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Synthesis of β-pyrrole and β-thiophene substituted 21,23-dithia and 21-monothiaporphyrins

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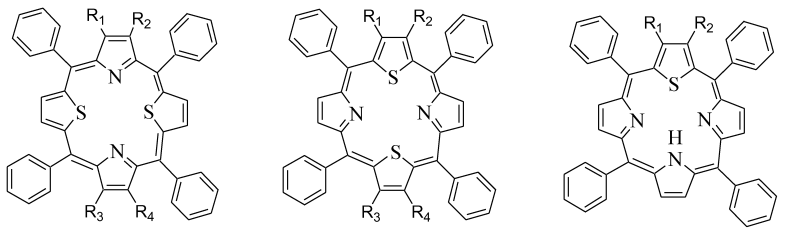
Abstract—A series of β-pyrrole and β-thiophene substituted porphyrins with N_2S_2 and N_3S porphyrin cores were synthesized and characterized. The introduction of substituents at β-pyrrole and β-thiophene carbons resulted in significant shifts in ^{1}H NMR, absorption and fluorescence maxima. These effects were attributed to alteration of the porphyrin ring current caused by substituents at β-positions.

1. Introduction

Porphines have two potential positions: *meso*- and β-positions at which substituents can be introduced. The electronic properties of porphyrins can be tuned at will by introducing suitable substituents at *meso*- or at β-positions. Generally, most of the porphyrins synthesized possess aryl groups at *meso* positions because they can be synthesized easily and they are very stable to handle for various applications.[1] Further introduction of substituents on *meso*-aryl groups does not much alter the electronic properties of the porphyrin ring since the substituents are not in direct conjugation with the porphyrin macrocycle. However, the introduction of substituents at the β-positions alters the electronic properties tremendously since these substituents are in direct conjugation with the porphyrin ring.[2] There are several reports on β-substituted porphyrins with an N_4 core. Both electron withdrawing and electron releasing substituents has been introduced and detailed spectral and electrochemical properties investigated.[3] Porphyrins bearing electron withdrawing substituents such as $-$Br, $-NO_2$ at β-pyrrole carbons have considerable potential as catalysts for epoxidation of alkenes and hydroxylation of alkanes.[4] Although there is extensive literature on β-substitution of porphyrins with an N_4 core, except a couple of reports by us,[5] there is no other report on β-substituted core modified porphyrins. The core-modified porphyrins resulting from the replacement of pyrrole with heterocycles such as thiophene, furan, selenophene and tellurophene have received less attention in spite of their novel properties such as stabilization of metals in unusual oxidation states.[6] We have been interested in the synthesis and the chemistry of new core-modified porphyrins for use in bioorganic and materials chemistry applications[7] and in this paper we



R_1, R_2, R_3, R_4 = Br : **1**

R_1, R_2, R_3, R_4 = Ph : **2**

R_1, R_3 = Ph; R_2, R_4 = NO_2 : **3**

R_1, R_3 = CH_3; R_2, R_4 = H : **4**

R_1, R_2, R_3, R_4 = CH_3 : **5**

R_1, R_3 = Ph; R_2, R_4 = H : **6**

R_1, R_2, R_3, R_4 = Ph : **7**

R_1 = CH_3, R_2 = H : **8**

R_1, R_2 = CH_3 : **9**

R_1 = Ph, R_2 = H : **10**

R_1, R_2 = Ph : **11**

Chart 1.

Keywords: β-Substituted porphyrins; Core-modified porphyrins; Bathochromic shifts; Non-planarity.
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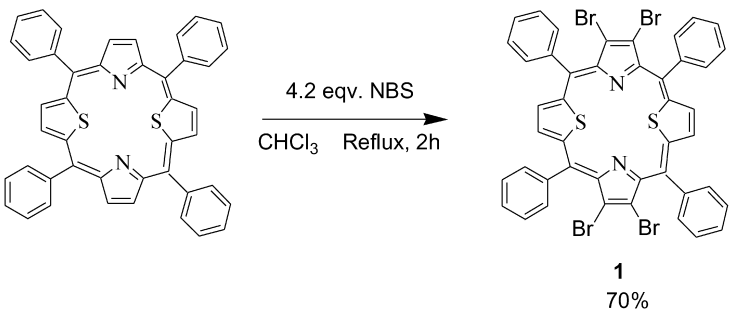


Scheme 1. Synthetic scheme for β-pyrrole substituted 21,23-dithiaporphyrin **1**.

report the synthesis and characterization of a series of β-substituted thiaporphyrins with N_2S_2 and N_3S porphyrin cores. The thiaporphyrins have two types of β-positions: β-pyrroles and β-thiophenes at which the substituents can be introduced. We successfully synthesized β-substituted thiaporphyrins in which the substituents were introduced at β-pyrrole as well as β-thiophene carbons independently (Chart 1) and investigated the effect of substituents on the spectral properties of the porphyrins.

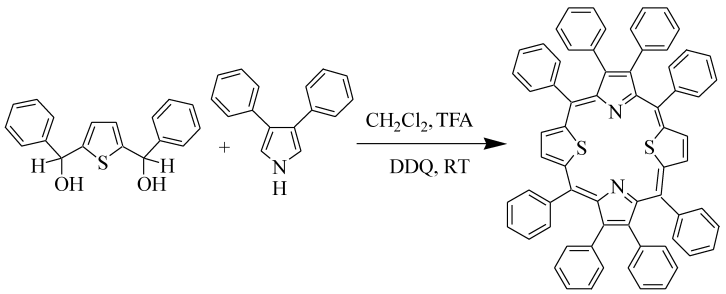
2. Results and discussion

2.1. β-Pyrrole substituted 21,23-dithiaporphyrins

Our initial goals were to introduce bromines at β-pyrrole carbons and use them as synthons for the synthesis of other β-substituted dithiaporphyrins via Suzuki coupling. Thus, we investigated the possibility of tetrabrominating the 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (S_2TPP). Treatment of S_2TPP with 4.2 equiv. of *N*-bromosuccinimide in chloroform gave (β-Br)$_4S_2$TPP, **1**, in 70% yield (Scheme 1). The tetrabrominated porphyrin, **1**, was purified by silica gel column using dichloromethane and characterized with ^{1}H NMR, mass, absorption and emission spectroscopies. The absence of the pyrrole signal in ^{1}H NMR indicated that the hydrogens were replaced by bromines at the β-positions of two pyrrole rings. The β-thiophene protons appeared as singlet indicating the symmetric nature of **1**. The thiophene protons in **1** experienced an upfield shift of 0.26 ppm compared to S_2TPP due to the change in ring current caused by the bromines at β-pyrrole carbons. The mass showed characteristic M^+ and $M-Br_n$ (n=1–4) peaks. The introduction of bromines at β-pyrrole carbons resulted in large red shifts and broadening of absorption bands (Table 1). This is because of the presence of bulky substituents at the β-pyrrole carbons which reduce the energy gap between HOMO and LUMO. The emission bands of **1** also experienced similar red shifts compared to S_2TPP. However, **1** was more weakly fluorescent than S_2TPP because of the presence of heavy halogens at the β-pyrrole carbons. To introduce aryl groups at β-pyrrole carbons, **1** was reacted with substituted phenyl boronic acids under Suzuki coupling conditions. This resulted in a complicated mixture of products and no attempts were made to separate and identify the products. We then diverted our attention to synthesize 3,4-disubstituted pyrroles for using them to synthesize β-substituted porphyrins. The 3,4-disubstituted pyrrole synthesis available in the literature is generally a multi-step process with low yields. However, Ono et al.[8] recently reported an easy and faster method of synthesizing 3,4-disubstituted pyrroles and then converting them to β-substituted porphyrins. Thus we prepared 3,4-diphenyl pyrrole following their method and condensed it with 2,5-bis(α-hydroxymethylphenyl)thiophene using $BF_3{\cdot}OEt_2$ in chloroform to obtain (β-Ph)$_4S_2$TPP, **2**, in 25% yield (Scheme 2). Ono et al.[8] reported that 3,4-diphenyl pyrrole was not reactive enough to form porphyrins with aromatic aldehydes. Hence they formylated and reduced it to the hydroxymethyl group and tetramerized it under acidic conditions to form porphyrins. However, in the present case the 3,4-diphenyl pyrrole reacted easily. The reactive functionality of 2,5-bis(hydroxymethyphenyl)thiophene[9] helped in the formation of **2** under normal porphyrin

Table 1. Absorption and emission data of porphyrins **1**–**11** along with S_2TPP and STPPH in toluene

Porphyrin	Soret band λ_{max} (nm) ($\varepsilon\times10^{-4}$)	Absorption Q-bands, λ_{max} (nm) ($\varepsilon\times10^{-4}$)				Fluorescence λ_{max} (λ_{ex}=440 nm)		
		IV	III	II	I	$Q_{(0,0)}$	$Q_{(0,1)}$	ϕ
S_2TPP	435 (25.0)	519 (2.60)	547 (0.70)	633 (0.22)	696 (0.45)	706	781	0.0076
1	440 (19.2)	521 (1.9)	—	633 (0.15)	698 (0.22)	740	—	$<10^{-4}$
2	440 (21.2)	519 (1.9)	—	637 (0.22)	700 (0.31)	735	—	0.0009
3	449 (18.1)	530 (1.70)	—	649 (0.18)	717 (0.23)	802	—	$<10^{-4}$
4	438 (17.5)	520 (2.07)	—	637 (0.13)	701 (0.32)	706	—	0.0015
5	446 (16.9)	527 (1.80)	—	646 (0.25)	714 (0.31)	744	—	0.0005
6	444 (13.0)	524 (1.37)	—	640 (0.13)	707 (0.21)	722	—	0.0020
7	454 (2.90)	524 (0.69)	—	654 (0.17)	715 (0.12)	736	—	0.0003
STPPH	429 (18.7)	513 (1.71)	547 (0.44)	618 (0.19)	678 (0.30)	678	760	0.0168
8	428 (23.7)	513 (2.07)	546 (sh)	614 (0.32)	674 (0.34)	682	—	0.0044
9	430 (15.9)	516 (1.43)	550 (sh)	618 (0.21)	678 (0.41)	693	—	0.0025
10	433 (14.3)	517 (1.37)	549 (sh)	619 (0.17)	680 (0.19)	688	—	0.0036
11	433 (17.2)	517 (2.65)	549 (sh)	619 (0.46)	679 (0.42)	693	—	0.0014



Scheme 2. Synthetic scheme for β-pyrrole substituted 21,23-dithiaporphyrin **2**.

forming conditions. The porphyrin **2** was characterized by ^{1}H NMR, mass, absorption and emission spectroscopies. In ^{1}H NMR, the pyrrole protons were absent as expected. The thiophene protons were also upfield shifted by 0.44 ppm compared to S_2TPP.[6] The product was further confirmed by the presence of the molecular ion peak in the mass spectrum. The absorption (Fig. 1) and emission bands (Fig. 2) were broadened and also red shifted compared to S_2TPP[6] (Table

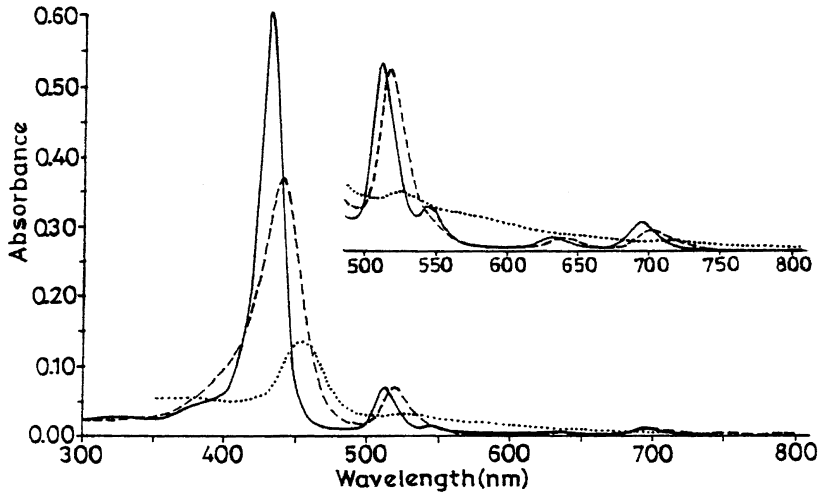


Figure 1. UV–visible spectra S_2TPP (—), **2** (- - -) and **7** (···) recorded in toluene.

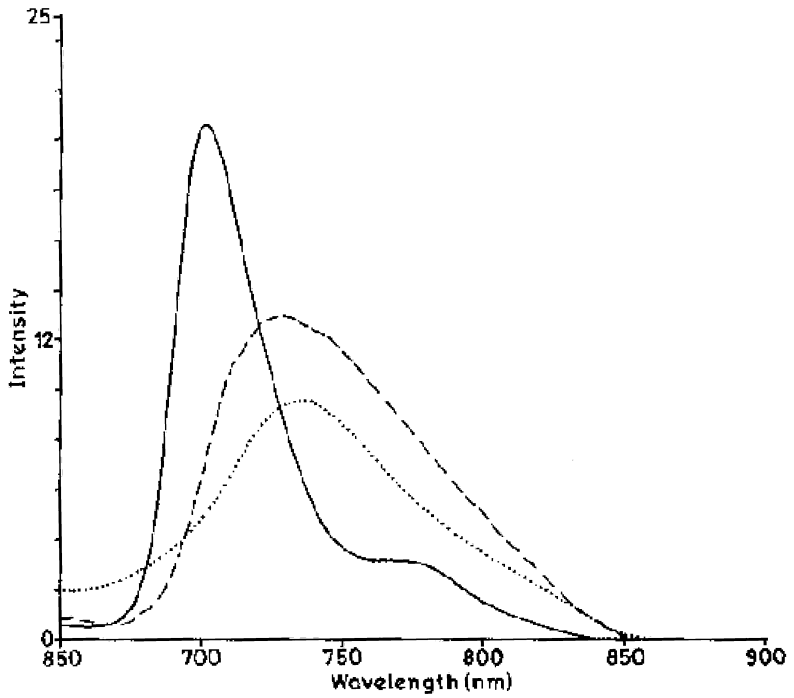
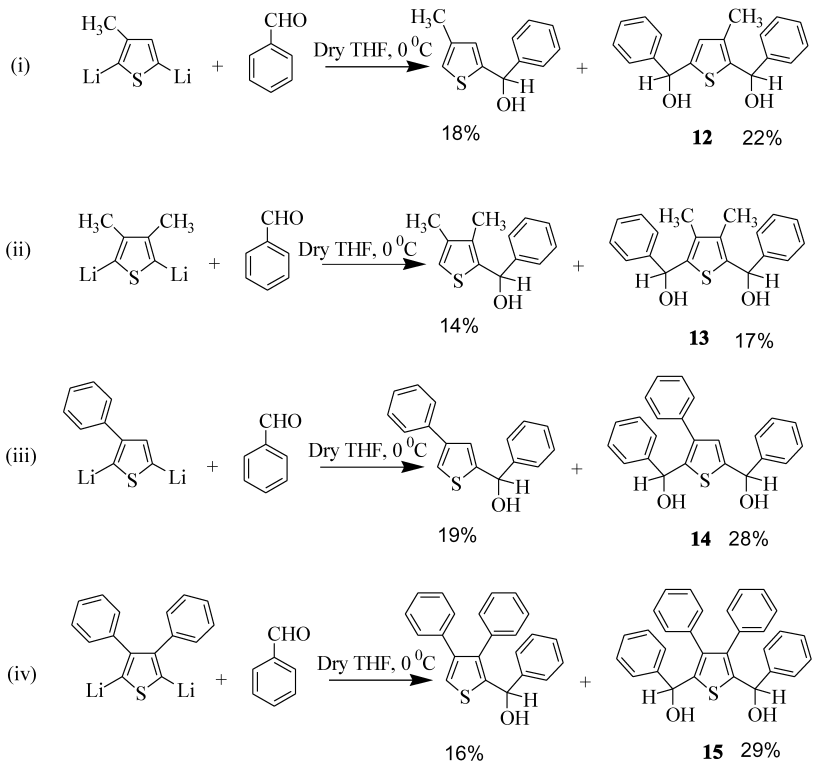


Figure 2. Fluorescence spectra of S_2TPP (—), **2** (- - -) and **7** (···) recorded in toluene at λ_{ex}=440 nm.

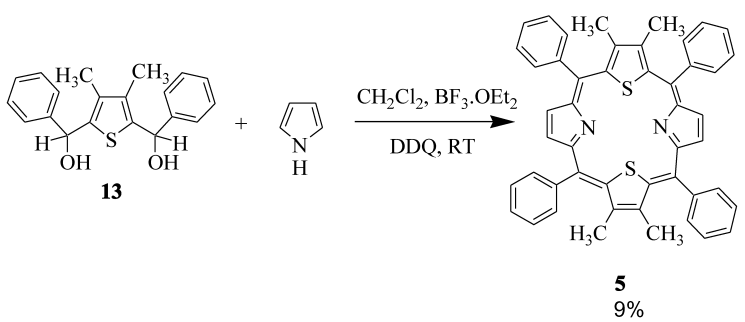


Scheme 3. Synthetic scheme for diols **12**, **13**, **14** and **15**.

1) indicating that the phenyl substituents at β-pyrrole carbons alter the energy levels. The molar absorption coefficients and fluorescence yields of **1** and **2** were reduced compared to S_2TPP. Similarly we prepared 3-phenyl-4-nitropyrrole following Ono's method[8] and condensed it with 2,5-bis(α-hydroxymethylphenyl) thiophene in the presence of $BF_3{\cdot}OEt_2$ in chloroform to obtain (β-Ph)(β-NO_2)S_2TPP, **3**, in 4.8% yield. The crude porphyrin **3** was purified by silica gel column chromatography using dichloromethane as an eluent. The ^{1}H NMR spectrum of **3** varied with the concentration since porphyrins with electron withdrawing substituents have a high tendency to aggregate. The mass spectrum showed an M^+ ion peak, hence confirming the product. The absorption and emission bands of **3** were broader and also red shifted with lower absorption coefficients and quantum yields than **1** and **2**.

2.2. β-Thiophene substituted 21,23-dithiaporphyrins

The substituents at the β-pyrrole carbons altered the porphyrin ring current which was reflected in the observed spectral properties. However, there is no report to understand the effect of substituents on ring current if the substituents are present at β-thiophene carbons instead of β-pyrrole carbons. Our preliminary study[5c] indicated that the substituents at β-thiophene carbons alter the porphyrin ring more effectively when compared to the same substituents at the β-pyrrole carbons. Thus we synthesized N_2S_2 porphyrins **4** and **5** containing two and four methyl groups, respectively, at the β-thiophene carbons. The required thiophene precursors, 3-methyl thiophene and 3,4-dimethyl thiophene were synthesized following known methodology.[10] The unknown diols **12** and **13** were synthesized as shown in Scheme 3 following Ulman and Manassen's method.[9] The 3-methyl or 3,4-dimethyl thiophene was first reacted with *n*-butyl lithium in *n*-hexane in the presence of TMEDA, followed by treatment with benzaldehyde in THF at 0 °C. The tlc analysis indicated the formation of diol **12** or **13** with small amounts of mono-ol and unreacted benzaldehyde. The diols **12** and **13** were purified by silica gel column chromatography using petroleum ether/ethyl acetate and to afford **12** as a semi-white solid in 22% and **13** as a



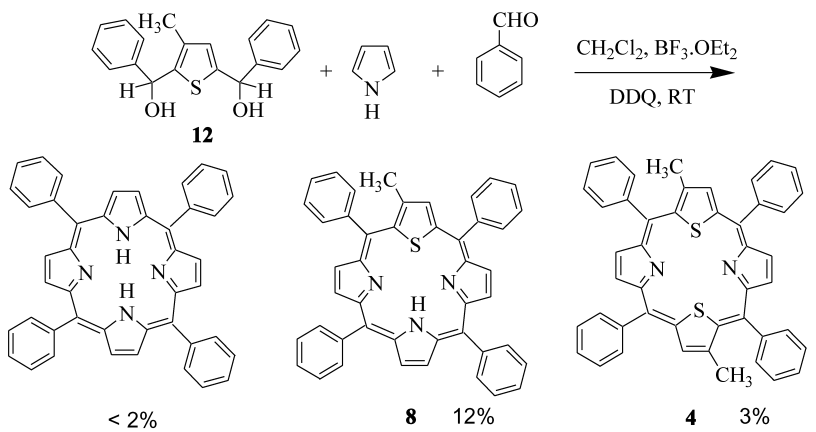
Scheme 4. Synthetic scheme for β-thiophene substituted 21,23-dithiaporphyrin **5**.

crystalline white solid in 17% yield. The N_2S_2 porphyrins **4** and **5** were synthesized by condensing the appropriate diol **12** and **13**, respectively, with pyrrole in CH_2Cl_2 in the presence of $BF_3{\cdot}OEt_2$ at room temperature, followed by oxidation with DDQ (Scheme 4). The crude porphyrins **4** and **5** were purified by silica gel column chromatography using petroleum ether/CH_2Cl_2 and the pure crystalline purple solids of porphyrins **4** and **5** were obtained in 8–9% yields. The porphyrins **4** and **5** were characterized by NMR, mass, absorption and fluorescence spectroscopies. The ^{1}H NMR spectrum of **4** in which one methyl group is present at the β-thiophene carbons showed a very interesting feature. The two thiophene protons, one on each thiophene of **4**, appeared as a singlet which was upfield shifted compared to S_2TPP.[6] Unlike in S_2TPP where pyrrole protons appear as a singlet, the pyrrole protons of **4** appeared as four separate signals: two doublets and two singlets indicating that the protons were not equivalent. The pyrrole protons of **4** were upfield shifted compared to S_2TPP. In porphyrin **5**, the thiophene protons disappeared due to the substitution of thiophene hydrogens by methyl groups. The pyrrole protons in **5** appeared as singlet and upfield shifted than pyrrole protons of S_2TPP. The absorption and emission bands of **4** and **5** were shifted bathochromically with low absorption coefficients and fluorescence yields compared to S_2TPP (Table 1). However, the magnitude of red shifts was larger for **5** than **4** due to the presence of more methyl groups at the β-thiophene carbons in **5** than in **4**.

The porphyrins with phenyl groups substituted at β-thiophene carbons **6** and **7** were synthesized using corresponding unknown diols **14** and **15**, respectively. The diols **14** and **15** were synthesized using 3-phenylthiophene and 3,4-diphenylthiophene, respectively, under identical *n*-butyl lithium conditions mentioned for diols **12** and **13** (Scheme 3). The diols **14** and **15** were purified by silica gel column chromatography and afforded as white solids in 28–29% yields. To prepare porphyrins **6** and **7**, 1 equiv. of diol **14** and **15**, respectively, was condensed with 1 equiv. of pyrrole under mild acidic conditions followed by oxidation with DDQ. The crude porphyrinic mixture was subjected twice to silica gel column chromatography to provide **6** in 4.8% and **7** in 2.3% yields as purple solids. The porphyrins **6** and **7** were confirmed by ^{1}H NMR and the molecular ion peak in mass spectra. In ^{1}H NMR, porphyrin **6** showed a singlet for thiophene protons which was upfield shifted by 0.11 ppm compared to S_2TPP. Porphyrin **7** did not show any thiophene signal as expected due to the presence of phenyl groups at β-thiophenes. The pyrrole protons in **6** appeared as three separate signals because of the unsymmetric substitution pattern whereas the pyrrole protons in **7** appeared as singlet, due to the symmetric substitution. Furthermore, the pyrrole protons in **7** experienced the maximum upfield shifts compared to any other β-substituted 21,23-dithiaporphyrin reported in this paper. This suggests that the four phenyl groups at β-thiophene carbons in **7** altered the porphyrin ring current more effectively compared to 21,23-dithiaporphyrins having four phenyl substituents at β-pyrrole carbons or any other β-substituted 21,23-dithiapophyrins. The absorption (Fig. 1) and emission bands (Fig. 2) of **7** also exhibited maximum red shifts (Table 1) and reduction in absorption coefficients and fluorescence yield.

2.3. β-Thiophene substituted 21-monothiaporphyrins

The thiophene diols **12** and **13** were also used to synthesize β-thiophene substituted 21-monothiaporphyrins **8** and **9**, respectively. The condensation of 1 equiv. of **12** with 2 equiv. of benzaldehyde and 3 equiv. of pyrrole gave a crude porphyrin mixture (Scheme 5). The tlc analysis showed the formation of three porphyrins: *meso*-5,10,15,20-tetraphenyl-β-2,12-dimethyl-21,23-dithiaporphyrin (N_2S_2 porphyrin **4**), the required *meso*-5,10,15,20-tetraphenyl-β-2-methyl-21-monothiaporphyrin (N_3S porphyrin **8**) and *meso*-5,10,15,20-tetraphenyl porphyrin (N_4 porphyrin). The mixture of three porphyrins was separated by silica gel column chromatography and the desired N_3S porphyrin **8** was collected as the second band using petroleum ether/CH_2Cl_2 in 12% yield. Similarly the condensation of 1 equiv. of diol **13** with 2 equiv. of benzaldehyde and 3 equiv. of pyrrole followed by column chromatography gave porphyrin **9** in 12% yield. Both porphyrins **8** and **9** were characterized by NMR, mass, absorption and fluorescence spectroscopic techniques. The thiophene proton of **8** in ^{1}H NMR appeared as a singlet and it was upfield shifted by 0.35 ppm compared to β-unsubstituted *meso*-5,10,15,20-tetraphenyl-21-monothiaporphyrin (STPPH).[6] The thiophene protons of **9** were absent as expected. The pyrrole protons of **8** and **9** appeared as five and three separate signals, respectively, and they were slightly upfield shifted compared to STPPH. The absorption spectra of porphyrins **8** and **9**



Scheme 5. Synthetic scheme for β-thiophene substituted 21- monothiaporphyrin **8**.

showed four Q-bands and one Soret band with negligible shifts in peak maxima compared to STPPH (Table 1).

Porphyrins **10** and **11** were synthesized similarly by condensing 1 equiv. of diol **14** and **15**, respectively, with 2 equiv. of benzaldehyde and 3 equiv. of pyrrole under porphyrin forming conditions. The crude porphyrins were subjected to silica gel column chromatography and pure porphyrins **10** and **11** were obtained in ~6% yields. In ^{1}H NMR, the thiophene proton appeared as singlet in **10** and it was absent in **11** due to substitution by phenyl groups. The pyrrole protons appeared as three signals in both **10** and **11** indicating the low symmetric nature of porphyrins. The absorption and emission peaks also experienced slight red shifts with a reduction in intensity compared to STPPH (Table 1).

3. Conclusions

In conclusion, we have prepared a series of β-pyrrole and β-thiophene substituted thiaporphyrins with N_2S_2 and N_3S porphyrin cores. The introduction of substituents at β-pyrrole and β-thiophene carbons alters the electronic properties of the porphyrins. The magnitude of the effect depends on the number of substituents. The substituents at β-positions of thiaporphyrins cause upfield shifts of thiophene and pyrrole protons in ^{1}H NMR, bathochromic shifts in absorption bands, and large red shifts with reduction in quantum yields of fluorescence bands compared to unsubstituted thiaporphyrin counterparts. We are presently investigating the metallation and electrochemical properties of these porphyrins.

4. Experimental

4.1. Data for compounds

4.1.1. *meso*-5,10,15,20-Tetraphenyl-β-7,8,17,18-tetrabromo-21,23-dithiaporphyrin (1). 5,10,15,20-Tetraphenyl-21,23-dithiaporphyrin (80 mg, 0.123 mmol) was dissolved in 20 ml of $CHCl_3$ in 100 ml one-necked round bottomed flask and 4.2 equiv. of freshly recrystallized *N*-bromosuccinimide (336 mg, 0.516 mmol) was added to it. The reaction mixture was refluxed for 2 h. The progress of the reaction was monitored with tlc and absorption spectroscopy. The solvent was removed on a rotary evaporator and the crude compound was purified by silica gel column chromatography using CH_2Cl_2 as eluent (74 mg, 70%). Mp >300 °C ^{1}H NMR ($CDCl_3$, δ in ppm) 7.80 (m, 12H, Ar), 8.06 (m, 8H, Ar), 9.39 (s, 4H, β-thiophene). ^{13}C NMR ($CDCl_3$, δ in ppm) 14.21, 29.45, 32.01, 113.03, 127.92, 133.62, 140.09, 149.30. LD-MS $C_{44}H_{24}N_2S_2Br_4$ calcd mass, 964.4. Obsd *m*/*z* 964.7 (M^+), 885.7 (M−1Br), 805.9 (M−2Br), 725.2 (M−3Br), 645 (M−4Br). Anal. calcd: C, 54.80; H, 2.51; N, 2.90. Found: C, 54.93; H, 2.42; N, 2.78. IR (neat, ν (cm^{-1})) 3276, 2934, 2861, 741.

4.1.2. *meso*-5,10,15,20-Tetraphenyl-β-7,8,17,18-tetraphenyl-21,23-dithia-porphyrin (2). 2,5-Bis(α-hydroxyphenylmethyl)thiophene (100 mg, 0.337 mmol) and 3,4-diphenylpyrrole (80 mg, 0.365 mmol) were dissolved in 25 ml CH_2Cl_2 in a 100 ml one-necked round bottomed flask fitted with an argon bubbler. Trifluoroacetic acid (96.3 μl) was added to initiate the condensation. The reaction mixture was stirred under argon at room temperature. The progress of the reaction was monitored using absorption spectroscopy. Aliquots of the reaction mixture were taken at regular intervals and oxidized with DDQ and the formation of the porphyrin was checked using absorption spectroscopy. The reaction was very slow and it took 10 h for completion. DDQ (100 mg, 0.440 mmol) was then added and the reaction mixture was stirred in air for 2 h. The solvent was removed under vacuum and the crude compound was dissolved in minimum amount of CH_2Cl_2 to prepare slurry powder by adding silica gel. The slurry was loaded on a silica gel column and eluted with CH_2Cl_2. The desired compound eluted very slowly and was collected and subjected to second silica gel column chromatography using CH_2Cl_2 as solvent to afford **2** in 25% yield. Mp >300 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) 6.90 (m, 8H, Ar), 7.06 (m, 4H, Ar), 7.21 (m, 8H, Ar), 7.52 (m, 8H, Ar), 7.71 (m, 8H, Ar), 7.80 (m, 4H, Ar), 9.23 (m, 4H, β-thiophene). LD-MS $C_{68}H_{44}N_2S_2$ calcd mass, 953.2. Obsd *m*/*z* 953.9 (M^+). Anal. calcd: C, 85.68; H, 4.65; N, 2.94. Found: C, 85.84; H, 4.56; N, 3.03. IR (KBr, ν (cm^{-1})) 3420, 3230, 2963, 741.

4.1.3. *meso*-5,10,15,20-Tetraphenyl-β-7,17-diphenyl-β-8,18-dinitro-21,23-dithia porphyrin (3). In a 500 ml one-necked round bottomed flask, 2,5-bis(hydroxyphenylmethyl) thiophene (500 mg, 1.687 mmol) and 2-nitro-3-phenylpyrrole (400 mg, 2.123 mmol) were dissolved in 250 ml $CHCl_3$ and argon was purged for 10 min. $BF_3{\cdot}OEt_2$ (660 ml of 2.5 M stock solution) was added and the reaction mixture was stirred for 1 h under argon at room temperature. The formation of porphyrin was confirmed with absorption spectroscopy by taking small amounts of reaction mixture and oxidizing with DDQ in toluene. DDQ (425 mg, 1.872 mmol) was added and the reaction mixture was stirred in air for 2 h. The solvent was removed on a rotary evaporator and the crude compound was purified twice by silica gel column chromatography using CH_2Cl_2 as solvent to afford a dark purple solid (35 mg, 4.6%). Mp >300 °C ^{1}H NMR ($CDCl_3$, δ in ppm) 7.10–7.30 (m, 30H, Ar), 7.50–7.70 (m, 4H, β-thiophene). LD-MS $C_{56}H_{34}N_4S_2O_4$ calcd mass 891.0, obsd *m*/*z* 892.7. Anal. calcd: C, 75.49; H, 3.85; N, 6.29. Found: C, 75.86; H, 3.79; N, 6.58; IR (KBr, ν (cm^{-1})) 3414, 2915, 1550, 741.

4.1.4. 2,5-Bis(hydroxymethylphenyl)-3-methylthiophene (12). In a 100 ml three-necked round bottomed flask fitted with a gas inlet tube, a reflux condenser and a rubber septum, dried and distilled *n*-hexane (10 ml) was placed. *N*,*N*′,*N*″,*N*‴-Tetramethylethylene diamine (TMEDA) (0.42 ml, 0.32 g, 2.76 mmol) and *n*-butyl lithium (4 ml of a 1.6 M solution in hexane) were injected into the stirred solution. 2-Methylthiophene (0.200 g, 2.04 mmol) was injected and the solution was refluxed gently for 1 h. In another three-necked 100 ml round bottomed flask fitted with gas inlet and outlet tube and septum, benzaldehyde (0.53 ml, 0.550 g, 5.20 mmol) was dissolved in 10 ml dry THF. The solution was cooled in an ice bath and nitrogen was bubbled for 15 min. The 2,5-dilithio-3-methylthiophene suspension from the first flask was added to

benzaldehyde solution in THF through siphon apparatus over a period of 10 min. After the addition was complete, the mixture was allowed to attain room temperature. An ice cold saturated NH_4Cl solution was added and the mixture was then extracted with ether (3×50 ml). The organic layers were combined, washed with brine and dried over anhydrous Na_2SO_4. The crude product obtained on evaporation of the solvent was subjected to silica gel column chromatography using petroleum ether/ethyl acetate mixture (4:1), which afforded the pure diol **12** as a semi-white solid (140 mg, 22%). Mp 125–127 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) 2.10 (s, 3H, CH_3), 2.42 (s, 2H, OH), 5.51 (s, 2H, CH), 7.18 (1H, thiophene) 7.32–7.51 (m, 10H, phenyl). ^{13}C NMR ($CDCl_3$, δ in ppm) 65.15, 70.70, 79.73, 126.81, 128.95, 139.59. ES-MS $C_{19}H_{18}O_2S$ calcd av. mass, 310.4. Obsd *m/z* 293.0 (M−OH). Anal calcd: C, 73.52; H, 5.84. Found: C, 73.97; H, 6.03. IR (KBr, ν (cm^{-1})) 3395 (OH), 2925, 1715, 1649, 1458, 1268, 1185, 1008, 750, 696, 530.

4.1.5. 2,5-Bis(hydroxymethylphenyl)-3,4-dimethylthiophene (13). 2,5-Dilithio-3,4-dimethyl thiophene was synthesized by lithiating 3,4-dimethyl thiophene (500 mg, 4.46 mmol) with *n*-butyl lithium (8.0 ml of 1.6 M solution in hexane) in dry hexane (25 ml) in the presence of TMEDA (1.6 ml, 1.24 g, 10.7 mmol) under similar reaction conditions as mentioned for compound **12**. The dilithiated salt of 3,4-dimethyl thiophene was then added to the solution of benzaldehyde (1.20 ml, 1.24 g, 11.6 mmol) in dry THF (25 ml) followed by similar work-up as mentioned for compound **12** gave crude diol **13**. Column chromatography on silica gel using petroleum ether/ethyl acetate mixture (4:1) and afforded pure diol **13** as a white solid (248 mg, 17%). Mp 141–143°C. ^{1}H NMR ($CDCl_3$, δ in ppm) 2.05 (s, 6H, $-CH_3$), 2.32 (s, 2H, −OH), 6.01 (s, 2H, −CH), 7.24–7.41 (m, 10H, phenyl). ^{13}C NMR ($CDCl_3$, δ in ppm) 13.11, 71.03, 126.35 127.71, 128.38, 134.32, 139.63, 142.68. FAB-MS $C_{20}H_{20}O_4S$ calcd av. mass, 324.4. Obsd *m/z* 324.0. Anal calcd: C, 74.04; H, 6.21. Found: C, 74.36; H, 6.53. IR (KBr, ν (cm^{-1})) 3293 (OH), 3062, 3027, 2915, 2860, 1493, 1452, 1198, 1080, 1007, 914, 852, 697, 582.

4.1.6. 2,5-Bis(hydroxymethylphenyl)-3-phenylthiophene (14). 2,5-Dilithio-3-phenyl thiophene was synthesized by stirring 3-phenyl thiophene (0.320 g, 2.00 mmol) with *n*-butyl lithium (4.0 ml of 1.6 M solution in hexane) in dry diethylether (15 ml) at room temperature. The dilithiated salt of 3-phenyl thiophene was added to the solution of benzaldehyde (0.460 ml, 0.439 g, 4.14 mmol) in dry THF (15 ml) followed by similar work-up as mentioned for compound **12** gave crude diol **14**. Column chromatography on silica gel using petroleum ether/ethyl acetate mixture (3:1) as eluent afforded pure **14** as a white solid (210 mg, 28%). Mp 128–130 °C ^{1}H NMR ($CDCl_3$, δ in ppm) 2.40 (s, 2H, −OH), 5.93 (d, *J*=7.2 Hz, 1H −CH), 6.04 (s, 1H, −CH), 6.75 (s, 1H, β-thiophene), 7.30–7.61 (m, 15H, phenyl). ^{13}C NMR ($CDCl_3$, δ in ppm) 19.60, 49.30, 59.52, 97.06, 128.05, 129.71, 129.97, 130.79, 131.53. ES-MS $C_{24}H_{20}O_2S$ calcd av. mass, 372.4. Obsd *m/z* 355.1 (M−OH). Anal calcd: C, 77.39; H, 5.41. Found: C, 77.52; H, 5.76. IR (KBr, ν (cm^{-1})) 3314 (OH), 3057, 3028, 2876, 1600, 1495, 1447, 1285, 1194, 1155, 1008, 847, 700, 533.

4.1.7. 2,5-Bis(hydroxymethylphenyl)-3,4-diphenylthiophene (15). 3,4-Diphenyl thiophene (0.236 g, 1.00 mmol) and *n*-butyl lithium (2 ml of a 1.6 M solution in hexane) were stirred in dry diethylether (10 ml) for 1 h at room temperature to get the dilithio salt of 3,4-diphenyl thiophene. The dilithiated salt of 3,4-diphenyl thiophene was added to the solution of benzaldehyde (0.230 ml, 0.243 g, 2.30 mmol) in 10 ml THF solution followed by similar work as mentioned for compound **12**. Column chromatography on silica gel using petroleum ether/ethyl acetate mixture (3:1) afforded pure **15** as a white solid (0.130 g, 29%). Mp 130–131 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) 2.32 (s, 2H, OH), 5.95 (s, 2H, CH), 7.04 (t, *J*=2.2 Hz, 4H, phenyl), 7.25–7.35 (m, 16H, phenyl). ^{13}C NMR ($CDCl_3$, δ in ppm) 70.80, 126.28, 127.04, 127.23, 127.73, 127.92, 128.38, 130.20, 135.48, 143.10. ES-MS $C_{30}H_{24}O_2S$ calcd av. mass, 448.5. Obsd *m/z* 449.0. Anal calcd: C, 80.33; H, 5.39. Found: C, 80.56; H, 5.44. IR (KBr, ν (cm^{-1})) 3348 (OH), 3060, 3028, 2920, 1602, 1492, 1449, 1274, 1133, 1010, 912, 768, 731, 700, 640.

4.1.8. *meso*-5,10,15,20-Tetraphenyl-β-2,12-dimethyl-21,23-dithiaporphyrin (4). A stream of argon was passed through dichloromethane (30 ml) in a 100 ml round-bottomed flask for 10 min. The diol **12** (0.100 g, 0.320 mmol) and pyrrole (25 μl, 0.360 mmol) were added and argon purging was continued for an additional 10 min. $BF_3{\cdot}OEt_2$ (20 μl of 2.5 M stock solution in CH_2Cl_2) was added and the reaction mixture was stirred for 1 h. The progress of the reaction was monitored by TLC and absorption spectroscopy. After 2 h stirring, DDQ (50 mg, 0.220 mmol) was added and the reaction was stirred in air for additional 1 h. The solvent was removed in vacuo and the crude compound was purified by silica column using petroleum ether/CH_2Cl_2 (3:7) mixture as eluent. The desired compound **4** was obtained as a purple solid (18 mg, 8.6%). Mp >300 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) 2.87 (s, 6H, CH_3), 7.72–7.80 (m, 12H, *m*,*p*-phenyl), 8.03–8.06 (m, 4H, *o*-phenyl), 8.20–8.22 (m, 4H, *o*-phenyl), 8.37 (s, 1H, β-pyrrole.), 8.44 (d, *J*=4.57 Hz, 1H, β-pyrrole), 8.56 (d, *J*=4.39 Hz, 1H, β-pyrrole), 8.63 (s, 1H, β-pyrrole), 9.40 (s, 2H, β-thiophene). ^{13}C NMR ($CDCl_3$, δ in ppm) 20.29, 29.78, 42.90, 127.71, 128.69, 133.42, 134.42, 134.38, 139.54. FAB-MS $C_{46}H_{32}N_2S_2$ calcd av. mass, 678.8. Obsd *m/z* 677.0. Anal. calcd: C, 81.62; H, 4.77; N, 4.14. Found: C, 81.91; H, 4.53; N, 3.89. IR (KBr, ν (cm^{-1})) 3396, 2922, 2857, 703.

4.1.9. *meso*-5,10,15,20-Tetraphenyl-β-2,3,12,13-tetramethyl-21,23-dithiaporphyrin (5). A solution of diol **13** (0.100 g, 0.306 mmol) and pyrrole (25 μl, 0.360 mmol) in 30 ml CH_2Cl_2 was treated with $BF_3{\cdot}OEt_2$ (10 μl of 2.5 M stock solution) under an argon atmosphere to initiate the condensation. After 1 h, DDQ (0.040 g, 0.176 mmol) was added and stirring was continued for an additional 1 h. Column chromatography on silica with petroleum ether/CH_2Cl_2 (3:7) gave solid purple colored porphyrin **5** (20 mg, 9%). Mp >300 °C ^{1}H NMR ($CDCl_3$, δ in ppm) 2.61 (s, 12H, CH_3), 7.74 (m, 12H, phenyl), 8.12 (m, 8H, phenyl), 8.26 (s, 4H, β-pyrrole). ^{13}C NMR ($CDCl_3$, δ in ppm) 18.44, 29.87, 32.10, 127.23, 127.35, 132.19, 133.75, 143.07, 144.67. ES-MS $C_{48}H_{36}N_2S_2$ calcd av. mass: 704.9. Obsd *m/z* 704.8. Anal. calcd: C, 81.78; H, 5.15; N, 3.97. Found: C, 81.42, H, 5.27, N, 3.95. IR (KBr, ν (cm^{-1})) 3435, 3059, 2929, 703.

4.1.10. *meso*-5,10,15,20-Tetraphenyl-β-2,12-diphenyl-21,23-dithiaporphyrin (6). In a 100 ml round bottomed flask, thiophene diol **14** (0.200 g, 0.534 mmol) and pyrrole (40 μl, 0.038 g, 0.56 mmol) were mixed in 50 ml CH_2Cl_2 under an argon atmosphere. $BF_3{\cdot}OEt_2$ (40 μl of 2.5 M stock solution) was added and the reaction was stirred for 1 h at room temperature. DDQ (90 mg, 0.396 mmol) was added and the reaction mixture was stirred in air for an additional 1 h. The solvent was removed on a rotary evaporator and the crude compound was purified twice using silica gel column chromatography with CH_2Cl_2 as solvent to afford **6** as a purple solid (21 mg, 4.8%). Mp >300 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) 7.28–7.34 (m, 4H, Ar), 7.42–7.58 (m, 6H, Ar), 7.72–7.84 (m, 12H, Ar), 8.21–8.38 (m, 8H, Ar), 8.48 (d, *J*=5.20 Hz, 2H, β-pyrrole), 8.53 (d, *J*=4.80 Hz, β-pyrrole), 8.66 (s, 1H, β-pyrrole), 9.56 (s, 2H, β-thio-phene). ^{13}C NMR ($CDCl_3$, δ in ppm) 29.89, 127.98, 128.33, 129.14, 129.51, 130.06, 131.18, 133.37, 134.69, 135.60, 136.44, 140.41. ES-MS $C_{56}H_{36}N_2S_2$ calcd av. mass, 801.0. Obsd *m/z* 801.3. Anal. calcd: C, 83.97; H, 4.53; N, 3.50: Found: C, 83.65; H, 4.67; N, 3.77. IR (KBr, ν (cm^{-1})) 3414, 3059, 2929, 697.

4.1.11. *meso*-5,10,15,20-Tetraphenyl-β-2,3,12,13-tetraphenyl-21,23-dithiaporphyrin (7). In a 100 ml round bottomed flask, diol **15** (0.200 g, 0.446 mmol) and pyrrole (40 μl, 0.038 g, 0.5 mmol) were dissolved in 45 ml CH_2Cl_2 and argon was purged for 10 min. $BF_3{\cdot}OEt_2$ (40 μl of 2.5 M stock solution) was added and the reaction was stirred for 1 h under argon at room temperature. DDQ (80 mg, 0.352 mmol) was added and the reaction mixture was stirred for 1.5 h in air. The solvent was removed on a rotary evaporator and the crude compound was purified twice by silica gel column chromatography using CH_2Cl_2 as solvent to give **7** as a purple solid (10 mg, 2.3%). Mp >300 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) 7.04–7.91 (m, 40H, phenyl), 8.10 (s, 4H, β-pyrrole). ^{13}C NMR ($CDCl_3$, δ in ppm) 14.31, 29.88, 128.66, 130.41, 132.06, 138.55. ES-MS $C_{68}H_{44}N_2S_2$ calcd av. mass: 953.2. Obsd *m/z*. 953.33. Anal. calcd: C, 85.68; H, 4.65; N, 2.94. Found: C, 85.37; H, 4.93; N, 3.13. IR (KBr, ν (cm^{-1})) 3321, 3063, 2931, 703.

4.1.12. *meso*-5,10,15,20-Tetraphenyl-β-2-methyl-21-monothiaporphyrin (8). A solution of diol **12** (312 mg, 1 mmol), benzaldehyde (0.220 ml, 2.05 mmol) and pyrrole (212 mg, 3.17 mmol) in 100 ml of CH_2Cl_2 were treated with $BF_3{\cdot}OEt_2$ (30 μl of 2.5 M stock solution) and stirred for 1 h under an argon atmosphere. DDQ (180 mg, 0.792 mmol) was added and reaction mixture was stirred for 1 h in air. The solvent was removed under reduced pressure. The TLC analysis of crude product showed the formation of three porphyrins as expected. The crude compound was loaded on silica and eluted with a mixture of petroleum ether/dichloromethane. The desired compound was collected as the second band using petroleum ether/CH_2Cl_2 (1:1). The solvent was removed on a rotary evaporator to afford **8** as a dark purple crystalline solid (78 mg, 12%). Mp >300 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) −2.56 (s, 1H, NH), 2.93 (s, 3H, CH_3), 7.77–7.80 (m, 12H, *m*,*p*-phenyl), 8.03–8.20 (m, 8H, *o*-phenyl), 8.43 (d, *J*=4.57 Hz, 1H, β-pyrrole), 8.52 (d, *J*=4.57 Hz, 1H, β-pyrrole.), 8.58 (d, *J*=4.57 Hz, 1H, β-pyrrole), 8.65 (d, *J*=4.57 Hz, 1H, β-pyrrole), 8.88 (s, 2H, β-pyrrole), 9.46 (s, 1H, β-thiophene). ^{13}C NMR ($CDCl_3$, δ in ppm) 14.33, 20.47, 29.90, 126.77, 127.18, 127.63, 128.01, 128.69, 132.87, 133.47, 134.33, 134.54, 134.91, 135.71, 137.87, 139.11, 141.39, 142.60, 143.79, 145.98, 154.99. FAB-MS $C_{45}H_{31}N_3S$ calc av. mass, 645.8. Obsd *m/z*: 646. Anal. calcd: C, 83.69; H, 4.84; N, 6.51. Found: C, 83.93; H, 5.05; N, 6.30. IR (KBr, ν (cm^{-1})) 3325, 3039, 2923, 707.

4.1.13. *meso*-5,10,15,20-Tetraphenyl-β-2,3-dimethyl-21-monothiaporphyrin (9). Diol **13** (200 mg, 0.617 mmol), benzaldehyde (140 μl, 148 mg, 1.40 mmol) and pyrrole (140 μl, 135 mg, 2.02 mmol) in CH_2Cl_2 (70 ml) were treated with $BF_3{\cdot}OEt_2$ (30 μl of 2.5 M stock solution) under an argon atmosphere. After 1 h, DDQ (110 mg, 0.484 mmol) was added and the reaction mixture was stirred for 1 h in air. Chromatography on silica gel with petroleum ether/CH_2Cl_2 (6:4) gave the desired compound **9** as a purple solid which moved as the second band (50 mg, 12%). Mp >300 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) −2.37 (s, 1H, –NH), 2.80 (s, 6H, $-CH_3$), 7.72–7.77 (m, 12H, *m*,*p*-phenyl), 8.08–8.21 (m, 8H, *o*-phenyl), 8.45 (d, *J*=4.39 Hz, 2H, β-pyrrole), 8.52 (d, *J*=4.39 Hz, 2H, β-pyrrole), 8.87 (m, 2H, β-pyrrole), ^{13}C NMR ($CDCl_3$, δ in ppm) 18.36, 29.79, 32.02, 53.49, 123.72, 126.66, 127.16, 128.38, 129.99, 133.17, 133.87, 134.46, 138.78, 142.51, 144.94, 154.48, 158.80. ES-MS $C_{46}H_{33}N_3S$ calc av. mass, 659.8, obsd *m/z* 660. Anal. calcd: C, 83.73; H, 5.04; N, 6.37. Found: C, 84.11; H, 5.32; N, 6.16. IR (KBr, ν (cm^{-1})) 3322, 3059, 2929, 710.

4.1.14. *meso*-5,10,15,20-Tetraphenyl-β-2-phenyl-21-monothiaporphyrin (10). 2,5-Bis(hydroxymethylphenyl)-3-phenylthiophene **14** (250 mg, 0.679 mmol), benzaldehyde (150 μl, 1.42 mmol) and pyrrole (150 μl, 2.17 mmol) were dissolved in 60 ml CH_2Cl_2. $BF_3{\cdot}OEt_2$ (40 μl of 2.5 M stock solution) was added to initiate the condensation and the reaction mixture was stirred for 1 h. DDQ (0.115 g, 0.509 mmol) was added and the reaction left stirring for 1 h in air. The solvent was removed on a rotary evaporator and the crude porphyrin was purified by silica gel column chromatography with petroleum ether/CH_2Cl_2 (1:1) to give the desired porphyrin **10** as a purple solid (30 mg, 6.3%). Mp >300 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) −2.51 (s, 1H, NH), 7.10–7.30 (m, 5H, aryl), 7.44 (m, 2H, *o*-phenyl), 7.75–7.83 (m, 12H, *m*,*p*-phenyl), 8.21–8.26 (m, 6H, *o*-phenyl), 8.49 (s, 2H, β-pyrrole), 8.62 (d, *J*=4.80 Hz, 2H, β-pyrrole), 8.70 (d, *J*=3.60 Hz, 1H, β-pyrrole), 8.92 (s, 1H, β-pyrrole), 9.65 (s, 1H, β-thiophene). ^{13}C NMR ($CDCl_3$, δ in ppm) 29.88, 123.72, 124.29, 126.82, 127.61, 128.05, 130.89, 132.54, 133.56, 134.37, 134.71, 135.13, 138.68, 139.65, 140.44, 141.21, 142.46, 144.47, 149.54, 155.09, 157.80. ES-MS $C_{50}H_{33}N_3S$ calcd av. mass, 707.8, obsd *m/z* 708.3. Anal. calcd: C, 84.84; H, 4.70; N, 5.94. Found: C, 84.98; H, 4.92; N, 6.12. IR (KBr, ν (cm^{-1})) 3332, 3059, 3923, 703.

4.1.15. *meso*-5,10,15,20-Tetraphenyl-β-2,3-diphenyl-21-monothiaporphyrin (11). 2,5-Bis(hydroxymethyl)-3,4-diphenylthiophene **15** (0.080 g, 0.178 mmol), benzaldehyde (40 μl, 0.398 mmol) and pyrrole (40 μl, 0.579 mmol) were dissolved in 30 ml CH_2Cl_2. $BF_3{\cdot}OEt_2$ (40 μl of 2.5 M stock solution) was added to initiate the cyclization and reaction mixture was stirred for 1 h. DDQ (0.115 g, 0.506 mmol) was added and stirred the reaction mixture in air for an additional 1 h. The solvent was removed on a rotary

evaporator and the crude porphyrin mixture was purified by column chromatography with petroleum ether/CH_2Cl_2 (1:4) to afford the desired porphyrin **11** as a purple solid (9 mg, 6.4%). Mp >300 °C. ^{1}H NMR ($CDCl_3$, δ in ppm) −2.29 (s, 1H, NH), 6.80–7.40 (m, 22H, aryl), 7.66–7.80 (m, 8H, aryl), 8.20 (m, 3H, β-pyrrole) 8.32 (m, 1H, β-pyrrole), 8.46 (m, 1H, β-pyrrole), 8.88 (s, 1H, β-pyrrole). ^{13}C NMR ($CDCl_3$, δ in ppm) 14.44, 22.70, 29.37, 29.70, 31.93, 123.54, 125.78, 125.94, 126.46, 126.64, 126.81, 127.83, 128.69, 132.03, 134.08, 134.43, 138.56, 139.11, 141.17, 141.73, 142.31, 150.01, 155.09, 159.18. ES-MS $C_{56}H_{37}N_3S$ calcd av. mass, 783.9. Obsd *m/z* 784.3. Anal. calcd: C, 85.79; H, 4.76; N, 5.36. Found: C, 85.96; H, 4.89; N, 5.54. (KBr, ν (cm^{-1})) 3319, 3053, 2858, 702.

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