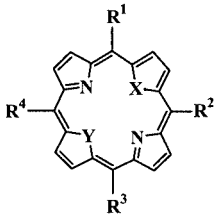
Synthesis and Structural Characterization of *meso*-Thienyl Core-Modified Porphyrins

Iti Gupta,[a] C.-Hsiung Hung,[b] and Mangalampalli Ravikanth*[a]

Keywords: Porphyrins / Sulfur / Supramolecular chemistry

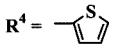
A series of *meso*-thienyl-substituted porphyrins with different porphyrin cores such as N_3S, N_2S_2 and N_3O were synthesized and characterized. The thienyl groups at the *meso*-carbon atoms change the electronic properties of the porphyrin ring. The X-ray structure solved for the N_2S_2 porphyrin with four *meso*-thienyl groups showed supramolecular assembly formation in the solid state due to C–H···N hydrogen bonding between the CH group of the *meso*-thienyl group of one porphyrin ring with the pyrrole N atom of another porphyrin ring. The X-ray analysis of the N_3S porphyrin with two *meso*-thienyl groups and two *meso*-aryl groups did not show any supramolecular assembly formation in the solid state.

Core-modified porphyrins resulting from the replacement of one or two pyrrole rings by heterocycles such as thiophene, furan, selenophene and tellurophene have received only little attention in spite of their novel properties such as stabilization of metal atoms in unusual oxidation states.[1] For example, it has been shown that 5,10,15,20-tetraphenyl-21-thiaporphyrin (N_3S core) can stabilize copper(I)[2] which is not possible with a normal 5,10,15,20-tetraphenylporphyrin (N_4 core). Most of the studies on core-modified porphyrins have been directed towards the synthesis and stabilization of metal atoms of copper, nickel and rhodium in unusual oxidation states.[2] There are no studies on the effects of introducing different kinds of substituents at *meso*- as well as β-positions on the electronic properties of the core-modified porphyrins. Recently, there have been reports on *meso*-tetrathienylporphyrins with N_4 porphyrin cores.[3] The *meso*-tetrathienylporphyrins showed very interesting film-forming and conductivity behaviour[4] and they were also good models for energy-transfer reactions.[3a] It was also shown that by introducing the five-membered thienyl groups in place of six-membered aryl groups at *meso*-carbon atoms, the electronic properties were altered dramatically.[3d] The interesting electronic properties of the *meso*-thienylporphyrins suggests that these porphyrins can be used as a substitute for *meso*-tetraarylporphyrins for various applications. Interestingly, there are no reports on core-modified porphyrins with five-membered heterocycles such as thienyl and furyl[5] at *meso*-carbon atoms to study their effect on the electronic properties of the porphyrins. In this paper, we report the synthesis and characterization of a series of porphyrins with two or four thienyl groups at the *meso*-carbon atoms of porphyrins with N_3S, N_2S_2 and N_3O



X = Y = S; $R^1 = R^2 = R^3 = R^4$ =  **: 1**

X = Y = S; $R^1 = R^2 = R^3 = R^4$ =  **: 2**

X = S; Y = NH; $R^1 = R^2 = R^3 = R^4$ =  **: 3**

X = S; Y = NH; $R^1 = R^2$ =  **; $R^3 = R^4$ =** **: 4**

X = S; Y = NH; $R^1 = R^2$ =  **; $R^3 = R^4$ =** **: 5**

X = Y = O; $R^1 = R^2 = R^3 = R^4$ =  **: 6**

X = O; Y = NH; $R^1 = R^2$ = **; $R^3 = R^4$ =** **: 7**

X = O; Y = NH; $R^1 = R^2$ = **; $R^3 = R^4$ =** **: 8**

[a] Department of Chemistry, Indian Institute of Technology, Powai, Mumbai 400076, India
E-mail: ravikanth@chem.iitb.ac.in
[b] Department of Chemistry, National Changhua University of Education, Changhua, Taiwan 50058, Republic of China

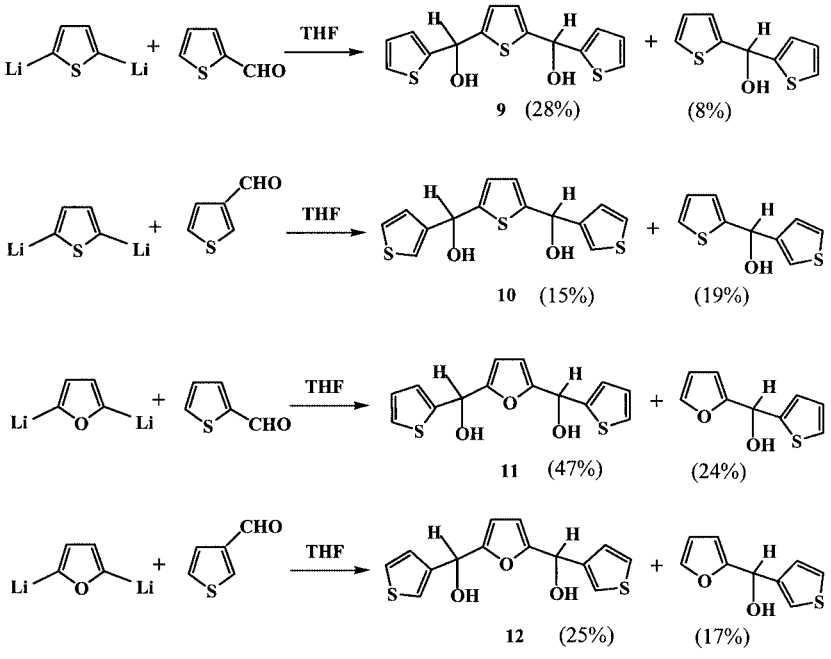
  DOI: 10.1002/ejoc.200300228

cores **1**−**8**. The electronic properties were altered by introduction of thienyl groups at the *meso*-carbon atoms and the effects were directly related to the number of *meso*-thienyl groups. Furthermore, the X-ray structure solved for the N_2S_2 porphyrin **1** with four *meso*-thienyl groups showed the formation of a ladder-type supramolecular assembly through C−H···N hydrogen-bonding interactions between the thienyl CH group of one porphyrin ring and the pyrrole N atom of another porphyrin ring.[6] Such hydrogen-bonded supramolecular assembly was not observed for the N_3S porphyrin **5** with two thienyl groups and two aryl groups at the *meso*-carbon atoms.

Results and Discussion

The unknown thiophenediols **9** and **10** were prepared according to the method of Ulman and Manassen;[7] 1 equiv. of 2,5-dilithiothiophene was condensed with 2 equiv. of thienyl-2-carboxaldehyde or thienyl-3-carboxaldehyde in ice-cold dry THF (Scheme 1). TLC analysis of the reaction mixture showed the formation of either the diol **9** or **10** along with some amount of mono-ol and unchanged aldehyde. The diol reaction mixtures were purified by silica gel column chromatography by using a petroleum ether/ethyl acetate mixture to afford diols **9** and **10** as white solids in 28 and 15% yields, respectively. The furandiols **11** and **12** were similarly prepared[8] by treating 2,5-dilithiofuran with thienyl-2-carboxaldehyde and thienyl-3-carboxaldehyde, respectively, in THF. The furandiols **11** and **12** were purified by silica gel column chromatography and afforded **11** and **12** as yellow oily compounds in 47 and 25% yields, respectively. All four diols were characterized by NMR and IR spectroscopy, mass spectrometry and elemental analysis; 1 equiv. of the diol **9** was condensed at room temperature with 1 equiv. of pyrrole in CH_2Cl_2 in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ under argon, followed by oxidation with DDQ in air.[9] The formation of the desired N_2S_2 porphyrin **1** was confirmed by the observation of a single green spot on TLC. Column chromatography on silica gel using CH_2Cl_2 gave **1** in 20% yield. Porphyrin **1** was characterized by NMR, absorption and fluorescence spectroscopy, mass spectrometry and elemental analysis. In the ^{1}H NMR spectrum, both thiophene and pyrrole protons appear as singlets, indicating the symmetric nature of the porphyrin **1** (Figure 1). However, the proton signals of both thiophene and pyrrole are shifted downfield in **1** by 0.20 ppm compared with 5,10,15,20-tetrakis(4-phenyl)-21,23-dithiaporphyrin (S_2TPP)[1a] suggesting that the π-delocalization of the porphyrin is altered by substituting the phenyl groups by thienyl groups at the *meso*-carbon atoms (Table 1). The absorption and emission bands (Figure 2) experience red shifts with dramatic changes in ε values (Table 2) and fluorescence yields (Table 3) compared to S_2TPP, supporting the alteration of π-delocalization of the porphyrin by the thienyl groups at the *meso*-carbon atoms.

The N_2S_2 porphyrin **2** was prepared similarly by condensing 1 equiv. of diol **10** with 1 equiv. of pyrrole in CH_2Cl_2 in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ followed by oxidation with DDQ.[9] The crude compound was purified by silica gel column chromatography. Downfield shifts of the thiophene and pyrrole proton signals in the ^{1}H NMR spectrum and red shifts of absorption and fluorescence bands compared to S_2TPP[1a] are observed for **2** but these are lower in magnitude than for **1**. The N_3S porphyrin **3** with four thienyl groups at the *meso*-positions was synthesized by condensing 1 equiv. of the diol **9** with 2 equiv. of



Scheme 1. Synthetic scheme for diols **9**−**12**

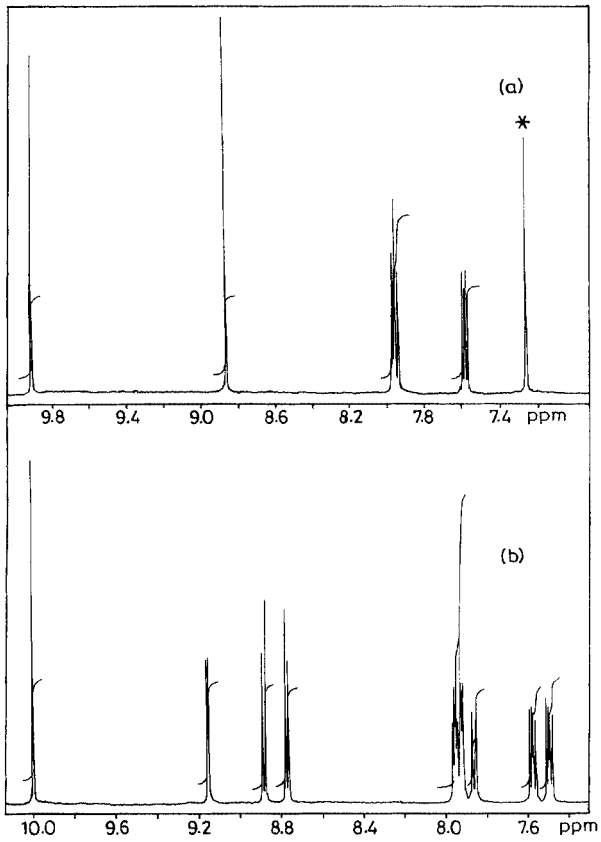


Figure 1. ^{1}H NMR spectra of **1** (a) and **3** (b) recorded in $CDCl_3$

Table 1. ^{1}H NMR chemical shifts (δ in ppm) of selected protons of porphyrins **1**−**8**

Porphyrin	Thiophene/Furan	Pyrrole
S_2TPP[a]	9.68 (s)	8.67 (s)
1	9.91 (s)	8.86 (s)
2	9.82 (s)	8.81 (s)
STPPH[a]	9.81 (s)	8.61 (d), 8.72 (d), 8.88 (s)
3	9.99 (s)	8.77(d), 8.88 (d), 9.15 (d)
4	9.98 (s)	8.60 (d), 8.86 (d), 8.90 (d)
5	9.88 (s)	8.61 (d), 8.79 (d), 8.92 (d)
OTPPH[a]	9.16 (s)	8.52 (d), 8.62 (d), 8.89 (s)
6	9.59 (s)	9.21 (d), 9.47 (bs)
7	9.62 (s)	8.43 (s), 8.88−8.83 (m)
8	9.30 (s)	8.63 (s), 8.86 (s)

[a] Data taken from ref.[1a]

thienyl-2-carboxaldehyde and 3 equiv. of pyrrole in CH_2Cl_2 in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ followed by oxidation with DDQ[9] (Scheme 2). The condensation resulted in the formation of three porphyrins[10] with three different porphyrin cores: the N_2S_2 porphyrin **1**, the desired N_3S porphyrin **3** and the N_4 porphyrin 5,10,15,20-tetrakis(2-thienyl)porphyrin. The three porphyrins were separated by column chromatography and their structures were confirmed by various spectroscopic techniques. The ^{1}H NMR spectrum of **3**, recorded in $CDCl_3$, shows a singlet for the thiophene protons, which is shifted downfield by 0.18 ppm relative to 5,10,15,20-tetrakis(4-phenyl)-21-thia-

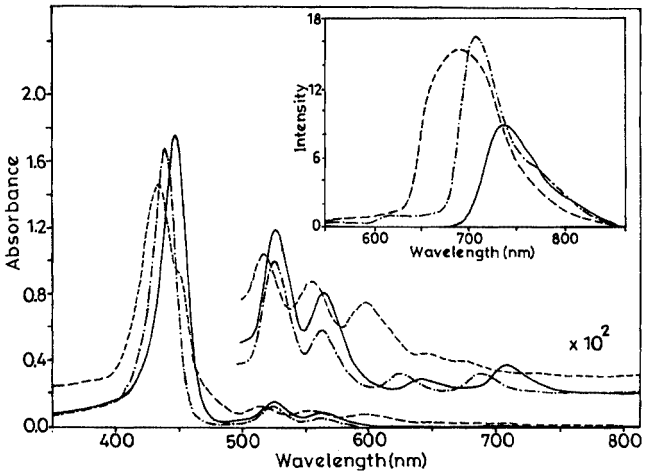


Figure 2. Absorption and fluorescence (inset) spectra of **1** (—), **3** (-·-·) and **6** (----) recorded in toluene

Table 2. Absorption data of *meso*-thienylporphyrins **1**−**8** recorded in toluene

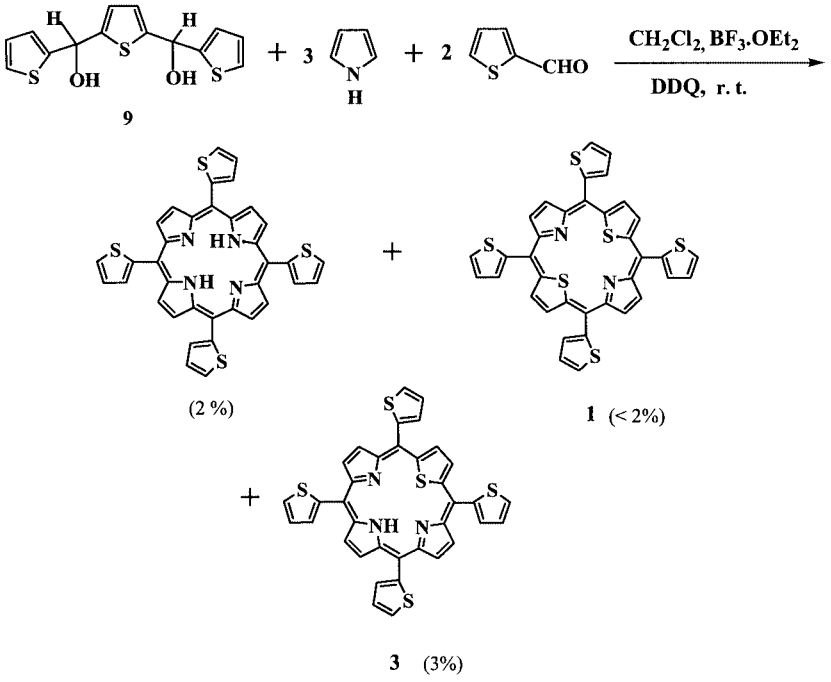
Porphyrin	Soret band λ [nm] (ε × 10^{-4})		Q-bands λ [nm] (ε × 10^{-3})		
	IV		III	II	I
S_2TPP[a]	435 (25.0)	514 (26.0)	547 (7.0)	633 (2.2)	696 (4.5)
1	447 (17.0)	525 (19.2)	563 (11.9)	642 (1.8)	713 (3.3)
2	440 (15.4)	519 (13.5)	554 (6.6)	638 (1.2)	704 (2.9)
STPPH[a]	429 (18.7)	513 (17.1)	547 (4.4)	618 (1.9)	675 (3.0)
3	440 (33.7)	523 (22.7)	562 (11.3)	627 (3.8)	692 (3.6)
4	437 (29.3)	520 (20.6)	557 (9.4)	622 (3.1)	684 (3.4)
5	432 (44.1)	517 (29.9)	552 (11.9)	621 (3.9)	683 (6.4)
OTPPH[a]	419 (21.9)	507 (9.9)	539 (3.0)	569 (2.6)	671 (2.8)
6	430 (10.1)	516 (5.5)	553 (3.0)	598 (2.1)	682 (0.98)
7	425 (13.1)	514 (7.3)	583 (5.0)	609 (4.3)	670 (2.1)
8	423 (27.1)	510 (22.8)	543 (5.5)	616 (3.1)	677 (3.8)

[a] Data taken from ref.[1a]

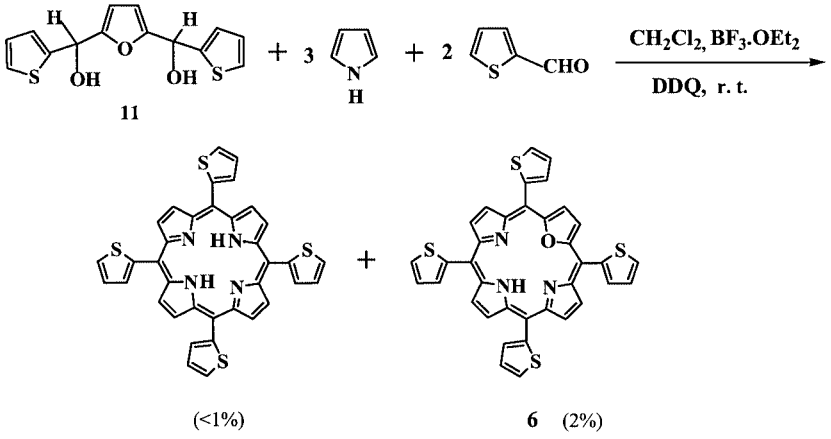
Table 3. Fluorescence data of *meso*-thienylporphyrins **1**−**8** in toluene

Porphyrin	Q(0,0) λ_{max} [nm]	Q(0,1) λ_{max} [nm]	φ_f [a]
S_2TPP[b]	706	781	0.00764
1	738	–	0.00041
2	717	–	0.00011
STPPH[b]	678	760	0.01683
3	709	–	0.00018
4	695	756	0.00016
5	693	755	0.00046
OTPPH[b]	676	–	0.07580
6	690		0.00468
7	687		0.00360
8	683		0.04480

[a] The fluorescence quantum yields were estimated by using 5,10,15,20-tetraphenylporphyrin (φ_f = 0.11) as a standard. [b] Data taken from ref.[1a]



Scheme 2. Synthetic scheme for N_3S porphyrin **3**



Scheme 3. Synthetic scheme for N_3O porphyrin **6**

porphyrin (STPPH).[11] The signals of the two pyrrole rings adjacent to the thiophene ring appear as AB doublets, and those of the pyrrole ring opposite to the thiophene ring appears as a doublet due to the coupling of the pyrrolic and NH protons. The signals of all three pyrrole ring protons are shifted to lower field by 0.16−0.27 ppm compared to STPPH (Table 1). The absorption spectrum of **3** shows four defined Q-bands and one Soret band (Figure 2). All the absorption bands are red-shifted and the absorption coefficients are significantly different from STPPH.[1a,11] The fluorescence bands of **3** also show bathochromic shifts (Figure 2) and a reduction in quantum yields relative to STPPH[12] (Table 3). The two N_3S porphyrins **4** and **5**, with two thienyl and two tolyl rings at the *meso*-carbon atoms, were synthesized by condensing 1 equiv. of the corresponding diol **9** and **10**, respectively, with 2 equiv. of *p*-tolylaldehyde and 3 equiv. of pyrrole in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ in CH_2Cl_2, followed by oxidation with DDQ. The condensations resulted in the formation of mixtures of three porphyrins and the required N_3S porphyrin **4** or **5**, which was separated from the mixture by column chromatography. The structures of the porphyrins **4** and **5** were confirmed by NMR, absorption and emission spectroscopy, mass spectrometry and elemental analysis. The presence of only two thienyl groups at the *meso*-carbon atoms results in less pronounced shifts of the peaks in the ^1H NMR, absorption and fluorescence spectra (Table 1−3).

The N_3O porphyrins **6**−**8** were prepared from the furandiols **11** and **12** (Scheme 1). The N_3O porphyrin **6**, with four thienyl groups at the *meso*-carbon atoms, was synthesized by condensing 1 equiv. of the furandiol **11** with 2 equiv. of thienyl-2-carboxaldehyde and 3 equiv. of pyrrole in CH_2Cl_2 in the presence of $BF_3{\cdot}OEt_2$ followed by oxidation with DDQ (Scheme 3). The reaction mixture showed the forma-

tion of only two porphyrins instead of the expected three porphyrins, as confirmed by TLC. The N_2O_2 porphyrin was not formed under any porphyrin-forming conditions. The desired N_3O porphyrin **6** was separated from the N_4 porphyrin 5,10,15,20-tetrakis(2-thienyl)porphyrin by column chromatography and its structure was confirmed by NMR spectroscopy, mass spectrometry and other spectral analyses. In the ^1H NMR spectrum, the furan protons appear as singlets which are shifted downfield (Table 1) relative to its aryl analogue, 5,10,15,20-tetrakis(4-phenyl)-21-oxaporphyrin (OTPPH).[1a] The absorption spectrum of **6** exhibits ill-defined Q-bands and a strong Soret band, which are red-shifted compared to OTPPH[12] (Table 2). The fluorescence band is very broad and red-shifted compared to OTPPH (Table 3).

The N_3O porphyrins **7** and **8**, with two *meso*-thienyl and two tolyl rings, were synthesized by condensing 1 equiv. of either the diol **11** or **12**, respectively, with 2 equiv. of *p*-tolylaldehyde and 3 equiv. of pyrrole in CH_2Cl_2 in the presence of $BF_3{\cdot}OEt_2$, followed by oxidation with DDQ. The reaction showed the formation of the desired N_3O porphyrin **7** or **8** along with the N_4 porphyrin, 5,10,15,20-tetrakis(2- or 3-thienyl) porphyrin, respectively. The N_3O porphyrins **7** or **8** were separated from their corresponding N_4 porphyrins by silica gel column chromatography and their structures were confirmed by NMR spectroscopy, mass spectrometry and elemental analysis. The shift of the peaks in the ^1H NMR, and absorption and fluorescence spectra noted for **7** and **8** were compared to OTPPH[13] and found to be lower in magnitude than for the N_3O porphyrin **6**.

Crystal-Structure Analysis of N_2S_2 Porphyrin 1 and N_3S Porphyrin 5

A single crystal of **1** suitable for X-ray analysis was obtained by slow concentration of a CH_2Cl_2/CH_3OH solution over a period of one week. The aerial and edge views of **1** are presented in Figure 3 and selected parameters and bond lengths and angles are reported in Tables 4 and 5, respectively. As shown in Figure 3, the molecule is almost planar. The four five-membered rings are in the same plane as the four *meso*-carbon atoms, with negligible deviation from planarity; the *meso*-thienyl substituents lie out of the plane of the porphyrin. Two of the *meso*-thienyl sulfur atoms lie above this plane and other two lie below the plane. The non-bonding N···N′ (4.61 Å) and S···S′ distances (3.058 Å) are shorter in **1** than in S_2TPP[13] (N···N′: 4.65 Å; S···S: 3.069 Å), indicating that **1** is more planar than S_2TPP. The bond lengths in the *meso*-thienyl rings are different to those in the free thiophene, suggesting that the π-delocalization of the porphyrin macrocycle is extended to the *meso*-thienyl rings. The $C_\beta-C_\beta$ distances of thiophene and pyrrole in **1** [1.353(5) and 1.331(6) Å, respectively] are significantly shorter than in S_2TPP, indicating that the π-delocalization is more altered in **1** as a result of introducing the thienyl substituents at the *meso* positions. The most novel feature of **1** is the observation of intermolecular hydrogen bonding holding the porphyrin rings in a supramolecular array.[6] The packing diagram presented in Figure 4 clearly shows the presence of a C−H···N hydrogen bond (Table 6) between the *meso*-thienyl CH group of one porphyrin ring and the pyrrole N atom of another one. This bonding is extended in the single strand to form a ladder-type supramolecular assembly; H bonding is not present between the strands.

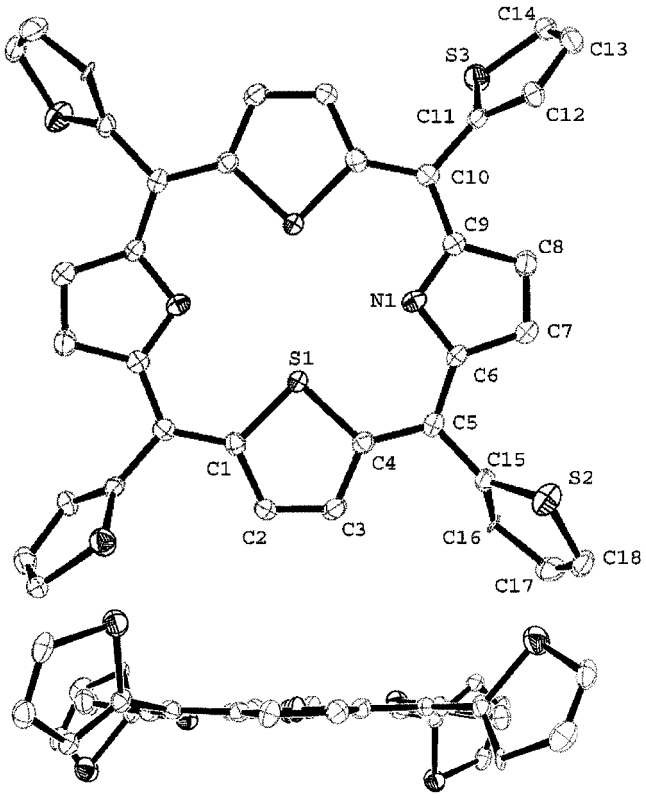


Figure 3. X-ray structure of **1**; top: aerial view; bottom: edge view

Table 4. Crystal data and data collection parameters for **1** and **5**

	1	**5**
Empirical formula	$C_{36}H_{20}N_2S_6$	$C_{42.75}H_{25}N_3S_{2.75}$
Formula mass	672.96	668.82
Dimensions [mm]	0.08 × 0.10 × 0.21	0.36 × 0.12 × 0.08
Crystal system	monoclinic	monoclinic
a [Å]	26.07(3)	19.66(16)
b [Å]	6.09(7)	8.74(7)
c [Å]	22.19(3)	20.12(16)
β [°]	124.2(2)	102.8(18)
V [Å^3]	2914.6(6)	3375(5)
Space group	*C*2/*c*	$P2_1/n$
Z	4	4
μ(Mo-K_α) [mm^{-1}]	0.152	0.241
*R*1	0.0514	0.0860
Reflections measured	3322	20076
T [K]	293	293 (2)

The structure of the N_3S porphyrin **5** (Figure 5) with two *meso*-thienyl and -tolyl rings was elucidated by a single-crystal X-ray diffraction analysis. The two *meso*-thienyl groups are disordered where one carbon and one sulfur atom occupy two positions. For one thienyl group, the oc-

Table 5. Selected X-ray structural data for porphyrins **1** and **5**

Porphyrin	Bond lengths [Å]	Bond angles [°]	Non-bonded distances [Å]
1	S1−C1 1.735(4) C1−C2 1.407(5) C2−C3 1.353(5) N1−C6 1.365(4) C6−C7 1.451(5) C7−C8 1.331(6)	C6−C5−C4 123.5(3) C5−C4−C3 128.1(3) C5−C4−S1 122.3(3) S1−C4−C3 109.6(3) C4−C3−C2 114.0(3) C1−S1−C4 91.8(18) C6−N1−C9 106.2(3) N1−C6−C7 109.6(3) C6−C7−C8 107.7(3) C7−C6−C8 126.7(3) N1−C6−C5 123.4(3) C9−C10−C1A 122.8(4)	S1···S1A 3.058(16) N1···N1A 4.618
5	S1−C1 1.732(6) C1−C2 1.431(8) C2−C3 1.362(8)	C1−S1−C4 93.6(3) S1−C1−C2 109.0(5) C1−C2−C3 114.2 (6) C2−C1−C20 126.5(6) S1−C1−C20 124.5(4) C1−C20−C19 121.8(5)	S1···N2 3.570 N1···N3 4.392

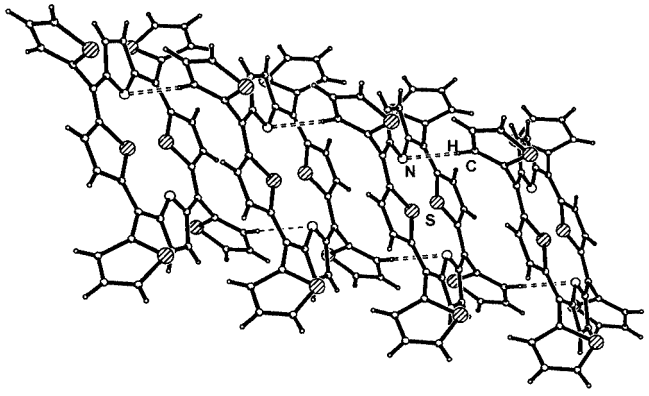


Figure 4. Molecular packing diagram of **1** showing C−H···N hydrogen bonding interactions

Table 6. Inter- and intramolecular hydrogen-bond data for porphyrins **1** and **5**

Porphyrin	H-bonded distances [Å]	Bond angles [°]
1	C12−H12···N1[a] 3.337(5)	152.8
5	N2−H2···S1[b] 3.570(5)	175.2
	N2−H2···N1[b] 3.042(7)	116.8
	N2−H2···N3[b] 2.911(6)	118.0

[a] Intermolecular hydrogen bond. [b] Intramolecular hydrogen bond.

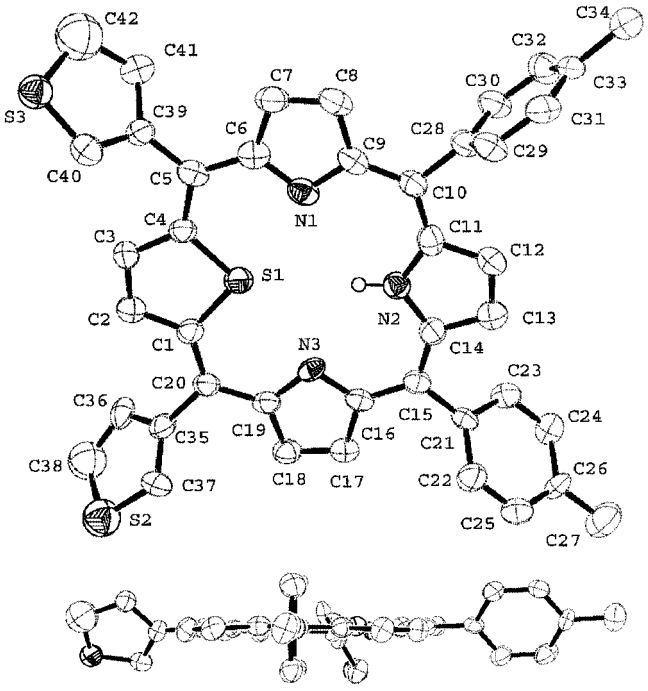


Figure 5. X-ray structure of **5**, top: aerial view, bottom: edge view

cupancy of carbon (C42) and sulfur (S3) is 50:50 and for the other thienyl group (C38 and S2), this ratio is 70:30. Comparing the structure of **5** with the reported aryl N_3S porphyrin STPPH[13] suggests that **5** is more planar than the slightly saddle-shaped STPPH. The non-bonding N(1)−N(3) distance (4.392 Å) is almost the same as that of STPPH but the non-bonding S−N(2) distance (3.570 Å) is longer than in STPPH (3.547 Å). The $C_\alpha-X$, $C_\alpha-C_\beta$ and $C_\beta-C_\beta$ bond lengths in **5** are slightly different than in STPPH, indicating that the π-delocalization has altered in the porphyrin macrocycle with thienyl substituents at the *meso* positions. The important feature of the structure is the presence of intramolecular hydrogen-bonding interactions in the cavity (Table 6).[6] There is no other hydrogen bonding noted for **5** in the packing diagram.

In conclusion, we have synthesized a series of *meso*-thienylporphyrins with different porphyrin cores such as N_3S, N_2S_2 and N_3O and compared their electronic properties with those of corresponding aryl analogues. The introduction of thienyl groups at the *meso*-carbon atoms alters the π-delocalization significantly as reflected in the downfield

shifts of the signals of the pyrrole and heterocycle protons in the ^{1}H NMR spectrum and the red shifts of the bands in the absorption and fluorescence spectra. Furthermore, the X-ray analysis of the N_2S_2 porphyrin with four 2-thienyl groups at the *meso*-carbon atoms showed the formation of a supramolecular assembly in the solid state because of intermolecular C−H···N hydrogen bonding between a *meso*-thienyl CH group and a pyrrole N atom. This unique hydrogen bonding, which helps the porphyrin rings to assemble in a supramolecular fashion, is not common to all *meso*-thienylporphyrins since such intermolecular hydrogen bonding was not observed for the N_3S porphyrin containing two tolyl and two 3-thienyl groups at the *meso*-carbon atoms. The N_3S porphyrin shows only intramolecular N−H···S and N−H···N hydrogen bonding. The *meso*-thienylporphyrins reported here have potential for several applications and we are currently studying their metallation, electrochemical and material properties in our laboratory.

Experimental Section

General: ^{1}H NMR spectra were recorded with a Varian 300 MHz instrument using tetramethylsilane as an internal standard. Absorption and fluorescence spectra were obtained with Perkin−Elmer Lambda-35 and Lambda-55 instruments, respectively. The FAB mass spectra were recorded with a JEOL SX 102/DA-6000 mass spectrometer using argon/xenon as the FAB gas. Toluene, THF and triethylamine were obtained from S. D. Fine chemicals, India, and were dried by standard procedures before use. All general chemicals were obtained from Qualigens, India. Benzaldehyde and thiophene, furan and pyrrole were obtained from Lancaster. Column chromatography was performed using 60−120 mesh silica obtained from Sisco Research Laboratories, India.

Thiophene-2,5-diylbis(thien-2-ylmethanol) (9): Dry, distilled *n*-hexane (40 mL) was added to a 250-mL three-necked, round-bottomed flask fitted with a rubber septum, gas inlet tube and reflux condenser and the flask was flushed with argon for 10 min. TMEDA (2.3 mL, 15.75 mmol) and *n*BuLi (18 mL of ca. 15% solution in hexane) were then added and the solution was stirred under argon for 10 min. Thiophene (0.5 mL, 6.302 mmol) was added and the solution was refluxed for 1 h. As the reaction progressed, a white turbid solution formed indicating the formation of the 2,5-dilithiated salt of thiophene. The reaction mixture was cooled to 0 °C in an ice bath and then an ice-cold solution of thiophene-2-carbaldehyde (1.40 mL, 15.12 mmol) in dry THF (40 mL) was added. The reaction mixture was stirred at 0 °C for 15 min and then brought to room temperature. The reaction was quenched by adding an ice-cold NH_4Cl solution (50 mL, ca. 1 M). The organic layer was washed with water and brine solution and dried with anhydrous Na_2SO_4. The solvent was removed in a rotary evaporator under reduced pressure to afford the crude compound. TLC analysis showed three spots corresponding to unchanged thiophene-2-carbaldehyde, monool and the desired diol **9**. The aldehyde and the mono-ol (90 mg, 8%) were removed by silica gel column chromatography using 5−15% ethyl acetate/petroleum ether and the diol **9** was collected with 20% ethyl acetate/petroleum ether as a white solid (287 mg, 28%). M.p. 62−65 °C. IR (KBr, film): $\tilde{\nu}$ = 3455 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): δ = 3.02 (br. s, 2 H, OH), 6.18 (s, 2 H, CH), 6.82 (d, J = 2.57 Hz, 2 H, thiophene), 6.94 (m, 2 H, thienyl), 6.98 (m, 2 H, thienyl), 7.25 (d, J = 1.10 Hz, 1 H, thienyl), 7.26 (d, J = 1.40 Hz, 1 H, thienyl) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 68.65, 124.67, 125.16, 125.60, 126.78, 146.90, 147.34 ppm. FAB-MS: $C_{14}H_{12}O_2S_3$, calcd. av. mass 308.4, obsd. m/z = 308 [M$^+$]. $C_{14}H_{12}O_2S_3$ (308.4): calcd. C 54.52, H 3.92, S 31.19; found C 54.35, H 3.90, S 31.13.

Thiophene-2,5-diylbis(thien-3-ylmethanol) (10): The 2,5-dilithiated thiophene was prepared by treating thiophene (0.5 mL, 6.302 mmol) with *n*BuLi (18 mL of ca. 15% solution in hexane) in the presence of TMEDA (2.3 mL, 15.75 mmol) in *n*-hexane (40 mL). The condensation of 2,5-dilithiothiophene with thiophene-3-carbaldehyde (1.70 g) under the same experimental conditions mentioned for diol **9**, afforded the diol **10** as a white solid (254 mg, 15%). M.p. 87−89 °C. IR (KBr, film): $\tilde{\nu}$ = 3337 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): δ = 2.51 (br. s, 2 H, OH), 6.05 (s, 2 H, CH), 6.78 (s, 2 H, thiophene), 7.08 (m, 2 H, thienyl), 7.29 (m, 4 H, thienyl) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 68.93, 122.02, 124.52, 126.27, 126.39, 144.32, 147.54 ppm. FAB-MS: $C_{14}H_{12}O_2S_3$, calcd. av. mass 308.4, obsd. m/z = 308 [M$^+$]. $C_{14}H_{12}O_2S_3$ (308.4): calcd. C 54.52, H 3.92, S 31.19; found C 54.19, H 3.18, S 31.23.

Furan-2,5-diylbis(thien-2-ylmethanol) (11): In a three-necked flask, furan (0.5 mL, 6.874 mmol) in *n*-hexane (40 mL) was treated with *n*BuLi (20 mL of a 15% solution in hexane) in the presence of TMEDA (2 g, 17.18 mmol) under inert conditions to give the 2,5-dilithiated salt of furan. Thiophene-2-carbaldehyde (1.9 g, 16.50 mmol) in dry THF (40 mL) was added slowly to the 2,5-dilithiated thiophene followed by workup and chromatography to afford the furandiol **11** as a yellow oil (950 mg, 47%). IR (neat): $\tilde{\nu}$ = 3379 cm^{-1}(OH). ^{1}H NMR ($CDCl_3$): δ = 2.89 (s, 2 H, OH), 5.99 (s, 2 H, CH), 6.17 (s, 2 H, furan), 6.96 (m, 2 H, thienyl), 6.99 (m, 2 H, thienyl), 7.26 (m, 2 H, thienyl) ppm. FAB-MS: $C_{14}H_{12}O_3S_2$ calcd. av. mass 292.4, obsd. m/z = 292 [M$^+$].

Furan-2,5-diylbis(thien-3-ylmethanol) (12): The condensation of 2,5-dilithiothiophene with thiophene-3-carbaldehyde (1.9 g, 16.50 mmol) under the same experimental conditions gave the furandiol **12** as a yellow oily compound (493 mg, 25%). IR (neat): $\tilde{\nu}$ = 3393 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.3 (br. s, 2 H, OH), 5.71 (d, J = 5.1 Hz, 2 H, furan), 5.96 (s, 2 H, CH), 7.01 (m, 2 H, thienyl), 7.21 (m, 4 H, thienyl) ppm. FAB-MS: $C_{14}H_{12}O_3S_2$, calcd. av. mass 292.4, obsd. m/z = 292 [M$^+$].

5,10,15,20-Tetrakis(2-thienyl)-21,23-dithiaporphyrin (1): A solution of the diol **9** (150 mg, 0.486 mmol) and pyrrole (30 μL, 0.432 mmol) in CH_2Cl_2 (50 mL) was added to a 100-mL one-necked round-bottomed flask fitted with an argon gas bubbler. After purging with argon for 15 min, the condensation of the diol and pyrrole was initiated at room temperature by addition of a catalytic amount of $BF_3{\cdot}OEt_2$ (20 μL of 2.5 M stock solution). The progress of the reaction was checked by taking aliquots of the reaction mixture, oxidizing the aliquots with DDQ in toluene and recording the absorption spectrum at regular intervals. After stirring for 1 h, DDQ (110 mg, 0.487 mmol) was added and the reaction mixture was stirred at room temperature in air for an additional 1 h. The solvent was removed in a rotary evaporator under low pressure and the crude compound was purified by silica gel column chromatography using CH_2Cl_2 as eluent to afford **1** as a green solid in (32 mg, 20%). ^{1}H NMR ($CDCl_3$): δ = 7.58 (m, 4 H, *meso*-thienyl), 7.95 (m, 8 H, *meso*-thienyl), 8.86 (s, 4 H, β-pyrrole), 9.91 (s, 4 H, β-thiophene) ppm. FAB-MS: $C_{36}H_{20}N_2S_6$ calcd. av. mass 672.9, obsd. m/z = 673 [M$^+$]. $C_{36}H_{20}N_2S_6$ (672.9): calcd. C 64.25, H 3.00, N 4.16, S 28.59; found C 64.13, H 2.97, N 4.25, S 28.39.

5,10,15,20-Tetrakis(3-thienyl)-21,23-dithiaporphyrin (2): Condensation of the diol **10** (150 mg, 0.486 mmol) and pyrrole (30 μL,

0.432 mmol) in CH_2Cl_2 (50 mL) was carried out under argon in the presence of $BF_3{\cdot}OEt_2$ (20 μL of 2.5 M stock solution) at room temperature. After 1 h, DDQ (110 mg, 0.486 mmol) was added and the reaction mixture was stirred for an extra 1 h. Chromatography with CH_2Cl_2 gave the required compound **2** as a purple solid (26 mg, 16%). ^{1}H NMR ($CDCl_3$): δ = 7.61 (m, 4 H, *meso*-thienyl), 7.81 (m, 8 H, *meso*-thienyl), 8.81 (s, 4 H, β-pyrrole), 9.82 (s, 4 H, β-thiophene) ppm. FAB-MS: $C_{36}H_{20}N_2S_6$, calcd. av. mass 672.9, obsd. *m*/*z* = 673 [M^+]. $C_{36}H_{20}N_2S_6$ (672.9): calcd. C 64.25, H 3.00, N 4.16, S 28.59; found C 64.32, H 3.07, N 4.23, S 28.52.

5,10,15,20-Tetrakis(2-thienyl)-21-thiaporphyrin (3): Diol **9** (500 mg, 1.621 mmol), thiophene-2-carbaldehyde (364 mg, 3.242 mmol) and pyrrole (340 μL, 4.863 mmol) were dissolved in CH_2Cl_2 (165 mL) in a 250-mL round-bottomed flask and the flask was purged with argon for 10 min. $BF_3{\cdot}OEt_2$ (70 μL of 2.5 M stock solution) was added and the reaction mixture was stirred at room temperature for 1 h. DDQ (550 mg, 2.432 mmol) was added and the reaction mixture was stirred for an additional 1 h in air. TLC analysis indicated the formation of three porphyrins namely the N_2S_2 porphyrin **1**, the desired N_3S porphyrin **3** and 5,10,15,20-tetrakis(2-thienyl)-porphyrin. The solvent was evaporated under reduced pressure, the crude reaction mixture was dissolved in CH_2Cl_2 and a dry slurry powder was prepared by adding a minimum amount of silica gel followed by removing traces of solvent under vacuum. The slurry was loaded onto a silica gel column and the column was eluted with petroleum ether. The N_4 porphyrin was removed as the first band and it was collected eluting with petroleum ether/CH_2Cl_2 (5:1). The desired N_3S porphyrin eluted as the second band using petroleum ether/CH_2Cl_2 (4:1). The solvent was removed in a rotary evaporator to afford **3** as a purple solid (26 mg, 3%). ^{1}H NMR ($CDCl_3$): δ = −2.60 (s,1 H, NH), 7.50 (m, 2 H, *meso*-thienyl), 7.58 (m, 2 H, *meso*-thienyl), 7.86 (m, 2 H, *meso*-thienyl), 7.92 (m, 2 H, *meso*-thienyl), 7.95 (m, 4 H, *meso*-thienyl), 8.77 (d, *J* = 4.76 Hz, 2 H, β-pyrrole), 8.88 (d, *J* = 4.76 Hz, 2 H, β-pyrrole), 9.15 (d, *J* = 2.19 Hz, 2 H, β-pyrrole), 9.99 (s, 2 H, β-thiophene) ppm. FAB-MS: $C_{36}H_{21}N_3S_5$ calcd. av. mass 655.9, obsd. *m*/*z* = 656 [M^+]. $C_{36}H_{21}N_3S_5$ (655.9): calcd. C 65.92, H 3.23, N 6.41, S 24.44; found C 65.90, H 3.21, N 6.38, S 24.41.

15,20-Bis(2-thienyl)-5,10-bis(*p*-tolyl)-21-thiaporphyrin (4): A solution of the diol **9** (150 mg, 0.486 mmol), *p*-toluenecarbaldehyde (117 mg, 0.973 mmol) and pyrrole (100 μL, 1.460 mmol) in CH_2Cl_2 (50 mL) was dissolved under argon in the presence of $BF_3{\cdot}OEt_2$ (20 μL of 2.5 M stock solution). After 1 h, DDQ (165 mg, 0.729 mmol) was added and the reaction mixture was stirred for an additional 1 h. The solvent was removed in a rotary evaporator under reduced pressure and the crude residue containing a mixture of three porphyrins was separated by silica gel column chromatography using a petroleum ether/CH_2Cl_2 mixture. The required N_3S porphyrin **4** was isolated as the second band eluting with petroleum ether/CH_2Cl_2 (4:1). Removal of the solvent from the fraction afforded **4** as a purple solid (28 mg, 9%). ^{1}H NMR ($CDCl_3$): δ = −2.52 (s, 1 H, NH), 2.70 (s, 6 H, CH_3), 7.56 (m, 6 H, *meso*-thienyl), 7.93 (m, 4 H, ArH), 8.06 (d, *J* = 8.06 Hz, 4 H, ArH), 8.60 (d, *J* = 4.39 Hz, 2 H, β-pyrrole), 8.86 (d, *J* = 4.76 Hz, 2 H, β-pyrrole), 8.90 (d, *J* = 1.83 Hz, 2 H, β-pyrrole), 9.98 (s, 2 H, β-thiophene) ppm. FAB-MS: $C_{42}H_{29}N_3S_3$ calcd. av. mass 671.9, obsd. *m*/*z* = 672 [M^+]. $C_{42}H_{29}N_3S_3$ (671.9): calcd. C 75.08, H 4.38, N 6.25, S 14.32; found C 75.12, H 4.31, N 6.32, S 14.29.

15,20-Bis(3-thienyl)-5,10-bis(*p*-tolyl)-21-thiaporphyrin (5): Diol **10** (150 mg, 0.486 mmol), *p*-toluenecarbaldehyde (117 mg, 0.973 mmol) and pyrrole (100 μL, 1.458 mmol) were dissolved in CH_2Cl_2 (50 mL) in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ (20 μL of 2.5 M stock solution) under argon for 1 h, followed by addition of DDQ (165 mg, 0.729 mmol) and the reaction mixture was stirred in air for an extra 1 h. Column chromatography on silica using petroleum ether/CH_2Cl_2 (4:1) gave the desired N_3S porphyrin **5** as a purple solid (25 mg, 8%). ^{1}H NMR ($CDCl_3$): δ = −2.63 (s, 1 H, NH), 2.70 (s, 6 H, CH_3), 7.55 (d, *J* = 7.69 Hz, 4 H, *meso*-thienyl), 7.81 (m, 2 H, *meso*-thienyl), 8.07 (m, 8 H, ArH), 8.61 (d, *J* = 4.39 Hz, 2 H, β-pyrrole), 8.79 (d, *J* = 4.39 Hz, 2 H, β-pyrrole), 8.92 (d, *J* = 1.83 Hz, 2 H, β-pyrrole), 9.88 (s, 2 H, β-thiophene) ppm. FAB-MS: $C_{42}H_{29}N_3S_3$, calcd. av. mass 671.9, obsd. *m*/*z* = 672 [M^+]. $C_{42}H_{29}N_3S_3$ (671.9): calcd. C 75.08, H 4.38, N 6.25, S 14.32; found C 75.16, H 4.40, N 6.31, S 14.30.

5,10,15,20-Tetrakis(2-thienyl)-21-oxaporphyrin (6): The furandiol **11** (500 mg, 1.709 mmol), thiophene-2-carbaldehyde (383 mg, 3.419 mmol) and pyrrole (360 μL, 5.127 mmol) were dissolved in CH_2Cl_2 (170 mL) under argon in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ (70 μL of 2.5 M stock solution) for 1 h, followed by oxidation with DDQ (578 mg, 2.559 mmol) in air for an additional 1 h. TLC analysis indicated the formation of two porphyrins, namely 5,10,15,20-tetrakis(2-thienyl)porphyrin and the required N_3O porphyrin **6**. The porphyrin **6** moved as the second band on a silica gel column when eluted with 3% CH_3OH/CH_2Cl_2. The solvent was removed in a rotary evaporator at reduced pressure to afford **6** as a green solid (16 mg, 2%). ^{1}H NMR ($CDCl_3$): δ = 8.67 (d, *J* = 4.40 Hz, 4 H, *meso*-thienyl), 8.80 (d, *J* = 4.67 Hz, 4 H, *meso*-thienyl), 9.06 (m, 4 H, *meso*-thienyl), 9.21 (d, *J* = 4.95 Hz, 2 H, β-pyrrole), 9.47 (br. s, 4 H, β-pyrrole), 9.59 (s, 2 H, β-furan) ppm. FAB-MS: $C_{36}H_{21}N_3OS_4$ calcd. av. mass 639.8, obsd. *m*/*z* = 640 [M^+]. $C_{36}H_{21}N_3OS_4$ (639.8): calcd. C 67.58, H 3.31, N 6.57, S 20.05; found C 67.52, H 3.29, N 6.54, S 20.12.

15,20-Bis(2-thienyl)-5,10-bis(*p*-tolyl)-21-oxaporphyrin (7): The diol **11** (200 mg, 0.684 mmol), *p*-toluenecarbaldehyde (164 mg, 1.368 mmol) and pyrrole (140 μL, 2.052 mmol) were dissolved in CH_2Cl_2 (70 mL) under argon in the presence of $BF_3{\cdot}OEt_2$ (30 μL of 2.5 M stock solution) followed by oxidation with DDQ (238 mg, 1.026 mmol) in air for an additional 1 h resulting in a mixture of two porphyrins. Chromatography of the mixture on silica gel using 3% CH_3OH/CH_2Cl_2 afforded the N_3O porphyrin **7** as a green solid (7 mg, 2%). ^{1}H NMR ($CDCl_3$): δ = 2.74 (s, 6 H, CH_3), 7.66 (m, 2 H, *meso*-thienyl), 7.69 (d, *J* = 7.33 Hz, 4 H, ArH), 8.05 (d, *J* = 5.14 Hz, 2 H, *meso*-thienyl), 8.29 (m, 6 H, *meso*-thienyl and ArH), 8.43 (s, 2 H, β-pyrrole), 8.85 (m, 4 H, β-pyrrole), 9.62 (s, 2 H, β-furan) ppm. FAB-MS: $C_{42}H_{29}N_3OS_2$ calcd. av. mass 655.8, obsd. *m*/*z* = 656 [M^+]. $C_{42}H_{29}N_3OS_2$ (655.8): calcd. C 76.92, H 4.46, N 6.41, S 9.78; found C 76.90, H 4.41, N 6.39, S 9.80.

15,20-Bis(3-thienyl)-5,10-bis(*p*-tolyl)-21-oxaporphyrin (8): The furandiol **12** (400 mg, 1.369 mmol), *p*-toluenecarbaldehyde (330 mg, 2.738 mmol) and pyrrole (290 μL, 4.107 mmol) were dissolved in CH_2Cl_2 (140 mL) under argon in the presence of $BF_3{\cdot}OEt_2$ (60 μL of 2.5 M stock solution) and the mixture was then oxidized in air with DDQ (465 mg, 2.053 mmol). Chromatography on silica gel using 3% CH_3OH/CH_2Cl_2 gave the desired porphyrin **8** as a brown solid (14 mg, 2%). ^{1}H NMR ($CDCl_3$): δ = 2.69 (s, 6 H, CH_3), 7.55 (d, *J* = 7.69 Hz, 4 H, ArH), 7.73 (m, 2 H, *meso*-thienyl), 7.95 (d, *J* = 4.40 Hz, 2 H, *meso*-thienyl), 8.05 (m, 6 H, *meso*-thienyl and ArH), 8.63 (s, 4 H, β-pyrrole), 8.86 (s, 2 H, β-pyrrole), 9.30 (s, 2 H, β-furan) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 22.0, 29.0, 112.60, 123.84, 127.53, 128.08, 128.61, 134.41, 134.62, 135.05, 137.59, 138.82, 139.45, 142.28, 154.63, 156.0, 156.98 ppm. FAB-MS: $C_{42}H_{29}N_3OS_2$ calcd. av. mass 655.8, obsd. *m*/*z* = 656 [M^+]. $C_{42}H_{29}N_3OS_2$ (655.8): calcd. C 76.92, H 4.46, N 6.41, S 9.78; found C 76.89, H 4.48, N 6.43, S 9.76.

X-ray Crystallography: CCDC-200918 (**1**) and -200919 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This research was supported by the Department of Atomic Energy (No. 2001/37/21/BRNS/797) and the Department of Science and Technology, Government of India, New Delhi. Mass spectra were obtained at CDRI, Lucknow and NMR spectra were obtained at RSIC, IIT-Bombay.

[1] [1a] L. Latos-Grazynski, in *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, vol. 2, pp. 361−416, and references cited therein. [1b] M. Ravikanth, T. K. Chandrashekar, *Struc. Bonding* **1995**, *82*, 105.

[2] [2a] L. Latos-Grazynski, J. Lisowski, M. M. Olmstead, A. L. Balch, *Inorg. Chem.* **1989**, *28*, 1183. [2b] L. Latos-Grazynski, J. Lisowski, M. M. Olmstead, A. Balch, *Inorg. Chem.* **1989**, *28*, 3328. [2c] P. Chmielewski, M. Grzeszczuk, L. Latos-Grazynski, J. Lisowski, *Inorg. Chem.* **1989**, *28*, 3546. [2d] L. Latos-Grazynski, E. Pacholska, P. J. Chmielewski, M. M. Olmstead, A. Balch, *Inorg. Chem.* **1996**, *35*, 566. [2e] L. Latos-Grazynski, E. Pacholska, P. J. Chmielewski, M. M. Olmstead, A. L. Balch, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2252. [2f] R. P. Pandian, T. K. Chandrashekar, *J. Chem. Soc., Dalton Trans.* **1993**, 119. [2g] L. Latos-Grazynski, M. M. Olmstead, A. L. Balch, *Chem. Eur. J.* **1997**, *3*, 268. [2h] Z. Gross, I. Saltsman, R. P. Pandian, C. M. Barzilay, *Tetrahedron Lett.* **1997**, *38*, 2383. [2i] B. Sridevi, S. J. Narayanan, A. Srinivasan, T. K. Chandrashekar, *J. Chem. Soc., Dalton Trans.* **1998**, 1979. [2j] B. Sridevi, S. J. Narayanan, A. Srinivasan, M. V. Reddy, T. K. Chandrashekar, *J. Porphyrins Phthalocyanines* **1998**, *2*, 69.

[3] [3a] M. S. Vollmer, F. Wurthner, F. Effenberger, P. Emele, D. U. Meyer, T. Stumpfig, H. Port, H. C. Wolf, *Chem. Eur. J.* **1998**, *4*, 260. [3b] N. Ono, H. Miyagawa, T. Ueta, T. Ogawa, H. Tani, *J. Chem. Soc., Perkin Trans. 1* **1998**, 1595. [3c] P. Bhavana, B. Varghese, P. Bhyrappa, *Acta Crystallogr., Sect. C* **2001**, *57*, 252. [3d] P. Bhyrappa, P. Bhavana, *Chem. Phys. Lett.* **2001**, *349*, 399. [3e] D.-F. Shi, R. T. Wheelhouse, *Tetrahedron Lett.* **2002**, *43*, 9341.

[4] H. Segawa, F.-P. Wu, N. Nakayama, S. Sagisaka, N. Higuchi, M. Fujitsuka, T. Shimidzu, *Synth. Met.* **1995**, *71*, 2151.

[5] I. Gupta, M. Ravikanth, *Tetrahedron Lett.* **2002**, *43*, 9453.

[6] G. R. Desiraju, T. Steiner, in *The Weak Hydrogen Bond*, Oxford Science Publications, Oxford, **1999**.

[7] A. Ulman, J. Manassen, *J. Am. Chem. Soc.* **1975**, *97*, 6540.

[8] Z. Gross, I. Saltsman, R. P. Pandian, C. M. Barzilay, *Tetrahedron Lett.* **1997**, *38*, 2383.

[9] J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearay, A. M. Marguerettaz, *J. Org. Chem.* **1987**, *52*, 827.

[10] [10a] D. Kumaresan, N. Agarwal, I. Gupta, M. Ravikanth, *Tetrahedron* **2002**, *58*, 5347. [10b] S. Santra, D. Kumaresan, N. Agarwal, M. Ravikanth, *Tetrahedron*, in press.

[11] L. Latos-Grazynski, J. Lisowski, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **1987**, *109*, 4428.

[12] [12a] R. P. Pandian, D. Reddy, N. Chidambaram, T. K. Chandrashekar, *Proc. Indian Acad. Sci.* **1999**, *102*, 307. [12b] R. P. Pandian, T. K. Chandrashekar, G. S. S. Saini, A. L. Verma, *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 677.

[13] B. Sridevi, S. J. Narayanan, A. Srinivasan, M. V. Reddy, T. K. Chandrashekar, *J. Porphyrins Phthalocyanines* **1998**, *2*, 69.

[14] L. Latos-Grazynski, J. Lisowski, L. Szterenberg, M. M. Olmstead, A. L. Balch, *J. Org. Chem.* **1991**, *56*, 4043.

Received April 12, 2003

