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Synthesis and crystal structure of 2,3,12,13-tetraalkoxy-21,23-dithiaporphyrins†

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21,23-Dithiaporphyrins with methoxy, butoxy, octyloxy and dodecyloxy substituents at β-thiophene carbons were synthesised for the first time and the crystal structure of the butoxy derivative indicated that the substituents at the β-thiophene carbons induce more planarity in the porphyrin ring.

One of the interesting modifications in porphyrin macrocycles is the replacement of the nitrogen with O, S, Se, Te and C. This class of compounds, named 'core modified porphyrins', show unique properties in terms of their physico-chemical properties and metal coordination chemistry.[1] The β-functionalization of porphyrins is of considerable chemical interest since many properties of the porphyrin macrocycle can be altered by small changes in the substituents. There are several reports on both electron releasing and electron withdrawing substituents at β-pyrrole carbons of N_4 porphyrin systems. Porphyrins with electron withdrawing substituents at β-pyrrole carbons are found to be robust catalysts for alkene epoxidation and alkane hydroxylation reactions.[2] Interestingly, except one report by us[3] in which we introduced substituents at β-pyrrole carbons of 21,23-dithiaporphyrins, there are no reports on β-fuctionalization of core modified porphyrins.

Herein, we wish to report the first synthesis of a series of β-alkoxy substituted 21,23-dithiaporphyrins, **1–4**. The alkoxy groups were introduced at four β-thiophene carbons of 21,23-dithiaporphyrins. The four β-substituted porphyrins synthesised were (Chart 1) 2,3,12,13-tetramethoxy-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin **(1)**, 2,3,12,13-tetrabutoxy-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin **(2)** , 2,3,12,13-tetraoctyloxy-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin **(3)** and 2,3,12,13-tetradodecyloxy-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin **(4)**. The X-ray structure solved for **2** indicates that it is more planar than the parent 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (S_2TPP).[4]

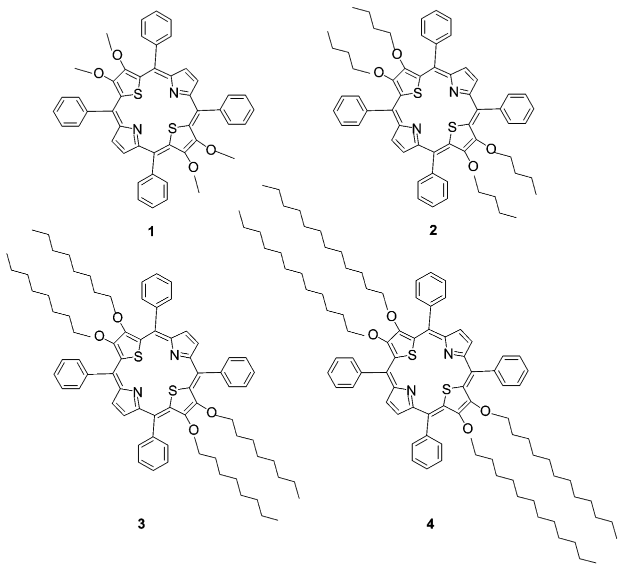
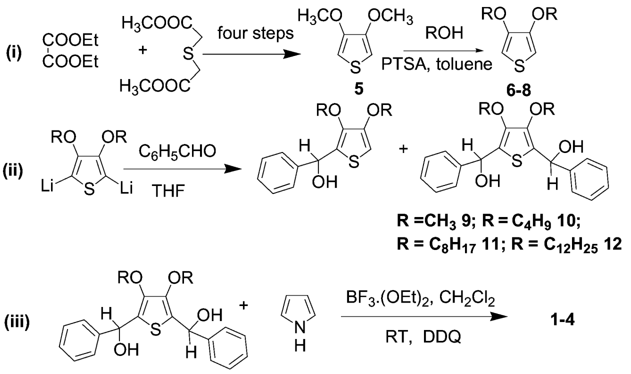


Chart 1

The suitable building blocks for the synthesis of β-alkoxy substituted 21,23-dithiaporphyrins were the corresponding 3,4-dialkoxy-2,5-bis(hydroxyphenylmethyl)thiophenes (thiophene diols). The synthetic methods followed here to prepare the thiophene diols and 2,3,12,13-tetraalkoxy-5,10,15,20-tetraphenyl-21,23-dithiaporphyrins are outlined in Scheme 1. The precursor 3,4-dimethoxythiophene, **5** was prepared according to the literature[5] by condensing the diethyloxalate with dimethylthioglycolate in the presence of sodium methoxide followed by decarboxylation using copper chromite as a catalyst in quinoline at 180 °C. Butoxy **6**, octyloxy **7**, and dodecyloxy **8** substituted thiophenes were prepared under *trans*-etherification conditions[6] in 41–54% yields by treating 3,4-dimethoxythiophene with 1-butanol, 1-octanol and 1-dodecanol, respectively, in the presence of *p*-toluenesulfonic acid in toluene.

The unknown thiophene diols, **9–12** were synthesised by treating one equivalent of 3,4 disubstituted-2,5-dilithiothiophene with 2.5 equivalents of benzaldehyde (Scheme 1).[7] The TLC analysis showed the formation of diol with some amount of mono-ol. The desired thiophene diols were separated from the mono-ols by silica gel column chromatography, using a petroleum ether(bp range 60–80 °C)–ethyl acetate mixture (7:3), as white soft solids in 23–33% yields. The diols were characterized by ^{1}H NMR, IR, Mass, C, H, N, S analysis.†

The porphyrins **1–4** were synthesised by condensing one equivalent of the corresponding thiophene diol with one equivalent of pyrrole in dichloromethane in the presence of a catalytic amount of BF_3-etherate followed by oxidation with DDQ. TLC analysis showed the single yellow spot of the required porphyrin with a small amount of polymeric compound at the origin. Column chromatography on silica gel using petroleum ether–dichloromethane (1:1) gave the desired por-



Scheme 1 Synthetic scheme for thiophene diols **9–12** and porphyrins **1–4**.

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† Electronic supplementary information (ESI) available: ^{1}H-NMR, LD-MS spectra and X-ray crystal structure data. See http://www.rsc.org/suppdata/cc/b2/b208017f/

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phyrins **1**–**4** in 8–14% yield. Porphyrins **1** and **2** are purple crystalline solids and porphyrins **3** and **4** are waxy purple solids. All four β- alkoxy 21,23-dithiaporphyrins, **1**–**4** were characterized by ^{1}H NMR, mass, absorption and emission spectroscopies.‡

The β-thiophene protons which usually appear at 9.679 ppm in S_2TPP[1] were absent in **1**–**4** due to the substitution of alkoxy groups at β-thiophene carbons. The pyrrole protons appeared as a singlet at 8.30 ppm, which was upfield, shifted by 0.35 ppm compared to S_2TPP. The mass spectra showed a corresponding molecular ion peak confirming the product. The absorption spectra of **4** along with S_2TPP recorded in toluene is shown in Fig. 1. All porphyrins showed three clear Q bands and a strong soret band which were bathochromically shifted (8–10 nm) compared to the parent S_2TPP. The fluorescence spectra (inset in Fig. 1) also experienced similar red shifts compared to S_2TPP and quantum yields are slightly increased with alkoxy substituents at β-thiophene carbons.

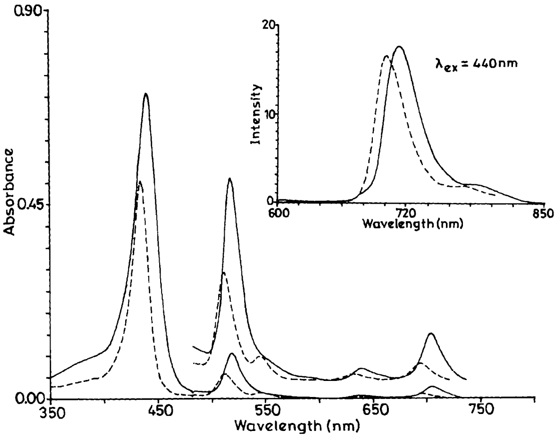

Fig. 1 Absorption and fluorescence (inset) spectra of **4** (——) along with S_2TPP (-------) recorded in toluene.

The structure of **2** was elucidated explicitly by a single-crystal X-ray diffraction analysis (Fig. 2). The structure is perfectly symmetrical but slightly disordered. Only half of the molecule is observed with the other half generated from symmetry. The butyl groups disordered into two positions with a ratio of 74/26. The butoxy substituents at β-thiophene carbons induce more planarity in **2** compared to the parent S_2TPP, the only other reported structure of free base 21,23-dithiaporphyrin (Latos-Grazynski *et al.*[4]). In S_2TPP, it was noted that the four five-membered rings are slightly deviated from the plane of the four *meso* carbons. Interestingly the structure of **2** is nearly planar and the four five-membered rings are in the same plane with four *meso* carbons with negligible deviation. The non-bonded $S\cdots S'$ distance is slightly increased and the $N\cdots N'$ distance is decreased compared to S_2TPP. The presence of substituents at β-positions also resulted in the decrease of the C_α–C_β and C_β–C_β distances of the thiophene rings compared to S_2TPP. The average distance between the porphyrin cores in the layered packing structure is 4.702 Å. There is no complete organized overlap packing on the n-butoxy chain for the β-substituents. However, the tail-to-tail organization between the dithiaporphyrin rings can be clearly seen from the packing diagram.†

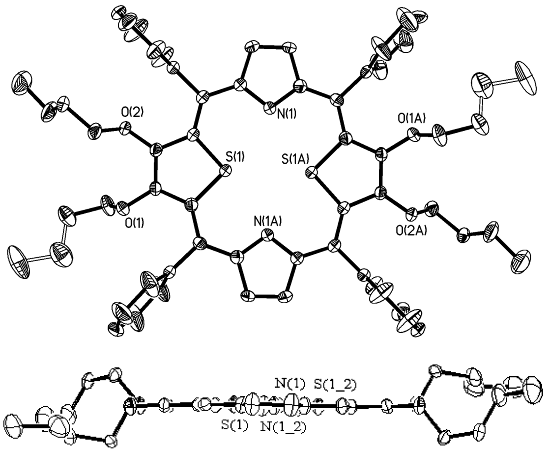

Fig. 2 Top: arial view ORTEP drawing (50% probability level) of **2**, Bottom: edge view emphasizing the planar nature of 21,23-dithiaporphyrin **2** (phenyl groups omitted for edge view for clarity). Crystallographic data: $C_{30}H_{30}NO_2S$, M = 468.61, Triclinic, a = 8.6153(9), b = 12.0456(13), c = 12.2567(14) Å, α = 97.985(2), β = $90.8\underline{4}0(2)$, γ = 97.106(2)°, V = 1249.3(2) Å^3, T = 150(2) K, space group $P1$, Z = 2, $\mu(\text{Mo–K}_a)$ = 0.157 mm^{-1}, 7923 reflections measured, 5514 unique (R_{int} = 0.0394) which were used in all calculations, Final R indices $[I > 2\sigma(I)]$ = R_1 = 0.0694, wR^2 = 0.1761, R indices (all data) = R_1 = 0.1264, wR^2 = 0.2127. CCDC 191919. See http://www.rsc.org/suppdata/cc/b2/b208017f/ for crystallographic data in CIF or other electronic format.

In conclusion, we synthesised for the first time the 2,3,12,13-tetraalkoxy substituted 21,23-dithiaporphyrins. The crystal structure solved for the butoxy derivative indicated that the porphyrin ring is more planar than the parent S_2TPP. The porphyrins bearing long chain alkoxy groups are promising liquid crystalline materials[8] and we are presently investigating the liquid crystalline properties of the reported β-alkoxy 21,23-dithiaporphyrins.

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Notes and references

‡ Selected spectroscopic data. **2**: yield = 8%, mp > 250 °C, UV-vis (toluene): $\lambda_{\max}$ (log ε) 441 (5.04), 519 (4.22), 555 (3.69), 639 (3.40) and 705 (3.58); fluorescence: $\lambda_{\max}$ 713 and 787 nm, ϕ = 0.013; ^{1}H-NMR (300 MHz, $CDCl_3$, δ in ppm) 8.38 (s, 4H, pyrrole), 8.11-8.14 (q, 8H, *o*-phenyl), 7.67–7.69 (m, 12H, *m,p*-phenyl), 4.11–4.12 (t, 8H, $-OCH_2$), 1.20–1.25 (m, 16H, CH_2), 0.85–0.89 (t, 12H, CH_3); LD-MS $C_{60}H_{60}N_2O_4S_2$ calc. mass 937.15, found *m*/*z*: 937.64. Anal. Calc.: C, 76.89; H, 6.45; N, 2.99; S, 6.84. Found: C, 76.38; H, 6.12; N, 3.11; S, 6.98%. **4**: yield = 13%, mp 195-196 °C, UV-vis (toluene): $\lambda_{\max}$ (log ε) 441 (5.24), 519 (4.41), 553 (3.49), 640 (2.71) and 705 (3.78); fluorescence: $\lambda_{\max}$ 713 and 789 nm, ϕ = 0.008; ^{1}H-NMR (300 MHz, $CDCl_3$, δ in ppm) 8.30 (s, 4H, pyrrole), 8.10–8.30 (q, 8H, *o*-phenyl), 7.67–7.69 (m, 12H, *m,p*-phenyl), 4.10–4.12 (q, 8H, $-OCH_2$), 1.25–1.28 (m, 80H, CH_2), 0.89–0.91 (t, 12H, CH_3); LD-MS $C_{92}H_{124}N_2O_4S_2$ calc. mass 1386.11, found *m*/*z*: 1386.02.

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