Synthesis of β-Thiophene-Substituted 21,23-Dithiaporphyrins

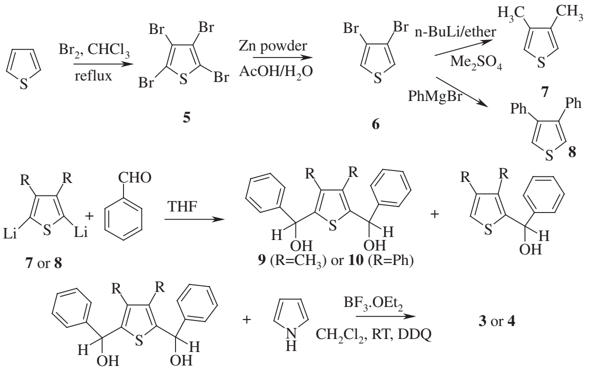
Neeraj Agarwal, Sarada P. Mishra, A. Kumar, and M. Ravikanth*
Department of Chemistry, Indian Institute of Technology, Powai, Mumbai-400076, India

(Received May 15, 2003; CL-030424)

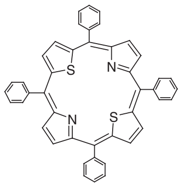
β-Thiophene-substituted 21,23-dithiaporphyrins with substituents like methyl and phenyl groups were synthesized and characterized.

The electronic properties of porphyrins can be tuned at will by introducing suitable substituents at *meso*- or β-positions. The porphyrins synthesized till today possess aryls groups at *meso* positions because they can be synthesized easily and they are very stable to handle for various applications. The introduction of substituents at β-positions alters the electronic properties tremendously since the substituents at β-positions are in direct conjugation with the porphyrin ring. There are several reports on N_4 porphyrins having both electron withdrawing and electron releasing substituents at β-positions and investigated the spectral and catalytic properties in detail.[1] Although there is extensive literature available on β-substituted N_4 porphyrins, the reports on β-substitution of core-modified porphyrins having porphyrin cores such as N_3O, N_3S, N_2S_2, N_2O_2 etc are very scarce. The N_2S_2 porphyrin such as **1** (S_2TPP) has two kinds of β-positions; β-pyrroles and β-thiophenes at which the substituents can be introduced. We recently synthesized some β-pyrrole-substituted 21,23-dithiaporphyrins[2] such as **2** and compared the electronic properties with β-unsubstituted S_2TPP **1**. In this paper, we report the synthesis of β-thiophene-substituted N_2S_2 porphyrins **3** and **4**. The comparision of electronic properties of **3** and **4** with that of β-pyrrole-substituted 21,23-dithiaporphyrin **2** indicates that the electronic properties were more altered by introducing substituents at β-thiophene carbons than β-pyrrole carbons.

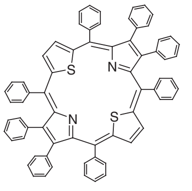
The required thiophene precursors 3,4-dimethyl thiophene and 3,4-diphenyl thiophene were synthesized[3] as shown in Scheme 1. The 2,3,4,5-tetrabromothiophene **5** was synthesized by refluxing thiophene in $CHCl_3$ with excess Br_2 followed by work up with ethyl acetate. The selective debromination of **5** to get 3,4-dibromo thiophene **6** was carried out by treating **5** with Zn powder in glacial acetic acid/water mixture (3:2) and purified by vacuum distillation. The 3,4-dimethyl thiophene **7** was obtained by treating **6** with *n*-BuLi followed by addition of excess cold dimethyl sulphate. Treating **6** with phenyl magnesium bromide in ether in the presence of [1,3-bis(diphenylphosphino) propane]dichloronickel(II) ($NidpppCl_2$) gave 3,4-diphenylthiophene **8**. The unknown diols **9** and **10** were synthesized[4] by treating the 2,5-dilithiated salt of **7** or **8** with benzaldehyde in THF at 0 °C. The diols were purified by silica gel column chromatography using petroleum ether/ethyl acetate and afforded diol **9** in 17% and diol **10** in 28% yields as white crystalline solids. The diols **9** and **10** were characterized by mp, IR, mass and NMR spectroscopic techniques.



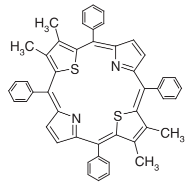
Scheme 1. Synthetic scheme for the preparation of 3,4-disubstituted thiophenes, corresponding diols and β-thiophene substituted porphyrins **3** and **4**.



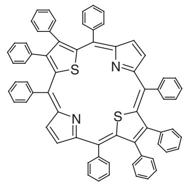
1



2



3



4

The N_2S_2 porphyrins **3** and **4** were synthesized by condensing one equivalent of corresponding diol **9** and **10** respectively with one equivalent of pyrrole in CH_2Cl_2 in the presence of catalytic amount of $BF_3.OEt_2$ at room temperature followed by oxidation with DDQ (Scheme 1).

The crude porphyrins **3** and **4** were purified by silica gel column chromatography and characterized by NMR, mass, C,H,N,S analysis and absorption spectroscopy.[5] The ^{1}H NMR spectrum of **3** in which methyl groups were present at β-thiophene carbons showed a singlet for pyrrole protons which was as upfield shifted by 0.42 ppm (appears at 8.26 ppm) compared to the pyrrole protons of **1** (appears at 8.67 ppm)[4] indicating that the methyl groups at β-thiophene carbons alters the π-delocalization (Table 1). The pyrrole protons of **4** in which phenyls were introduced at β-thiophene carbons were further upfield shifted (appears at 8.10 ppm) due to more effective alteration of π-delocalization caused by phenyl groups at β-thiophene carbons. The mass spectra showed M^+ ion peak confirming the composition of **3** and **4**.

The absorption spectra of **1**, **2**, **3** and **4** recorded in toluene for both Q-bands and Soret band are presented in Figure 1 and the data is tabulated in Table 1.

Table 1. ^{1}H NMR chemical shifts of thiophene and pyrrole protons in $CDCl_3$ and absorption data in toluene for porphyrins **1**-**4**

Porphyrin			Absorption				
	^{1}HNMR (δ in ppm)		Soret	Q-bands λ_{nm} ($\varepsilon \times 10^{-4}$)			
	Thiophene	pyrrole		IV	III	II	I
1	9.67(s)	8.67(s)	435	514	547	633	696
			(25)	(2.6)	(0.70)	(0.22)	(0.45)
2	9.23(s)	—	440	519	—	637	700
			(21.2)	(1.9)	—	(0.22)	(0.31)
3	—	8.26(s)	444	524	—	640	707
			(7.5)	(0.85)	—	(0.15)	(0.15)
4	—	8.10(s)	454	524	—	654	715
			(2.9)	(0.69)	—	(0.17)	(0.12)

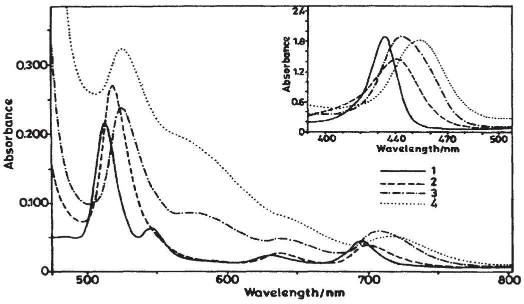


Figure 1. Q-bands and Soret band (inset) absorption spectra of **1**-**4** recorded in toluene.

Porphyrin **2** in which phenyls were introduced at β-pyrrole carbons exhibited three well defined Q-bands and one Soret band which were broad and red shifted compared to unsubstituted parent S_2TPP. The introduction of methyl groups at β-thiophene carbons as in **3** resulted in more broadening and further red shifts of absorption bands. However as shown in Figure 1, the maximum shifts and broadening of absorption bands were observed for **4** in which phenyl groups were present at β-thiophene carbons. The presence of bulky substituents at the β-positions (pyrrole and thiophene carbons) alters the energy levels resulted in broadening and red shifts of absorption bands. The maximum red shifts observed for **4** indicates that the introduction of bulky substituents at β-thiophene carbons alters the energy levels more effectively compared to the introduction of the same substituents at β-pyrrole carbons.

In conclusion, we prepared β-thiophene-substituted 21,23-dithiaporphyrins under mild conditions. The comparison of electronic properties of β-thiophene-substituted porphyrins with that of previously prepared β-pyrrole-substituted 21,23-dithiaporphyrins indicated that the substituents at β-thiophene carbons alter π-delocalization of porphyrin ring more effectively compared to same substituents at β-pyrrole carbons.

Financial assistance from Department of Science and Technology to MR is greatfully acknowledged.

References and Notes

1 a) G. Hariprasad, S. Dahal, and B. G. Maiya, *J. Chem. Soc., Dalton Trans.*, **1996**, 3429. b) P. E. Ellis and J. E. Lyons, *Coord. Chem. Rev.*, **105**, 181 (1990). c) P. Bhyrappa and V. Krishnan, *Inorg. Chem.*, **30**, 239 (1991). d) F. D'Souza, G. R. Deviprasad, and M. E. Zandler, *J. Chem. Soc., Dalton Trans.*, **1997**, 3699.

2 a) M. Ravikanth, *Chem. Lett.*, **2000**, 480. b) N. Agarwal, S. P. Mishra, A. Kumar, C.-H. Hung, and M. Ravikanth, *J. Chem. Soc., Chem. Commun.*, **2002**, 2642.

3 K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato, and K. Suzuki, *Tetrahedron*, **38**, 3347 (1982).

4 A. Ulman and J. Manassen, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 106.

5 Characterization of porphyrin **3**: ^{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 (77.1 MHz, $CDCl_3$, δ in ppm) 18.44, 29.87, 32.10, 127.23, 127.35, 132.19, 133.75, 143.07, 144.67. Anal. Calcd: C, 81.78; H, 5.15; N, 3.97; S, 9.10. Found: C, 80.87; H, 5.27; N, 3.95; S, 9.01. ESI-MS $C_{48}H_{36}N_2S_2$ Calcd, av. mass: 704.94; obsd *m/z*: 704.87. **4**: ^{1}H NMR ($CDCl_3$, δ in ppm) 7.54-7.91 (m, 40H, phenyl), 8.10 (s, 4H, β-pyrrole). Anal. Calcd: C, 85.68; H, 4.65; N, 2.94; S, 6.73. Found: C, 86.28; H, 4.93; N, 3.13; S, 6.82. ESI-MS $C_{68}H_{44}N_2S_2$ calcd av, mass: 953.22; obsd *m/z*: 953.33.

Published on the web (Advance View) July 21, 2003; DOI 10.1246/cl.2003.744