M. Spectra were recorded at 25°C and λ_{ex}=450 nm.

Table 4. Fluorescence data of *meso*-furyl porphyrins **1**–**7** recorded in toluene

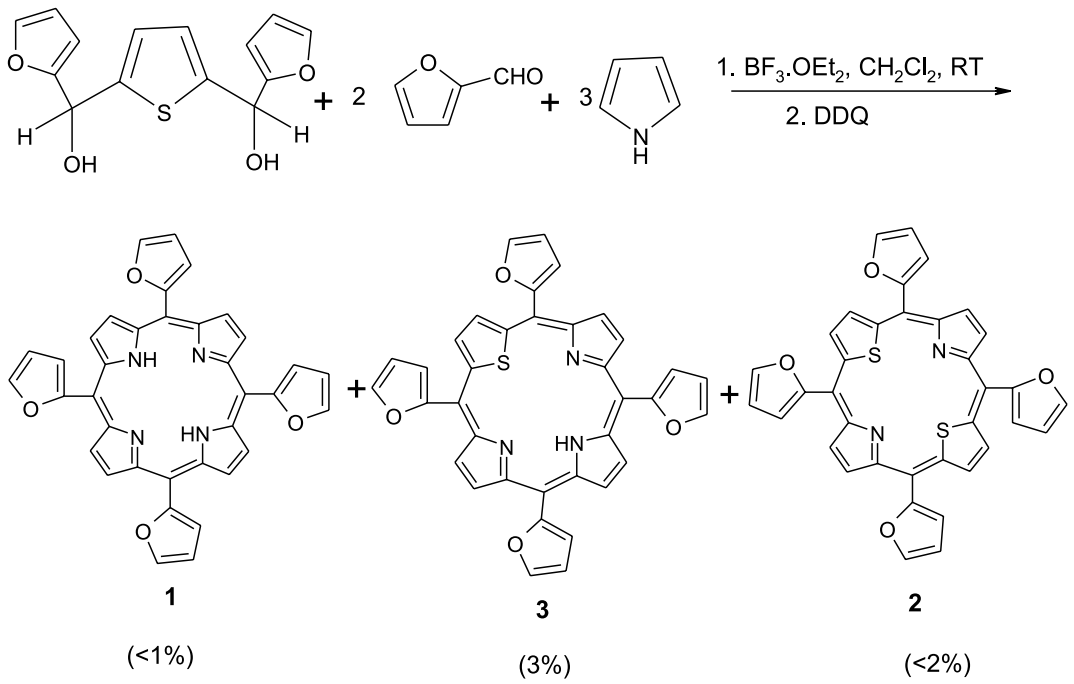
Porphyrin	λ_{em} (nm)	ϕ_f
H_2TPP	652, 718	0.11
1	697	0.047
S_2TPP	706, 781	0.0076
2	773	0.0025
STPPH	678, 760	0.0168
3	708	0.0139
4	706	0.0063
5	704	0.0090
6	709	0.0108
OTPPH	676	0.0758
7	690	0.0274

from toluene to afford a white crystalline solid in 47% yield. The diol **8** was characterized by NMR, IR, mp, mass spectrometry and C, H, N, S analysis.

The N_2S_2 porphyrin **2** was prepared by condensing 1 equiv. of diol **8** with 1 equiv. of pyrrole in CH_2Cl_2 at room temperature under mild acid conditions. TLC analysis showed a single spot indicating the formation of **2** as the sole product. Chromatography on silica gel with CH_2Cl_2 gave **2** in 13% yield. The formation of **2** was confirmed by a *m*/*z* peak at 608.5 in the mass spectrum. In ^{1}H NMR, the pyrrole and thiophene protons have appeared as sharp singlets and they were downfield shifted compared to 5,10,15,20-tetrakis(phenyl)-21,23-dithiaporphyrin[4b] (S_2TPP) (Table 1) indicating the extension of the π-electron



Scheme 1. Synthetic scheme for diols **8** and **9**.



Scheme 2. Synthetic scheme for the preparation of N_3S porphyrin **3**.

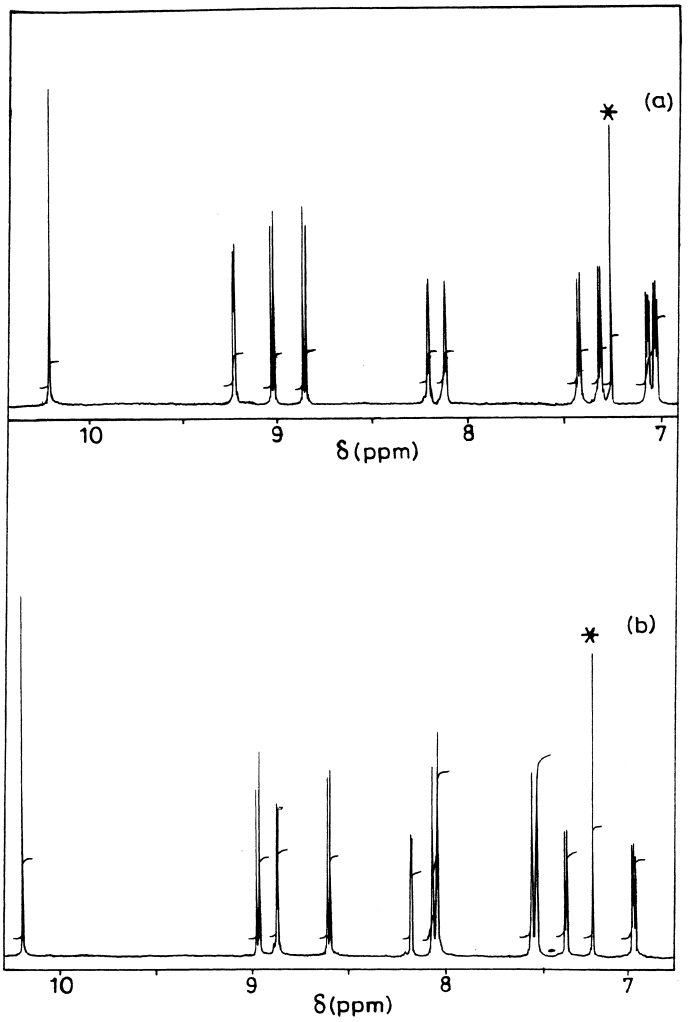
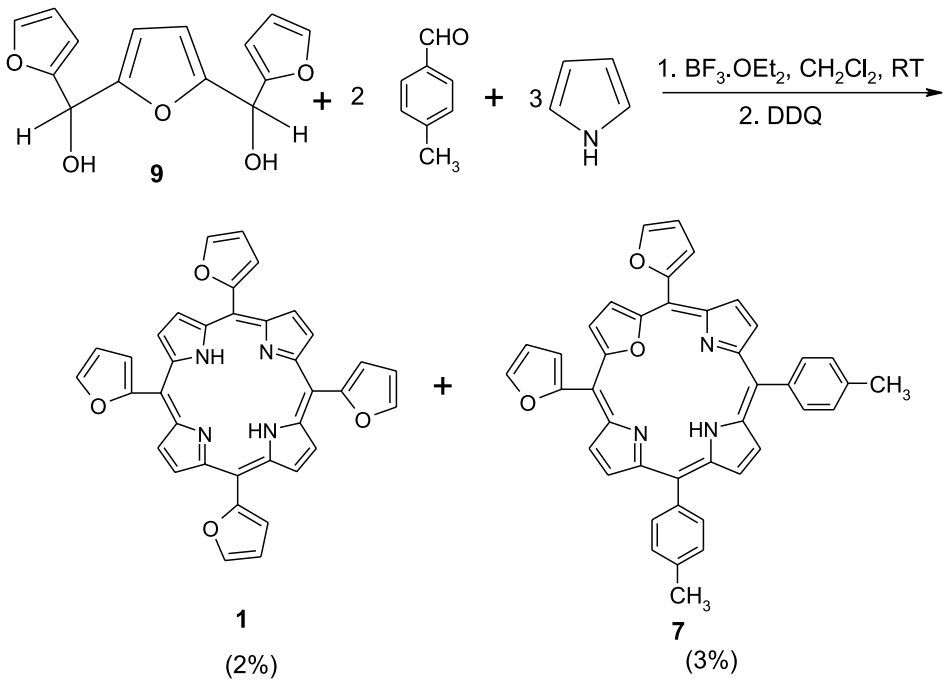


Figure 3. ^{1}H NMR spectra of (a) **3** and (b) **4** recorded in $CDCl_3$. (*) indicates solvent impurity.



Scheme 3. Synthetic scheme for the preparation of N_3O porphyrin **7**.

cloud of porphyrin to the *meso*-furyl groups. The absorption and emission bands of **2** were also red shifted compared to S_2TPP[4] with reduction in ε-values and quantum yields, respectively (Figs. 1 and 2). The dication of **2** showed simplified Q-band spectra and significant red shifts of the both Q- and soret bands (Fig. 1a).

2.3. *meso*-Furyl porphyrins with N_3S porphyrin cores 3–6

The N_3S porphyrin 5,10,15,20-tetrakis(2-furyl)-21-monothiaporphyrin **3** was prepared condensing 1 equiv. of diol **8** with 2 equiv. of furan-2-aldehyde and 3 equiv. of pyrrole in CH_2Cl_2 in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ (Scheme 2). The condensation resulted in the formation of mixture of three porphyrins[7] with three different porphyrin cores: N_4 (**1**), N_3S (**3**) and N_2S_2 (2). The mixture was separated easily by silica gel column chromatography using CH_2Cl_2, and the desired N_3S porphyrin **3** was moved as the first band (3% yield). The presence of a strong *m*/*z* peak at 591.7 and clean ^{1}H NMR as shown in Figure 3(a) and close C, H, N, S analysis confirmed the proposed structure and composition. In ^{1}H NMR, the thiophene protons appeared as singlet and downfield shifted compared to 5,10,15,20-tetrakis(phenyl)21-monothiaporphyrin (STPPH).[4,8] The three pyrroles in **3** appeared as three separate doublets, like in STPPH, indicating the lower symmetric nature of **3**. The pyrrole protons and NH proton were also downfield shifted compared to STPPH. Porphyrins **4** and **6** containing two furyl groups and two six-membered aryl groups in *cis* fashion were prepared by condensing 1 equiv. of diol **8** with 2 equiv. of corresponding aldehyde and 3 equiv. of pyrrole under standard porphyrin forming conditions. Porphyrin **5** was prepared similarly using 1 equiv. of known diol, 2,5-bis(phenylhydroxymethyl) thiophene[6] and condensing with 2 equiv. of furan-2-aldehyde and 3 equiv. of pyrrole. The condensation resulted in the formation of three porphyrins and the desired N_3S porphyrin was separated from other two by silica gel column chromatography. The N_4 porphyrin moved as the first band followed by *cis* N_3S porphyrin as the second band in 2–5% yields. The porphyrins were characterized by all spectroscopic methods. Porphyrins **4**–**6** also exhibited down-field shifts of thiophene, pyrrole and NH protons (Table 1) in ^{1}H NMR (Fig. 3b) and red shifts of optical and emission bands compared to STPPH (Tables 2–4). The magnitude of these shifts compared to STPPH were much lower in porphyins **4**–**6** than N_3S porphyrin **3**. This is due to presence of only two furyl groups at *meso* carbons of **4**–**6** whereas **3** contains four furyl groups at *meso* positions and the magnitude of shifts were directly proportional to number of furyl groups at *meso* carbons.

2.4. *meso*-Furyl porphyrins with N_3O porphyrin core 7

The unknown furan diol, 2,5-bis(2-furylhydroxymethyl)-furan **9** required to synthesize oxaporphyrins was prepared by treating 2,5-dilithiated salt of furan with furan-2-aldehyde in THF (Scheme 1).[9] The diol **9** was separated from mono-ol by silica gel column chromatography. Our attempts to synthesize meso-5,10,15,20-tetrafuryl-21,23-dioxaporphyrin were failed. We did not even find traces of 21,23-dioxaporphyrin under standard porphyrin forming conditions. The N_3O porphyrin **7** was prepared by condensing 1 equiv. of diol **9** with 2 equiv. of *p*-tolylaldehyde and 3 equiv. of pyrrole under mild acid conditions. The TLC analysis showed the formation of **7** along with N_4 porphyrin (Scheme 3). The porphyrin **7** was purified by silica gel column chromatography and characterized by NMR, mass, C, H, N analysis, absorption and fluorescence spectroscopic techniques. In ^{1}H NMR, the furan and pyrrole protons were down-field shifted compared to the furan and pyrrole protons of 5,10,15,20-tetraphenyl-21-oxaporphyrin (OTPPH) indicating furyl groups at *meso* positions altering

the π-delocalisation of the porphyrin ring (Table 1).[10] The optical bands of **7** were red shifted with a reduction in extinction coefficients compared to OTPPH (Table 2). The absorption bands of the dication of **7** generated by the addition of a drop of trifluoroacetic acid to porphyrin **7** in toluene also experienced red shifts of absorption bands with reduction of extinction coefficients compared to $OTPPH_3^{2+}$(-Table 3). The emission bands of **7** were red shifted with low quantum yields compared to OTPPH (Table 4).

3. Conclusions

In conclusion, we have prepared a series of *meso*-furyl porphyrins with N_4, N_3S, N_2S_2 and N_3O porphyrin cores for the first time. The substitution of six-membered aryl groups by furyl groups at the *meso* positions groups causes downfield shifts of thiophene, furan, pyrrole and inner NH protons in ^{1}H NMR, bathochromic shifts of absorption bands and large red shifts with reduction in quantum yields of fluorescence bands. These results indicates that π-delocalisation of porphyrin ring was altered effectively by furyl groups at the *meso* positions. These compounds can be used in place of *meso*-aryl porphyrins and have potential for applications in various fields. A detailed metallation and electrochemical study of *meso*-furyl porhyrins are presently under investigation in our laboratory.

4. Experimental

4.1. General

NMR spectra were recorded on a varian 300 MHz using tetramethylsilane as internal standard. Absorption and fluorescence spectra were obtained with Perkin–Elmer Lambda 35 and Perkin–Elmer Lambda 55 models respectively. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon as the FAB gas. Toluene, THF and triethylamine, *N*,*N*′*N*″*N*‴-tetramethylethylene diamine (TMEDA) were obtained from S.D Fine chemicals, India, and dried by standard procedures before use. All general chemicals were obtained from Qualigens, India. Benzaldehyde, *p*-tolylaldehyde, pyridine-4-carboxaldehyde, furan-2-aldehyde, thiophene and pyrrole were obtained from Lancaster. Column chromatography was performed using 60–120 mesh silica obtained from Sisco Research Laboratories, India.

4.1.1. *meso*-5,10,15,20-Tetrakis(2-furyl)porphyrin (1). In a 500 ml one necked round bottom flask fitted with argon bubbler, furan-2-aldehyde (286 mg, 2.98 mmol) and pyrrole (210 μl, 2.98 mmol) were dissolved in 300 ml of CH_2Cl_2. After purging argon for 10 min, the condensation of furan-2-aldehyde and pyrrole was initiated by adding catalytic amount of $BF_3{\cdot}OEt_2$ (120 μl of 2.5 M stock solution). The reaction mixture was stirred at room temperature for 1 h. The progress of the reaction was checked by taking aliquots of the reaction mixture at regular intervals and oxidize with DDQ and record the absorption spectra which clearly confirmed the formation of porphyrin. After 1 h, DDQ (674 mg, 2.98 mmol) was added and the reaction mixture was stirred in air for additional 1 h. The solvent was removed under reduced pressure and the crude compound was purified by silica gel column chromatography using CH_2Cl_2 (62 mg, 12%). Mp >300°C. ^{1}H NMR ($CDCl_3$, δ in ppm) −2.59 (s, 2H, NH), 7.04 (m, 4H, furyl), 7.32 (m, 4H, furyl), 8.14 (s, 4H, furyl), 9.16 (s, 8H, β-pyrrole). LD-MS $C_{36}H_{22}N_4O_4$ calcd av. mass, 574.6, obsd. *m*/*z* 574.7 (M^+). Anal. calcd C, 75.25; H, 3.86; N, 9.75. Found: C, 75.31; H, 3.92; N, 9.65.

4.1.2. 2,5-Bis(2-furylhydroxymethyl)thiophene (8). In a three necked round bottomed flask equipped with rubber septum, gas inlet tube and reflux condenser, a dry, distilled *n*-hexane (40 ml) was taken. A positive pressure of argon was maintained and after purging argon for 15 min, TMEDA (2.3 ml, 15.75 mmol) and *n*-butyl lithium (18 ml of ca. 15% solution in hexane) were added into the stirred solution. Thiophene (530 mg, 6.30 mmol) was added and the reaction mixture was refluxed for 1 h. After 1 h, the 2,5-dilithiated thiophene mixture was cooled to 0°C in an ice bath and an ice cold solution of furan-2-aldehyde (1.5 g, 15.12 mmol) in dry THF (40 ml) was added. The mixture was stirred for 15 min and ice cold NH_4Cl (50 ml, ca. 1 M) was added to quench the reaction. The organic layer was extracted with ether and washed several times with water and brine solution and dried over anhydrous Na_2SO_4. TLC analysis of crude compound showed the formation of diol with small amounts of mono-ol and unreacted aldehyde. The crude compound was purified by silica gel column chromatography in petroleum ether/ethyl acetate (5:1) mixture and the diol **8** was obtained. The compound was recrystallized twice from toluene to afford diol **8** as white solid in 47% yield. Mp 72–73°C (d). IR (KBr film, cm^{-1}) 3367 (OH). ^{1}H NMR ($CDCl_3$, δ in ppm) 2.75 (bs, 2H, OH), 5.91 (s, 2H, CH), 6.31 (m, 2H, furyl), 6.35 (m, 2H, furyl), 6.80 (s, 2H, thiophene), 7.32 (m, 2H, furyl). ^{13}C NMR ($CDCl_3$, δ in ppm) 66.44, 107.47, 110.32, 124.88, 142.52, 144.62, 154.48. FAB-MS $C_{14}H_{12}SO_4$, calcd av. mass, 276.2 obsd. *m*/*z* 276 (M^+). Anal. calcd C, 60.86; H, 4.38; S, 11.61. Found: C, 60.54; H, 4.08; S, 11.7.

4.1.3. *meso*-5,10,15,20-Tetrakis(2-furyl)21,23-dithiaporphyrin (2). Samples of diol **8** (246 mg, 0.89 mmol) and pyrrole (60 μl, 0.89 mmol) were dissolved in 90 ml CH_2Cl_2 taken 250 ml one necked round bottomed flask and argon was purged for 15 min. $BF_3{\cdot}OEt_2$ (40 μl of 2.5 M stock solution) was added to initiate the reaction and the reaction mixture was stirred for 1 h under argon atmosphere. DDQ (200 mg, 0.89 mmol) was added and reaction mixture was stirred in air for additional 1 h. TLC analysis showed the formation of the required compound as the sole product. The solvent was removed on rotavapor under reduced pressure and the crude compound was purified by silica gel column chromatography using CH_2Cl_2 as eluent to afford fluorescent green solid (35 mg, 13%). ^{1}H NMR ($CDCl_3$, δ in ppm) 7.07 (m, 4H, furyl), 7.42 (m, 4H, furyl), 8.20 (m, 4H, furyl), 8.97 (s, 4H, β-pyrrole), 10.05 (s, 4H, β-thiophene). LD-MS $C_{36}H_{20}N_2S_2O_4$, calcd av. mass, 608.7. obsd. *m*/*z* 608.5 (M^+). Anal. calcd C, 71.04; H, 3.31; N, 4.6; S, 10.54. Found: C, 71.12; H, 3.36; N, 4.7; S, 10.61.

4.1.4. *meso*-5,10,15,20-Tetrakis(2-furyl)21-monothiaporphyrin (3). Samples of 1 equiv. of diol **8** (350 mg, 1.27 mmol), 2 equiv. of furan-2-aldehyde (244 mg, 2.54 mmol) and 3 equiv. of pyrrole (260 μl, 3.81 mmol)

were dissolved in CH_2Cl_2 (132 ml) under argon in a one neck round bottom flask. After 10 min purging with argon, $BF_3{\cdot}OEt_2$ (53 μl of 2.5 M stock solution) was added to initiate the condensation. The reaction mixture was stirred for 1 h under an argon atmosphere. Then DDQ (430 mg, 1.91 mmol) was added and stirring was continued for an additional 1 h. The formation of porphyrins was verified by absorption spectroscopy. TLC analysis of crude reaction mixture indicated the formation of three porphyrins with three different porphyrin cores: N_4, N_3S and N_2S_2. The solvent was removed under reduced pressure and crude solid was dissolved in CH_2Cl_2. A dark powdered slurry was then prepared by adding silica gel and dried. The powder was loaded on a silica column and eluted slowly with CH_2Cl_2. The desired N_3S porphyrin **3** moved as the first band followed by N_4 (**1**) porphyrin as second band and N_2S_2 (**2**) porphyrin as third band. The solvent was removed from the desired compound to afford **3** as green solid (20 mg, 3%). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.41 (s, 1H, NH), 7.02 (m, 2H, furyl), 7.06 (m, 2H, furyl), 7.31 (d, 2H, J=2.6 Hz, furyl), 7.42 (d, 2H, J=4.4 Hz, furyl), 8.11 (s, 2H, furyl), 8.20 (s, 2H, furyl), 8.85 (d, 2H, J=4.7 Hz, β-pyrrole), 9.01 (d, 2H, J=4.4 Hz, β-pyrrole), 9.22 (s, 2H, β-pyrrole), 10.21 (s, 2H, β-thiophene). ^{13}C NMR ($CDCl_3$, δ in ppm) 29.8, 111.9, 112.8, 114.4, 116.9, 122.6, 127.0, 133.7, 134.9, 144.5, 145.4, 148.9. LD-MS $C_{36}H_{21}N_3SO_4$, calcd av. mass, 591.6 obsd. m/z 591.7 (M^+). Anal. calcd C, 73.08; H, 3.58; N, 7.1; S, 5.42. Found: C, 73.12; H, 3.51; N, 6.9; S, 5.39.

4.1.5. *meso*-5,10-Ditolyl-15,20-bis(2-furyl)-21-monothiaporphyrin (4). A solution of diol **8** (300 mg, 1.09 mmol), *p*-tolylaldehyde (262 mg, 2.18 mmol) and pyrrole (230 μl, 3.27 mmol) in 100 ml, CH_2Cl_2 were condensed under argon atmosphere in the presence of $BF_3{\cdot}OEt_2$ (44 ml of 4.5 M stock solution). After 1 h, DDQ (370 mg, 1.64 mmol) was added and stirred for an additional 1 h in air. The solvent was removed and the crude porphyrin mixture of three porphyrins was separated by silica gel column chromatography using petroleum ether/CH_2Cl_2 (3:1) solvent mixture. The desired N_3S porphyrin **4** was moved as a second band. Removal of solvent under reduced pressure gave **4** as purple solid in 5% yield (28 mg). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.32 (s, 1H, NH), 2.70 (s, 6H, CH_3), 7.04 (m, 2H, furyl), 7.38 (m, 2H, furyl), 7.55 (d, 4H, J=7.46 Hz, Ar), 8.05 (d, 4H, J=8.06, Hz, Ar), 8.17 (m, 2H, furyl), 8.60 (d, 2H, J=4.76 Hz, β-pyrrole), 8.86 (d, 2H, J=1.83 Hz, β-pyrrole), 8.97 (d, 2H, J=4.39 Hz, β-pyrrole), 10.19 (s, 2H, β-thiophene). FAB-MS: $C_{42}H_{29}N_3SO_2$, calcd av. mass, 639.8. obsd. m/z 640 (M^+). Anal. calcd C, 78.85; H, 4.57; N, 6.57; S, 5.01. Found: C, 78.81; H, 4.53; N, 6.54.; S, 4.90. ^{13}C NMR ($CDCl_3$, δ in ppm) 21.61, 40.08, 107.24, 110.35, 112.59, 116.30, 119.34, 124.77, 127.50, 129.06, 132.78, 134.49, 134.64, 135.91, 137.79, 139.46, 142.46, 142.02, 145.11, 147.03, 154.14.

4.1.6. *meso*-5,10-Diphenyl-15,20-bis(2-furyl)-21-monothiaporphyrin (5). A solution of 2,5-bis(phenylhydroxymethyl) thiophene (300 mg, 1.01 mmol), furan-2-aldehyde (195 mg, 2.02 mmol) and pyrrole (210 μl, 3.04 mmol) in 100 ml of CH_2Cl_2 was treated under argon atmosphere with $BF_3{\cdot}OEt_2$ (44 μl of 2.5 M stock solution). After 1 h, DDQ (339 mg, 1.52 mmol) was added and stirring was continued for an extra 1 h in air. The crude porphyrin mixture containing three porphyrins were separated by silica gel column chromatography and the desired N_3S porphyrin **5** was collected as second band using petroleum ether/CH_2Cl_2 (3:1) solvent mixture. The solvent was evaporated to afford **5** as purple solid (20 mg, 5%). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (s, 1H, NH), 7.03 (m, 2H, furyl), 7.30 (m, 4H, furyl), 7.82 (m, 4H, Ar), 8.10 (m, 2H, Ar), 8.25 (m, 4H, Ar), 8.73 (d, 2H, J=4.76 Hz, β-pyrrole), 8.88 (d, 2H, J=4.76 Hz, β-pyrrole), 9.30 (d, 2H, J=1.83 Hz, β- pyrrole), 9.75 (s, 2H, β-thiophene). ^{13}C NMR ($CDCl_3$, δ in ppm): 29.7, 111.8, 116.8, 127.6, 128.0, 128.4, 133.9, 134.3, 134.6, 134.8, 139.6, 140.7, 141.8, 144.2, 147.6, 154.5, 155.4, 157.3. FAB-MS $C_{40}H_{25}N_3SO_2$, calcd av. mass, 611.5. obsd. m/z 612 (M^+). Anal. calcd C, 78.54; H, 4.12; N, 6.87; S, 5.24. Found: C, 78.41; H, 4.01; N, 6.68; S, 5.16.

4.1.7. *meso*-5,10-Bis(4-pyridyl)-15,20-bis(2-furyl)-21-monothiaporphyrin (6). Samples of diol **8** (300 mg, 1.087 mmol), pyridine-4-carboxaldehyde (234 mg, 2.174 mmol) and pyrrole (230 μl, 3.261 mmol) were dissolved in propionic acid (75 ml) and refluxed for 2 h. The propionic acid was distilled off under low pressure and the crude solid was washed several times with hot water and dried overnight. The mixture of three porphyrins were separated by silica gel column chromatography. The N_3S porphyrin **6** was collected as a second band using CH_2Cl_2/CH_3OH (7:3) solvent mixture. The N_3S porphyrin **6** was obtained as brownish purple solid in 2% yield (12 mg). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.43 (s, 1H, NH), 7.08 (m, 2H, furyl), 7.43 (m, 2H, furyl), 8.13 (m, 4H, Ar), 8.21 (d, 2H, J=1.1 Hz, furyl), 8.54 (d, 2H, J=4.7 Hz, β-pyrrole), 8.84 (m, 2H, β- pyrrole), 9.05 (m, 6H, β-pyrrole and Ar), 10.26 (s, 2H, β-thiophene). FAB-MS $C_{38}H_{23}N_5SO_2$ calcd av. mass, 613.7 obsd. m/z 614 (M^+). Anal. calcd C, 74.37; H, 3.78; N, 11.41; S, 5.23. Found: C, 74.41; H, 3.74; N, 11.39; S, 5.27.

4.1.8. 2,5-Bis(2-furylhydroxymethyl)furan (9). The diol **9** was prepared by following the same method given for diol **8** by using *n*-hexane (40 ml), TMEDA (2.5 ml, 17.18 mmol), *n*-BuLi (17 ml of ca. 15% solution in hexane) and furan (468 mg, 6.874 mmol) for 2,5-dilithiofuran salt which was added to ice cold solution of furan-2-aldehyde (1.40 ml, 16.498 mmol) in dry 40 ml THF. The crude diol was purified by column chromatography in petroleum ether/ethyl acetate (5:1) solvent mixture. The solvent was removed to afford furan diol **9** as an orange oil in 11% yield (190 mg). IR (neat, cm^{-1}) 3403 (OH). ^{1}H NMR ($CDCl_3$, δ in ppm) 3.3 (bs, 2H, OH), 5.81 (s, 2H, CH), 6.26 (s, 2H, furan), 6.32 (s, 2H, furyl), 6.35 (s, 2H, furyl) 7.40 (s, 2H, furyl). ^{13}C NMR ($CDCl_3$, δ in ppm) 63.3, 107.4, 108.1, 110.1, 142.1, 152.9, 153.1. FAB-MS $C_{14}H_{12}O_5$, calcd av. mass, 260.2 obsd. m/z 260 (M^+). Anal. calcd C, 64.61; H, 4.65. Found: C, 64.53; H, 4.69.

4.1.9. *meso*-5,10-Ditolyl-15,20-bis(2-furyl)-21-monooxaporphyrin (7). The furan diol **9** (233 mg, 0.89 mmol), *p*-tolylaldehyde (215 mg, 1.79 mmol) and pyrrole (186 μl, 2.68 mmol) were condensed in 90 ml of CH_2Cl_2 under nitrogen in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ (40 ml of 2.5 M stock solution). The reaction mixture was stirred under nitrogen for 1 h and DDQ (304 mg, 1.34 mmol) was added and stirring was continued in air for extra 1 h. TLC and UV–Visible spectroscopy analysis of

crude mixture showed the formation of two types of porphyrins: 5,10,15,20-tetratolylporphyrin (N_4) and the desired N_3O porphyrin **7**. The crude mixture was purfied by silica gel column chromatography using CH_2Cl_2/CH_3OH (9: 1) as eluent. The N_3O porphyrin **7** was moved as second band and the solvent was removed on rotary evaporator to afford **7** as green solid (10 mg, 2%). ^1H NMR ($CDCl_3$, δ in ppm) 2.74 (s, 6H, CH_3), 7.14–6.99 (m, 2H, furyl), 7.66 (m, 6H, furyl and Ar), 8.19 (m, 6H, furyl and Ar), 8.71 (s, 2H, β-pyrrole), 8.94 (bs, 2H, β-pyrrole), 9.08 (bs, 2H, β-pyrrole), 9.87 (s, 2H, β-furan). FAB-MS $C_{42}H_{29}N_3O_3$ calcd av. mass, 623.7 obsd. *m/z* 624 (M^+). Anal. calcd C, 80.88; H, 4.69; N, 6.74. Found: C, 80.83; H, 4.65; N, 6.70. ^{13}C NMR ($CDCl_3$, δ in ppm) 14.28, 21.65, 104.38, 113.25, 120.37, 127.30, 128.45, 130.09, 130.56, 130.96, 133.87, 137.40, 139.58, 142.22, 143.11, 146.50, 153.13, 156.06, 157.39.

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