

The Synthesis and Crystal Structure of β-Substituted Thiaporphyrins with Novel Cyclic Substituents

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21,23-Dithiaporphyrins and 21-monothiaporphyrins with propane-1,3-diyldioxy and its derivatives at the β-thiophene carbons were synthesized and characterized. The cyclic substituents introduced at the β-thiophene carbons altered the electronic properties of the porphyrins. The X-ray structure for 2,3-bis(2,2-dibenzylpropane-1,3-diyldioxy) substituted 21-monothiaporphyrin showed a more planar structure compared to the saddle shaped structure reported for β-unsubstituted 21-monothiaporphyrins.

Porphyrins are a unique class of compounds with potential applications in all disciplines of science, including medicine.[1] The electronic properties of porphyrins can be tuned at will by introducing suitable substituents on the *meso*-aryls or at the β-positions. The substituents on the *meso*-aryl positions do not alter the electronic properties of the porphyrin ring significantly since they are not in the direct conjugation with the porphyrin macrocycle. However, the substituents at the β-pyrrole carbons are in direct conjugation with the porphyrin and hence influence the electronic properties drastically.[2] Both electron-withdrawing and electron-releasing substituents have been introduced at the β-pyrrole carbons of regular N_4 porphyrins and the effect of β-substituents on the electronic properties of porphyrins has been studied in detail.[3] The other way to alter the electronic properties of porphyrins is by substituting the inner pyrrolic 'N' with hetero atoms such as C, O, S, Se, and Te. This class of compounds are known as core modified porphyrins,[4] which can stabilize metals in unusual oxidation states such as copper and nickel in the +1 oxidation state.[4] In spite of their novel physico-chemical properties, the reports on new derivatives of this unique class of compounds are scarce. Recently, we synthesized 21,23-dithiaporphyrins having long linear alkoxy groups at the β-thiophene carbons to study their liquid crystalline properties.[5] In continuation of our efforts to synthesize new derivatives of core-modified porphyrins to understand their potential for various applications in place of regular N_4 porphyrins, we report here the synthesis of 21,23-dithiaporphyrins **1–3** and 21-monothiaporphyrins **4–6** having cyclic propane-1,3-diyldioxy group(s) and its ethyl and benzyl derivatives at the β-thiophene carbons (Fig. 1). The electronic properties of the porphyrins were slightly altered due to the change in porphyrin π-delocalization caused by the β-substituents at the thiophene carbons.

Results and Discussion

3,4-Substituted Thiophenes and Thiophene Diols (7–12). The required thiophene precursors for thiophene diols, 3,4-(propane-1,3-diyldioxy)thiophene (**7**) and it's ethyl (**8**) and benzyl (**9**) derivatives, were synthesized[6] as shown in Scheme 1. By a standard transetherification reaction between 3,4-dimethoxythiophene and 1,3-propanediol or 2,2-disubstituted 1,3-propanediol, the thiophenes **7–9** were synthesized in 60–70% yields. The precursors, 1,3-propanediol, 2,2-diethyl-1,3-propanediol, and 2,2-dibenzyl-1,3-propanediol, were synthesized starting from diethyl malonate (Scheme 1). The thiophenes **7–9** were characterized by melting point, NMR, and elemental analysis. The unknown diols **10–12** were synthesized by following Ulman and Manassen's method[7] with some modifications (Scheme 2). The thiophenes were first reacted with *n*-BuLi in hexane in the presence of TMEDA followed by treatment with benzaldehyde in THF at 0 °C. The TLC analysis indicated the formation of the diol with a small amount of mono-ol. The diol was easily separated from the mono-ol by silica-gel column chromatography using a petroleum ether/ethyl acetate mixture to give diols **10**, **11**, and **12** as white solids in 17–30% yields. The thiophene diols **10–12** were characterized by melting point, NMR, mass spectrometry, IR, and elemental analysis.

21,23-Dithiaporphyrins with Cyclic Substituents at β-Thiophene Carbons (1–3). The 21,23-dithiaporphyrins **1–3** were synthesized by condensing one equivalent of the appropriate diol, **10–12**, with one equivalent of pyrrole in dichloromethane in the presence of $Et_2O{\cdot}BF_3$ followed by oxidation with DDQ at room temperature (Scheme 3). The crude 21,23-dithiaporphyrins were purified by silica-gel column chromatography using dichloromethane as an eluent. The crystalline purple compounds **1–3** were obtained in 8–12% yields. The porphyrins were characterized by spectroscopic methods.

The ^{1}H NMR spectrum of **3** recorded in $CDCl_3$ is shown in Fig. 2(a). The comparison of the NMR spectra of **1–3** with β-thiophene unsubstituted 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (S_2TPP),[4] indicated that the ring current was greatly altered due to the substituents at the β-thiophene carbons. The β-thiophene protons, which generally appear as a singlet at $\delta =$

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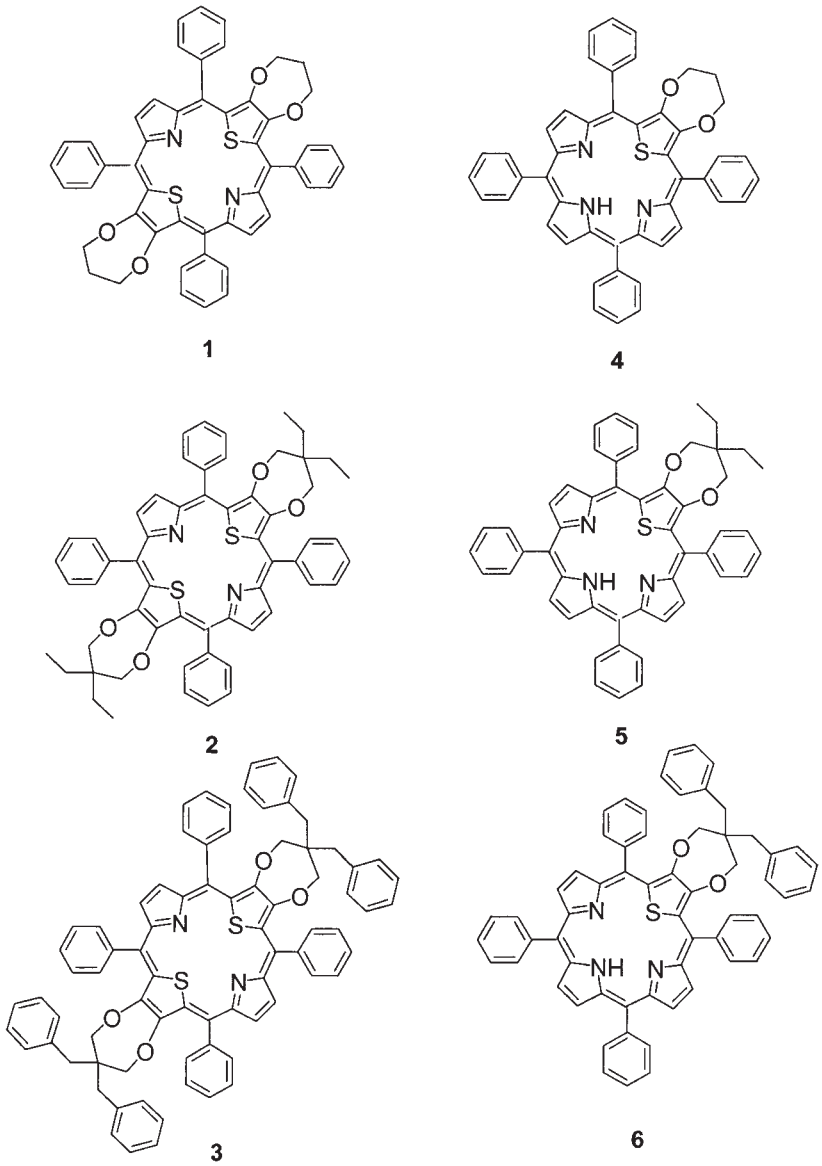
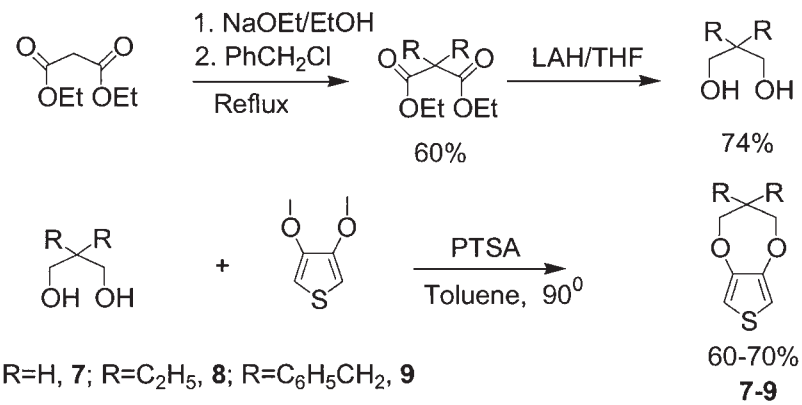
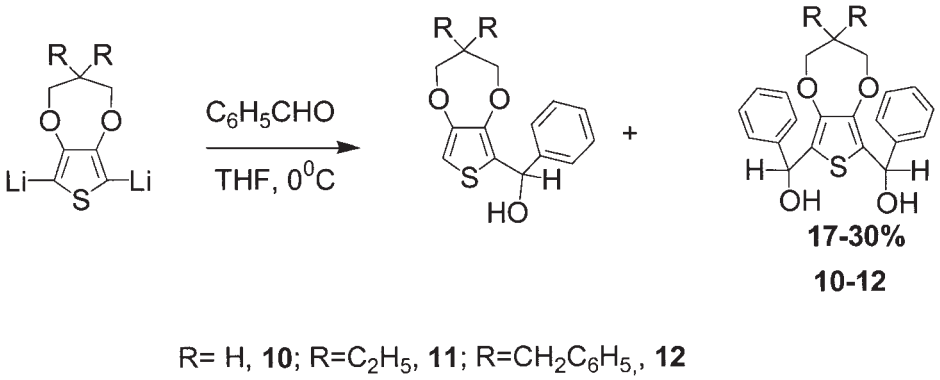


Fig. 1. Structures of β-thiophene substituted thiaporphyrins **1**–**6**.



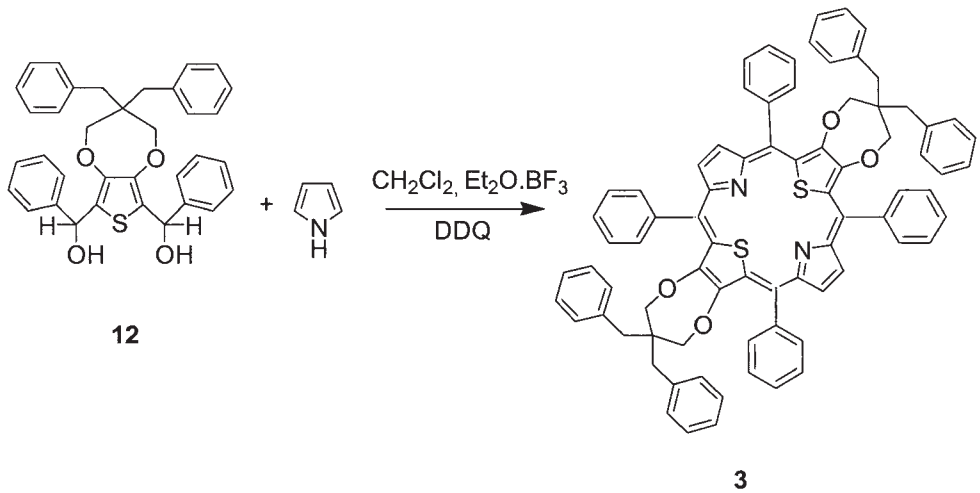
Scheme 1. Synthetic scheme for 3,4-propane-1,3-diyldioxy substituted thiophenes and its derivatives **7**–**9**.

9.679 in S_2TPP were absent in **1**–**3** due to the introduction of the cyclic propane-1,3-diyldioxy groups at the β-thiophene carbons. The β-pyrrole protons appeared as one singlet, indicating a symmetric nature in the dithiaporphyrins **1**–**3**. However, the β-pyrrole protons in **1**–**3** experienced an upfield shift of ~0.26 ppm compared to S_2TPP, which was attributed to the



R= H, **10**; R=C_2H_5, **11**; R=$CH_2C_6H_5$, **12**

Scheme 2. Synthesis of thiophenediols **10**–**12**.



Scheme 3. Synthesis of 21,23-dithiaporphyrin **3**.

change in ring current caused by the propane-1,3-diyldioxy substituents at the β-thiophene carbons. The *meso* phenyl protons also experienced similar upfield shifts compared with S_2TPP. The analytical and mass spectral data were in agreement with the proposed composition of **1**–**3**. The comparison of the absorption spectra of **3** along with S_2TPP recorded in toluene is shown in Fig. 3. Both Q-bands and the Soret band of **1**–**3** were exhibited 10–15 nm bathochromic shifts compared with S_2TPP. The emission bands of **1**–**3** also experienced a similar magnitude of red shifts (Fig. 3 inset).

The protonation of pyrrole nitrogen by the addition of 1% trifluoroacetic acid to porphyrins **1**–**3** in toluene resulted in red shifts of the Soret and Q-bands. The magnitude of the red shift and the number of absorption bands on protonation of **1**–**3** was different from the protonation of S_2TPP[8] (Table 1). The emission bands of **1**–**3** were also experienced similar red shifts on protonation (Table 2).[9]

21-Monothiaporphyrins with Cyclic Substituents at the β-Thiophene Carbons (4–6). The β-substituted 21-monothiaporphyrins **4**–**6** were synthesized by condensing one equivalent of the corresponding diol **10**–**12**, with two equivalents of benzaldehyde and three equivalents of pyrrole in dichloromethane in the presence of $Et_2O{\cdot}BF_3$ at room temperature, followed by oxidation with DDQ (Scheme 4). Interestingly, this condensation resulted in the formation of a mixture of three porphyrins with different porphyrin cores:[10] N_4, N_3S, and N_2S_2. It is known that the absorption and emission peak maxima shift to red as the porphyrin core changes from N_4, to N_3S to N_2S_2. Thus, absorption and emission spectroscopy were used in identifying the required N_3S porphyrins. The 21-thiaporphyrins **4**–**6** were purified by silica-gel column chromatography and isolated in 7–9% yields.

The ^{1}H NMR spectrum of **6** is shown in Fig. 2(b), and the data of the 21-thiaporphyrins **4**–**6** was compared with that of the β-thiophene unsubstituted 5,10,15,20-tetraphenyl-21-monothiaporphyrin, STPPH.[4] Unlike the 21,23-dithiaporphyrins **1**–**3**, which showed a singlet for both the pyrrole ring protons, the 21-monothiaporphyrins **4**–**6** showed one singlet for pyrrole (opposite thiophene) and one quartet for the two pyrrole ring protons (adjacent to thiophene) indicating the low symmetric nature of the 21-monothiaporphyrins. Furthermore, the pyrrole ring protons of **4**–**6** experienced an upfield shift compared with STPPH due to the alteration of the ring current caused by the propane-1,3-diyldioxy substituent at the β-thiophene carbons. The phenyl protons of **4**–**6** also experienced similar upfield shifts compared with STPPH. Mass and elemental analysis proved the proposed molecular composition of **4**–**6**. The absorption and emission bands of **4**–**6** were bathochromically shifted compared with STPPH (Tables 2 and 3). The addition of trifluoroacetic acid to **4**–**6** to form the dications of **4**–**6** in toluene resulted in large red shifts of both the absorption[8] and emission bands[9] compared with $STPPH_3^{2+}$.

Table 1. Absorption Data of β-Thiophene Substituted Porphyrins **1**–**6** Recorded in Toluene

Porphyrin	Soret band	Q-bands λ/nm (log ε)			
	λ/nm (log ε)	IV	III	II	I
S_2TPP	435 (5.40)	514 (4.41)	547 (3.84)	633 (3.34)	696 (3.65)
1	441 (4.58)	522 (4.05)	552 (sh)	644 (2.62)	709 (3.87)
1H_2^{2+}	471 (4.93)		735 (4.38)		
2	444 (4.82)	524 (4.04)	554 (3.23)	645 (2.97)	710 (3.57)
2H_2^{2+}	470 (5.80)		738 (4.22)		
3	443 (4.95)	522 (3.95)	553 (3.06)	643 (2.89)	708 (3.45)
3H_2^{2+}	472 (4.74)		737 (4.12)		
STPPH	429 (5.27)	513 (4.23)	547 (3.64)	618 (3.27)	675 (3.47)
4	430 (4.80)	514 (4.07)	547 (3.39)	618 (3.27)	679 (3.42)
4H_3^{2+}	459 (4.90)		703 (4.30)		
5	432 (5.27)	516 (4.36)	551 (3.41)	620 (3.43)	681 (3.78)
5H_3^{2+}	457 (5.27)		703 (4.70)		
6	432 (5.29)	515 (4.37)	550 (3.40)	619 (3.42)	680 (3.76)
6H_3^{2+}	458 (5.28)		704 (4.56)		

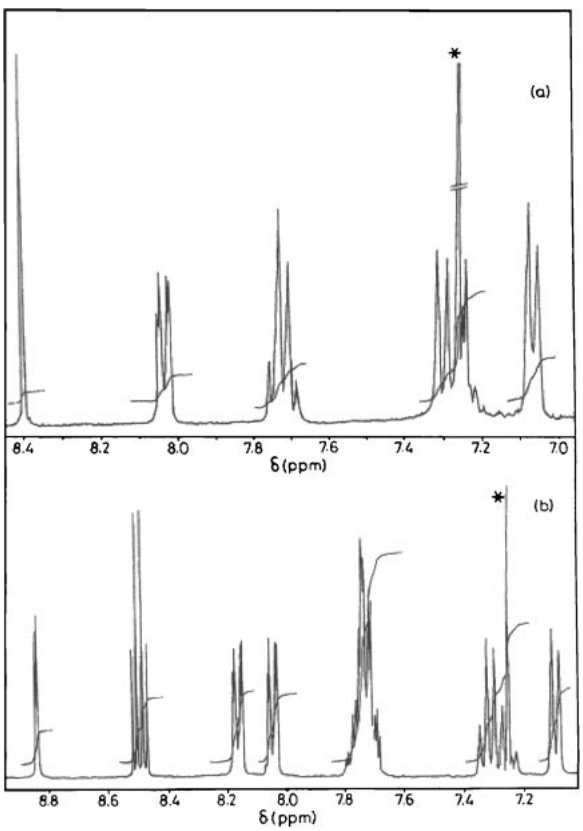


Fig. 2. ^{1}H NMR of (a) **3** and (b) **6** recorded in $CDCl_3$.

The structure of **6** was elucidated by a single crystal X-ray diffraction analysis (Fig. 4) (CCDC No. 207348). A disordered solvated toluene molecule was found in the unit cell of **6**. Comparing the structure of **6** with the reported β-unsubstituted N_3S porphyrin 5,20-diphenyl-10,15-bis(*p*-nitrophenyl)-21-thiaporphyrin[4] (STPPH) suggested that **6** was more planar than the slightly saddle shaped STPPH. This is best described by comparing the dihedral angle of **6** with STPPH. The dihedral angles

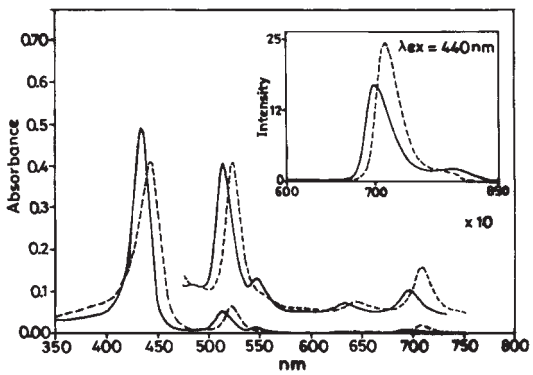
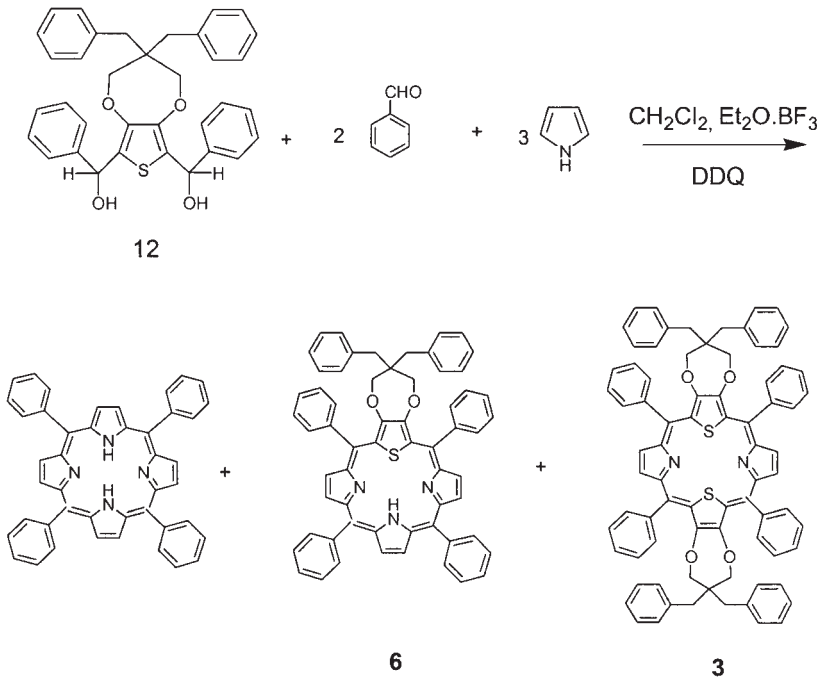


Fig. 3. Absorption and emission (inset) spectra, recorded in toluene, for S_2TPP (———) and **3** (- - - -).

Table 2. Fluorescence Data of β-Thiophene Substituted Porphyrins **1**–**6** in Toluene

Porphyrin	Q(0,0) λ_{max}/nm	Q(0,1) λ_{max}/nm	ϕ_f[a)]
S_2TPP	706	781	0.0076
1	712	787	0.0019
1H_2^{2+}	683	—	$<10^{-4}$
2	716	792	0.0214
2H_2^{2+}	657	764	$<10^{-5}$
3	713	790	0.0178
3H_2^{2+}	780	—	$<10^{-5}$
STPPH	678	760	0.0168
4	684	—	0.0048
4H_3^{2+}	683	—	$<10^{-4}$
5	685	757	0.0368
5H_3^{2+}	689	740	$<10^{-5}$
6	683	757	0.0399
6H_3^{2+}	—	745	$<10^{-5}$

a) The fluorescence quantum yields (ϕ_f) were estimated by taking 5,10,15,20-tetraphenylporphyrin as the standard ($\phi_{H_2TPP} = 0.11$).



Scheme 4. Synthesis of 21-thiaporphyrin **6**.

Table 3. Selected Bond Distances (Å) of Porphyrin **6** and STPPH

	STPPH	**6**
Pyrrole		
N···C_α	1.369(6)	1.392(5)
C_α···C_β	1.445(6)	1.433(6)
C_β···C_β	1.347(5)	1.345(6)
Thiophene		
S···C_α	1.740(4)	1.760(4)
C_α···C_β	1.421(4)	1.424(5)
C_β···C_β	1.365(7)	1.388(6)
Non-bonded distances		
N1···N3	4.40(1)	4.401
S···N2	3.547(8)	3.562

Table 4. Intramolecular Hydrogen Bonding Data for Porphyrin **6**

	H-bonded distances/Å	Bond angles/°
N2–H2A···S1	3.562(4)	175.00
N2–H2A···N1	2.985(6)	118.00
N2–H2A···N3	2.983(5)	118.00

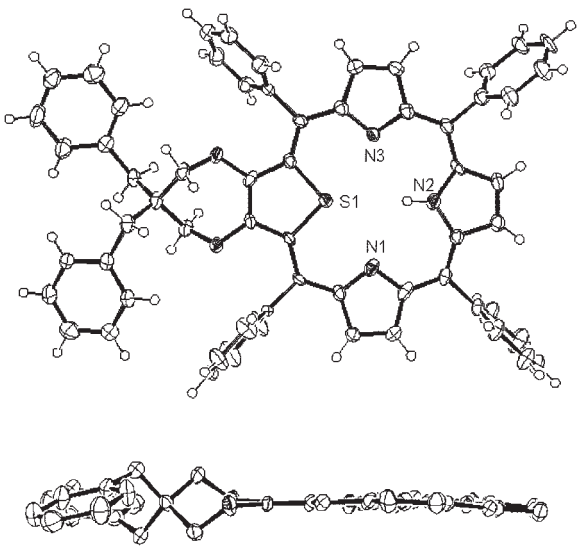


Fig. 4. ORTEP drawing for **6** (top, plane view; bottom, side view). Crystal data: $C_{64.5}H_{49}N_3O_2S$, purple needles, triclinic, space group = $P1$, $a = 9.6630(11)$, $b = 14.6111(16)$, $c = 18.876(2)$ Å, $V = 2438.1(5)$ Å^3, $Z = 2$, density = 1.2667 g/cm^3, $T = 293(2)$ K, $F(000) = 978$, $R = 0.0691$, $wR2 = 0.2417$.

between the plane of the *meso* carbon atoms and the four five-membered rings of **6** and STPPH respectively are: thiophene, 2.6° and 14.1°; pyrrole N(1), −4.9° and −11.5°; N(2), 5.6° and 10.0°; N(3), 0° and −7.4°. The hydrogen atom bond to N(2) was located and refined. The non-bonded N(1)–N(3) distance in **6** is almost the same as that of STPPH, but the non-bonded S–N(2) distance in **6** is slightly lower compared with STPPH (Table 3). The C_α–X, C_α–C_β, and C_β–C_β bond lengths of both the pyrrole and thiophene rings of **6** were slightly altered compared with STPPH indicating that the π-delocalization was altered in the porphyrin macrocycle due to the presence of the substituent at the β-thiophene carbons. Unlike some other N_3S porphyrins, in which we observed both inter and intra molecular hydrogen bonding,[11] only intramolecular hydrogen bonding (Table 4) was observed for **6**, as evident from the packing diagram of **6** presented in Fig. 5.

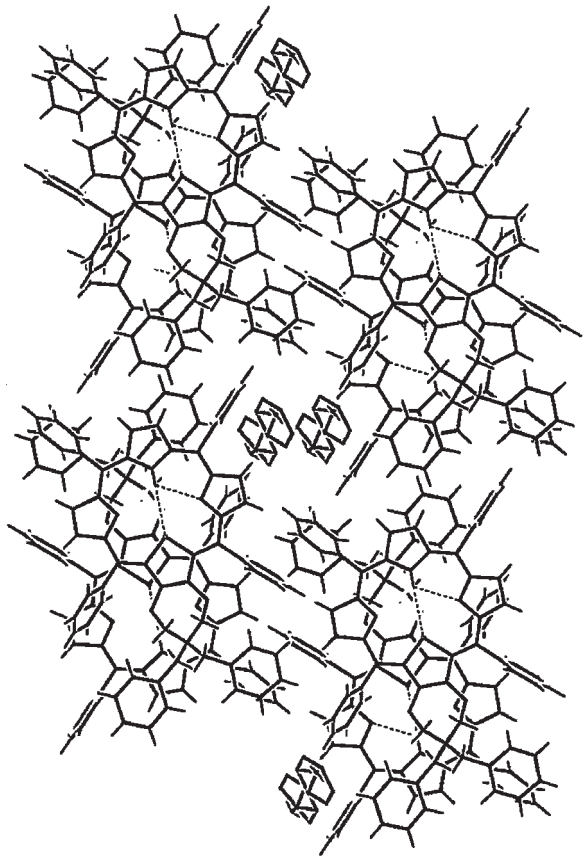


Fig. 5. Packing diagram of porphyrin **6**. (Dotted line shows the intramolecular hydrogen bonding inside the porphyrin core.)

Conclusions

In conclusion, we synthesized and characterized a series of 21,23-dithia- and 21-monothiaporphyrins with cyclic propane-1,3-diyldioxy groups at the β-thiophene carbons. The cyclic substituents at the β-thiophene carbons slightly alter the π-conjugation of the porphyrin macrocycle, as reflected in the spectral shifts. The moderate changes in the spectral properties of the porphyrins were due to the flexible nature of the cyclic substituents at the β-thiophene carbons. The X-ray structure for the dibenzyl derivative of propane-1,3-diyldioxy substituted 21-monothiaporphyrin (**6**) indicated that it is more planar compared with the β-unsubstituted N_3S porphyrin, STPPH.[4] A detailed metallation, and electrochemical and photophysical studies of these compounds are in progress in our laboratory.

Experimental

General. ^{1}H NMR spectra were recorded on a Varian 300 MHz using tetramethylsilane as an internal standard. Chemical shifts were reported on the δ scale. Coupling constants (*J*) were reported in hertz (Hz). Absorption and emission spectra were obtained with a Perkin-Elmer Lambda-35 and Lambda-55, respectively. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon as the FAB gas. ESMS spectra were recorded on a Q-TOF Micromass using dichloromethane as a solvent. Toluene, tetrahydrofuran (THF), triethylamine, and N,N′N″N‴-tetramethylethylenediamine (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, thiophene, furan, and pyrrole were obtained from Lancaster. Column chromatography was performed using 60–120 mesh silica obtained from Sisco Research Laboratories, India.

3,4-(Propane-1,3-diyldioxy)thiophene 7. Toluene (100 mL) was added to a three necked 250 mL round bottom flask fitted with a refluxing condenser and argon inlet and outlet and stirred under argon for 10 min. 3,4-Dimethoxythiophene (2 g, 13.9 mmol) was added to it followed by 1,3-propanediol (1.37 g, 18.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid (238 mg, 1.39 mmol) and the reaction mixture was stirred for 30 h at 80 °C under an argon atmosphere. The excess solvent was removed using a rotary evaporator, and the crude compound was extracted with ethyl acetate. The organic layer was washed several times with water and dried on anhy. Na_2SO_4. The solvent was removed using a rotary evaporator, and the crude compound was purified by silica-gel column chromatography using petroleum ether/ethyl acetate (10:1) to afford thiophene **7** as a white crystalline solid in 69% yield. mp 76–78 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 6.45 (s, 2H), 4.05 (t, $J = 6.0$, 4H), 2.25 (q, 2H); Anal. Calcd for $C_7H_8O_2S$: C, 53.82; H, 5.16%. Found: C, 53.45; H, 5.82%.

3,4-(2,2-Diethyl-propane-1,3-diyldioxy)thiophene 8. Compound **8** was similarly prepared as described for **7** by refluxing 3,4-dimethoxythiophene with 2,2-diethyl-1,3-propanediol (1.2 g, 9.02 mmol) in toluene in the presence of a catalytic amount of *p*-toluenesulfonic acid (120 mg, 0.69 mmol) at 80 °C for 35 h followed by extraction with ethyl acetate. The crude compound was purified by silica-gel column chromatography using petroleum ether/ethyl acetate to afford compound **8** as a white solid in 60% yield. mp 45 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 6.48 (s, 2H), 3.73 (s, 4H), 1.02 (q, 4H), 0.91 (t, $J = 6.5$, 6H); Anal. Calcd for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60%. Found: C, 62.57; H, 7.90%.

3,4-(2,2-Dibenzyl-propane-1,3-diyldioxy)thiophene 9. Compound **9** was similarly prepared by refluxing 3,4-dimethoxythiophene (2 g, 13.9 mmol) with 2,2-dibenzyl-1,3-propanediol (4.6 g, 18.0 mmol) in toluene in the presence of *p*-toluenesulfonic acid (130 mg, 0.694 mmol) for 48 h at 80 °C. After extraction with ethyl acetate, the crude sticky compound was purified by silica-gel column using petroleum ether/5% ethyl acetate to afford **9** as a white solid in 67% yield (3.1 g). mp 176–178 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 7.20 (m, 10H), 6.50 (s, 2H), 3.80 (s, 4H), 2.90 (s, 4H); Anal. Calcd for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99%. Found: C, 74.85; H, 5.74%.

2,5-Bis(hydroxyphenylmethyl)-3,4-(propane-1,3-diyldioxy)-thiophene 10. A three necked 100 mL round bottom flask was dried thoroughly and flushed with argon for 15 min before charging with reagents. Dry hexane (10 mL) was added to the flask equipped with a gas inlet tube, a reflux condenser, and a rubber septum. A small amount of argon based positive pressure was maintained through out the reaction. TMEDA (0.635 mL, 4.2 mmol) and *n*-BuLi (3.5 mL of 1.6 M stock solution) were added to the stirred solution, followed by 3,4-(propane-1,3-diyldioxy)thiophene (312 mg, 2 mmol) followed by refluxing for 1 h. The reaction mixture changed slowly into a white curdy solution indicating the formation of the 2,5-dilithiated salt of 3,4-(propane-1,3-diyldioxy)thiophene. In another three necked 100 mL round bottom flask, benzaldehyde (0.45 mL, 4.43 mmol) was dissolved in 10 mL of dry THF and the solution was cooled in an ice bath under argon for 15 min. The 2,5-dilithiated thiophene suspension was added to benzaldehyde solution through a siphon apparatus over a period of 15 min. After the addition was completed, the reaction mixture was

brought to room temperature. Ice cold aqueous NH_4Cl was added with stirring to quench the reaction. The two liquid phases separated, and the water layer was washed thoroughly with additional water. All organic layers were combined, washed with water and saturated brine, and dried over anhy. Na_2SO_4. TLC analysis indicated the formation of the diol along with some of the mono-ol and unreacted aldehyde. The crude product was purified by silica-gel column chromatography using a petroleum ether/ethyl acetate mixture (3:1) to afford the diol **10** as a white solid (212 mg, 28% yield). mp 130–132 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 7.29–7.52 (m, 10H, phenyls), 5.71 (s, 2H, –CH), 3.70 (t, $J = 4.6$, 4H, $-OCH_2$), 2.04 (s, 2H, –OH), 1.94 (s, 2H, $-CH_2$); FAB-MS Calcd exact mass 368.4. Found 368 (M^+). Anal. Calcd for $C_{21}H_{20}O_4S$: C, 68.46; H, 5.47%. Found: C, 69.12, H, 5.54%.

3,4-(2,2-Diethylpropane-1,3-diyldioxy)-2,5-bis(hydroxyphenylmethyl)thiophene 11. Diol **11** was prepared by following the same procedure as mentioned for diol **10** using hexane (10 mL), TMEDA (0.46 mL, 3.06 mmol), *n*-BuLi (2.5 mL of 1.6 M solution) and 3,4-(2,2-diethylpropane-1,3-diyldioxy)thiophene (310 mg, 1.46 mmol) to prepare the 2,5-dilithiated suspension which was added to the solution of benzaldehyde (0.37 mL, 3.65 mmol) in 10 mL dry THF. The diol was purified by silica-gel column chromatography using petroleum ether/ethyl acetate (5:1) as the eluent. The diol was further recrystallized from toluene to afford diol **11** as a white flake solid in 30% yield (190 mg). mp 136–138 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 7.39–7.42 (m, 4H, *o*-phenyl), 7.25–7.34 (m, 6H, *m*,*p*-phenyls), 6.02 (d, $J = 3.66$, 2H, –CH), 3.85 (q, 4H, $-OCH_2$), 2.63 (d, $J = 3.62$, 2H, –OH), 1.48 (m, 4H, $-CH_2$), 0.88 (q, 6H, $-CH_3$); IR (cm^{-1}) 3341 (–OH); FAB-MS Calcd exact mass 424.5. Found 424 (M^+). Anal. Calcd for $C_{25}H_{28}O_4S$: C, 70.73; H, 6.65%. Found: 70.98; H, 6.51%.

3,4-(2,2-Dibenzylpropane-1,3-diyldioxy)-2,5-bis(hydroxyphenylmethyl)thiophene 12. The 2,5-dilithiated salt of 3,4-(2,2-dibenzylpropane-1,3-diyldioxy)thiophene was prepared by the addition of substituted thiophene (220 mg, 0.654 mmol) to the mixture of TMEDA (0.200 mL, 1.33 mmol) and *n*-BuLi (2 mL of ca. 1.6 M solution) in dry hexane. The dilithio salt of the thiophene was transferred to the ice cold solution of benzaldehyde (0.17 mL, 1.64 mmol) and stirred for 1 h. After standard work as mentioned for diol **10**, the crude diol was purified by silica-gel column chromatography using a 3:1 mixture of the petroleum ether/ethyl acetate. Recrystallization from toluene yielded the pure diol **12** as a white solid in 17% yield (130 mg). mp 139–142 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 7.10–7.37 (m, 20H, phenyls), 6.01 (s, 2H, –CH), 4.02 (s, 4H, $-OCH_2$), 2.82 (s, 4H, $-CH_2$), 2.69 (s, 2H, –OH); IR (cm^{-1}) 3437 (–OH); FAB-MS Calcd exact mass 548.6. Found 548 (M^+). Anal. Calcd for $C_{35}H_{32}O_4S$: C, 76.61; H, 5.87%. Found: C, 76.47; H, 5.91%.

***β*-2,3,12,13-Bis(propane-1,3-diyldioxy)-*meso*-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin 1.** Samples of diol **10** (100 mg, 0.274 mmol) and pyrrole (25 μL, 0.32 mmol) were dissolved in 25 mL CH_2Cl_2 in a one necked round bottom flask and purged with argon for 10 min. $Et_2O{\cdot}BF_3$ (20 μL of 2.5 M solution in CH_2Cl_2) was added to initiate the reaction, and the flask was shielded with aluminium wrapper to protect from light exposure. The reaction mixture was stirred at room temperature under argon for 1 h. The progress of the reaction was monitored by absorption spectroscopy by taking aliquots of the reaction mixture at regular intervals and oxidizing with DDQ in toluene. After 1 h, DDQ (45 mg, 0.200 mmol) was added, and the reaction mixture was stirred at room temperature in open air. Triethylamine was added to neutralize the reaction mixture. The solvent was removed using a rotary evaporator and the crude porphyrin was purified by silica-gel column chromatography using a petroleum ether/CH_2Cl_2 (3:7) mixture. The porphyrin, with small amounts of impurities, was subjected to another silica-gel column chromatography run with the same solvent mixture to afford the pure porphyrin **1** as a purple solid in 12% yield (27 mg). mp >300 °C, ^{1}H NMR ($CDCl_3$, δ in ppm) 8.43 (s, 4H, pyrrole), 8.12–8.24 (m, 8H, *o*-phenyl), 7.67–7.70 (m, 12H, *m*,*p*-phenyl), 4.05 (t, 8H, $-OCH_2$), 1.36 (s, 4H, $-CH_2$). FAB-MS Calcd exact mass 792.9. Found 793 (M^+). Anal. Calcd for $C_{50}H_{36}N_2O_4S_2$: C, 75.73; H, 4.58; N, 3.53%. Found: C, 75.98; H, 4.76; N, 3.22%.

***β*-2,3,12,13-Bis(2,2-diethylpropane-1,3-diyldioxy)-*meso*-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin 2.** Diol **11** (100 mg, 0.235 mmol) and pyrrole (20 μL, 0.300 mmol) were dissolved in 25 mL of CH_2Cl_2 and stirred under argon atmosphere for 10 min. $Et_2O{\cdot}BF_3$ (20 μL of 2.5 M solution in CH_2Cl_2) was added, and the reaction mixture was stirred for 1 h. DDQ (60 mg, 0.264 mmol) was added, and the reaction mixture was stirred at room temperature in open air for an additional 1 h. After neutralization of the reaction mixture with triethylamine, the crude compound was subjected to silica-gel column chromatography twice using a petroleum ether/CH_2Cl_2 (2:1) mixture, and the pure porphyrin **2** was obtained as a purple solid in 9.3% yield (20 mg). mp >300 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 8.40 (s, 4H, pyrrole), 8.03 (m, 8H, *o*-phenyl), 7.65 (m, 12H, *m*,*p*-phenyl), 3.98 (s, 8H, $-OCH_2$), 1.25 (s, 8H, $-CH_2$), 0.84 (t, 12H, $-CH_3$); FAB-MS Calcd exact mass 905.1. Found 905 (M^+). Anal. Calcd for $C_{58}H_{52}N_2O_4S_2$: C, 76.96; H, 5.79; N, 3.09%. Found: C, 77.09; H, 5.89; N, 3.12%.

***β*-2,3,12,13-Bis(2,2-dibenzylpropane-1,3-diyldioxy)-*meso*-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin 3.** A solution of diol **12** (140 mg, 0.255 mmol) and pyrrole (20 μL, 0.29 mmol) in 30 mL of CH_2Cl_2 was stirred under argon for 10 min. $Et_2O{\cdot}BF_3$ (10 μL of a 2.5 M stock solution in CH_2Cl_2) was added, and the reaction mixture was stirred under argon at room temperature. After 1 h, DDQ (58 mg, 0.255 mmol) was added, and the reaction mixture was stirred for an additional 1 h. The reaction mixture was neutralized with triethylamine, and the solvent was removed using a rotary evaporator. The crude compound was purified by silica-gel column chromatography using petroleum ether/CH_2Cl_2 (3:1) to afford the pure purple compound **3** in 8% yield (25 mg). mp >300 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 8.39 (s, 4H, pyrrole), 8.01 (m, 8H, *o*-phenyl), 7.72 (m, 12H, *m*,*p*-phenyl), 7.28–7.31 (m, 8H, *o*-outerphenyl), 7.05 (d, $J = 6.96$, 12H, *m*,*p*-outerphenyl), 3.98 (s, 8H, $-OCH_2$), 2.77 (s, 8H, $-CH_2$); FAB-MS Calcd exact mass 1153.4. Found 1154 (M^+). Anal. Calcd for $C_{78}H_{60}N_2O_4S_2$: C, 81.22; H, 5. 24; N, 2.43%. Found: C, 81.57; H, 5.69; N, 2.86%.

***β*-2,3-(Propane-1,3-diyldioxy)-*meso*-5,10,15,20-tetraphenyl-21-monothiaporphyrin 4.** In a 100 mL round bottom flask, a solution of diol **10** (200 mg, 0.55 mmol), benzaldehyde (120 μL, 1.20 mmol), and pyrrole (120 μL, 1.75 mmol) in 30 mL CH_2Cl_2 was stirred at room temperature under argon for 10 min. $Et_2O{\cdot}BF_3$ (20 μL of a 2.5 M stock solution in CH_2Cl_2) was added as a catalyst to initiate the condensation. The reaction flask was covered with aluminium wrapper to protect from light exposure. The reaction mixture was stirred at room temperature under argon atmosphere for 1 h. The color of the reaction mixture changed from a pale yellow solution to dark brown. Completion of the reaction was confirmed by recording absorption spectra at regular intervals and oxidizing with DDQ in toluene. DDQ (93 mg, 0.41 mmol) was added to oxidize the porphyrinogen to the porphyrin, and the reaction mixture was stirred for another 1 h at room temperature in open air. After completion of the reaction, the reaction mixture was neu-

tralized with triethylamine. The solvent was removed using a rotary evaporator, and TLC analysis of the crude compound showed the formation of the expected three porphyrins. The crude compound was loaded on a silica-gel column and eluted with a petroleum ether/CH_2Cl_2 mixture. The N_4 porphyrin moved as the first band followed by the desired N_3S porphyrin **4** collected with petroleum ether/CH_2Cl_2 (4:6). The solvent was removed to afford **4** as a purple solid in 8% yield (31 mg). mp >300 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 8.84 (s, 2H, pyrrole), 8.50 (q, 4H, pyrrole), 8.16 (d, $J = 6.22$, 4H, *o*-phenyl), 8.06 (d, $J = 3.66$, 4H, *o*-phenyl), 7.65–7.73 (m, 12H, *m*,*p*-phenyl), 4.15 (t, 6H, –OCH_2), −2.57 (s, 1H, –NH); ESMS Calcd exact mass 703.8. Found 704.2 (M^+). Anal. Calcd for $C_{47}H_{33}N_3O_2S$: C, 80.20; H, 4.73; N, 5.97%. Found: C, 79.95; H, 4.84; N, 6.05%.

β-2,3-Bis(2,2-diethylpropane-1,3-diyldioxy)-*meso*-5,10,15,20-tetraphenyl-21-monothiaporphyrin 5. Samples of diol **11** (100 mg, 0.235 mmol), benzaldehyde (50 μL, 0.471 mmol), and pyrrole (50 μL, 0.746 mmol) in 30 mL of CH_2Cl_2 were stirred under an argon at room temperature for 10 min. The reaction was initiated with a catalytic amount of $Et_2O{\cdot}BF_3$ (10 μL of 2.5 M solution in CH_2Cl_2) and stirred under an argon atmosphere for 1 h. DDQ (65 mg, 0.286 mmol) was added, and the reaction mixture was stirred for an additional 1 h. The crude porphyrin mixture was purified by silica-gel column chromatography, and the desired N_3S porphyrin **5** was collected as the second band with a petroleum ether/CH_2Cl_2 (6:4) mixture. The solvent was removed using a rotary evaporator, giving **5** as a purple solid in 9% yield (16 mg). mp >300 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 8.83 (s, 2H, pyrrole), 8.49 (q, $J = 4.02$, 4H, pyrrole), 8.16 (d, $J = 5.85$, 4H, *o*-phenyl), 8.04 (d, $J = 3.29$, 4H, *o*-phenyl), 7.64–7.66 (m, 12H, *m*,*p*-phenyl), 4.06 (s, 4H, –OCH_2), 1.25 (s, 4H, –CH_2), 0.87 (t, $J = 7.32$, 6H, –CH_3), −2.55 (s, 1H, –NH); FAB-MS Calcd exact mass 759.9. Found 759. Anal. Calcd for $C_{51}H_{41}N_3O_2S$: C, 80.60; H, 5.44; N, 5.53%. Found: C, 80.77; H, 5.53; N, 5.59%.

β-2,3-Bis(2,2-dibenzylpropane-1,3-diyldioxy)-*meso*-5,10,15,20-tetraphenyl-21-monothiaporphyrin 6. A solution of diol **12** (100 mg, 0.182 mmol), benzaldehyde (0.040 mL, 0.37 mmol), and pyrrole (0.040 mL, 0.55 mmol) in 25 mL of CH_2Cl_2 were stirred for 10 min at room temperature under argon atmosphere. $Et_2O{\cdot}BF_3$ (10 μL of 2.5 M solution in CH_2Cl_2) was added, and the reaction mixture was stirred for 1 h. DDQ (35 mg, 0.154 mmol) was added, and the reaction mixture was stirred in open air at room temperature for an additional 1 h. The crude porphyrin mixture of the three porphyrins were separated by silica-gel column chromatography, with the desired N_3S porphyrin **6** as the second band with petroleum ether/CH_2Cl_2 (7:3). The solvent was removed using a rotary evaporator to afford the purple compound **6** in 8% yield (12 mg). mp >300 °C; ^{1}H NMR ($CDCl_3$, δ in ppm) 8.83 (s, 2H, pyrrole), 8.49 (q, 4H, pyrrole), 8.15 (d, $J = 5.80$, 4H, *o*-phenyl), 8.04 (d, $J = 6.22$, 4H, *o*-phenyl), 7.71–7.76 (m, 12H, *m*,*p*-phenyl), 7.30–7.34 (m, 6H, *m*,*p*-outerphenyl), 7.10 (d, $J = 6.59$, 4H, *o*-outerphenyl), 4.07 (s, 4H, –OCH_2), 2.80 (s, 8H, –CH_2), −2.59 (s, 1H, –NH); ^{13}C NMR 44.9, 39.4, 124.0, 126.6, 126.3, 127.0, 127.8, 128.2, 132.0, 132.5, 132.9, 134.3, 134.9, 136.6, 138.6, 142.4, 152.5, 158.4; FAB-MS: Calcd exact mass 884.10. Found 884 (M^+). Anal. Calcd for $C_{61}H_{45}N_3O_2S$: C, 82.87; H, 5.13; N, 4.75%. Found: C, 82.96; H, 5.23; N, 4.87%.

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