

Tetrahedron Letters 43 (2002) 9453-9455

## Synthesis of meso-furyl porphyrins

Iti Gupta and M. Ravikanth\*

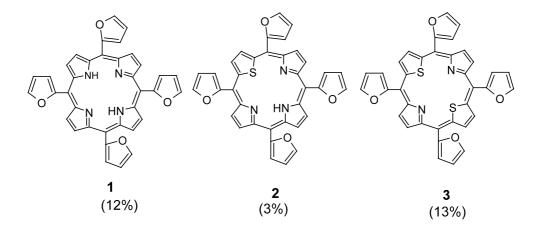
Department of Chemistry, Indian Institute of Technology, Powai, Mumbai 400 076, India Received 22 July 2002; revised 26 September 2002; accepted 4 October 2002

Abstract—Three *meso*-furyl porphyrins with  $N_4$ ,  $N_3S$  and  $N_2S_2$  porphyrin cores were synthesized and characterized. The absorption bands of *meso*-furyl porphyrins experienced large red shifts compared to *meso*-aryl porphyrins and the maximum red shifts were observed for the *meso*-furyl porphyrin with the  $N_2S_2$  core. © 2002 Elsevier Science Ltd. All rights reserved.

Porphyrins serve as a functional group in a wide variety of biological systems, the most common being chlorophyll and the heme proteins.<sup>1</sup> Porphyrins, besides being helpful in understanding crucial biological processes, have enormous potential for applications including those in catalysis of organic reactions,<sup>2a</sup> magnetic resonance imaging<sup>2b</sup> and photodynamic therapy.<sup>2c</sup> Porphyrin macrocycles are very flexible and by introducing substituents selectively at the  $\beta$ - or *meso*-positions, the properties can be tuned at will for any application. meso-Tetraarylporphyrins offer attractive features in this context and have been used in a wide variety of model systems owing to their ease of synthesis and facile functionalization. However, the reports on porphyrins having *meso* substituents like five-membered heterocycles such as pyrrole, thiophene, furan etc are scarce. In recent times, there have been a few reports on meso-tetrathienylporphyrins because of their unique

energy transfer and electrochemical properties.<sup>3</sup> To the best of our knowledge, there are no reports on the synthesis of porphyrins containing furyl groups at the *meso* carbons. In this paper we report for the first time, the synthesis and characterization of novel *meso*-tetra-furylporphyrins with three different porphyrin cores:  $N_4$  (1),  $N_3S$  (2) and  $N_2S_2$  (3). The electronic properties of *meso*-tetrafuryl porphyrins are very different from tetra-aryl porphyrins and they have the potential to have wide applications in materials chemistry.

The *meso*-tetrafuryl porphyrin with the  $N_4$  core, 5,10,15,20-tetrakis(2-furyl)porphyrin (H<sub>2</sub>TFP), **1** was prepared by condensing 1 equiv. of furfural with 1 equiv. of pyrrole in chloroform at room temperature in the presence of a catalytic amount of BF<sub>3</sub>·OEt<sub>2</sub>. The crude compound showing a single spot on TLC was purified by silica gel column chromatography using



\* Corresponding author.

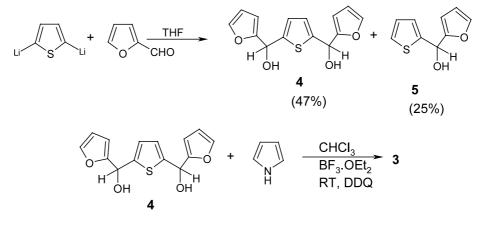
0040-4039/02/\$ - see front matter @ 2002 Elsevier Science Ltd. All rights reserved. PII: S0040-4039(02)02258-X

 $CH_2Cl_2$  as eluent to give 1 in 12% yield. The porphyrin 1 was confirmed by the presence of a strong m/z peak at 574.7 and the appearance of the pyrrole protons as a sharp singlet at 9.16 ppm in the <sup>1</sup>H NMR spectrum.<sup>4</sup> To prepare *meso*-furyl porphyrins with  $N_3S$  and  $N_2S_2$ porphyrin cores, an easy access to the unknown diol, 2,5-bis(2-furyl hydroxymethyl)thiophene 4 was required. The diol 4 was prepared by treating 1 equiv. of 2,5-dilithiothiophene with 2 equiv. of furfural in THF as shown in Scheme 1.5 TLC analysis showed the formation of the diol along with mono-ol 5. The monool and diol mixture were separated by silica gel column chromatography using a petroleum ether/ethyl acetate mixture. The mono-ol was moved as the first band in petroleum ether/15% ethyl acetate (25% yield) and the diol was then collected as a second band in petroleum/ 20% ethyl acetate. The diol 4 was recrystallized twice from toluene to afford a white crystalline solid in 47% vield.6

Condensation of 1 equiv. of diol 4 with 2 equiv. of furfural and 3 equiv. of pyrrole in  $CHCl_3$  in the pres-

ence of a catalytic amount of BF<sub>3</sub>·OEt<sub>2</sub> gave a crude mixture of three porphyrins: 1–3. Purification on silica gel using CH<sub>2</sub>Cl<sub>2</sub> gave the desired compound, 5,10,15,20 - tetrakis(2 - furyl) - 21 - monothiaporphyrin (STFPH), 2 as the first band in 3% yield. The presence of a strong m/z peak at 591.7 and clean <sup>1</sup>H NMR spectrum confirmed the proposed structure and composition.<sup>7</sup> 5,10,15,20-Tetrakis(2-furyl)-21,23-dithiaporphyrin ( $S_2TFP$ ) **3** was prepared by condensing 1 equiv. of 4 with 1 equiv. of pyrrole in  $CHCl_3$  in the presence of BF<sub>3</sub>·OEt<sub>2</sub> (Scheme 1). TLC analysis showed a single spot indicating the formation of 3 as the sole product. Chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> gave 3 in 13% yield. The presence of sharp singlet peaks at 8.97 ppm and 10.1 ppm in the <sup>1</sup>H NMR for the pyrrole and thiophene protons, respectively, and a m/z peak at 608.5 in the mass spectrum confirms the  $N_2S_2$  porphyrin **3**.<sup>8</sup>

The absorption spectra of 1-3 recorded at very dilute concentration are presented in Fig. 1. All three porphyrins showed two to three Q-bands and one Soret



Scheme 1. Synthetic scheme for the preparation of diol 4 and porphyrin 3.

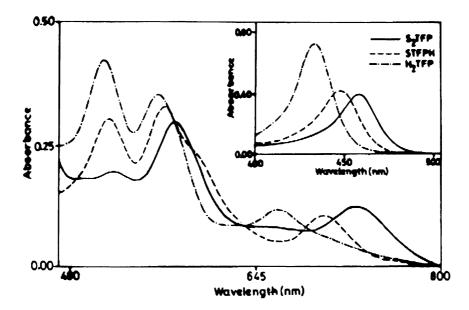


Figure 1. Q-bands and Soret band (inset) absorption spectra of 1-3 recorded in toluene.

band unlike tetraryl porphyrins which showed four clear Q-bands and one Soret band. The absorption bands are broad and experienced a 25 to 30 nm red shift compared to tetraaryl porphyrins. The absorption bands of 1-3 are red shifted as the porphyrin core changes from  $N_4$  to  $N_3S$  to  $N_2S_2$  and the maximum shifts were observed for 3. Similar red shifts of the absorption bands were observed for 5,10,15,20-tetrakis(2-thienyl)porphyrin compared to 5,10,15,20-tetraphenylporphyin.<sup>3d</sup> The X-ray structure was solved for 5,10,15,20-tetrakis(2-thienyl) porphyrinato zinc(II) which showed clearly that the thienyl rings were not co-planar with the porphyrin macrocycle.3c The observed red shifts of the absorption bands of tetrathienyl porphyrins compared to tetraaryl porphyrins was then attributed to the inductive effect of the thienyl rings. We have not yet been successful in obtaining suitable crystals of 1-3 for structure analysis. The structure of the porphyrin is expected to change as the porphyrin core<sup>1</sup> changes from  $N_4$  to  $N_3S$  to  $N_2S_2$ . We are presently exploring the possibility of the structure analysis of 1-3 to understand the cause for the red shifts of the absorption bands.

In conclusion, we have prepared three *meso* furyl porphyrins with three different porphyrin cores. A detailed electrochemical and photophysical study of *meso*-furyl porphyrins are presently under investigation in our laboratory.

## Acknowledgements

This work was supported by a grant from the Council of Scientific and Industrial Research (CSIR) and Department of Science & Technology (DST), Govt. of India, New Delhi.

## References

- 1. Ravikanth, M.; Chandrashekar, T. K. Struct. Bond. 1995, 82, 105 and references cited therein.
- (a) Meunier, B. Chem. Rev. 1992, 92, 1411; (b) Lauffer, R.
  B. Chem. Rev. 1987, 87, 901; (c) Bonnett, R. Chem. Soc. Rev. 1995, 24, 19.
- (a) Vollmer, M. S.; Wurthner, F.; Effenberger, F.; Emele, P.; Meyer, D. U.; Stumpfig, T.; Port, H.; Wolf, H. C. *Chem. Eur. J.* **1998**, *4*, 260; (b) Ono, N.; Miyagawa, H.; Ueta, T.; Ogawa, T.; Tani, H. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1595; (c) Bhavana, P.; Varghese, B.; Bhyrappa, P. *Acta Crystallogr.* **2001**, *C57*, 252; (d) Bhyrappa, P.; Bhavana, P. *Chem. Phys. Lett.* **2001**, *349*, 399.
- Compound 1: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): -2.59 (s, 2H, NH), 7.04 (m, 4H, furan), 7.32 (m, 4H, furan), 8.14 (s, 4H, furan), 9.16 (s, 8H, β-pyrrole). LD-MS C<sub>36</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> calcd av, mass: 574.6; obsd *m/z*: 574.7. UV-vis λ<sub>max</sub>/nm (ε/mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>): 433 (172001), 526 (7579), 571 (6893), 670 (1612).
- Kumaresan, D.; Agarwal, N.; Ravikanth, M. J. Chem. Soc., Perkin Trans. 1 2001, 1644.
- Compound 4: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): 2.70 (s, 2H, OH), 5.91 (s, 2H, CH), 6.22 (s, 4H, furan), 6.80 (s, 2H, thiophene), 7.32 (s, 2H, furan). Anal. calcd: C, 60.86; H, 4.38; S, 11.61. Found: C, 60.54; H, 4.28; S, 11.37%. IR (KBr, ν): 3367 cm<sup>-1</sup>.
- 7. Compound **2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): -2.41 (s, 1H, NH), 7.02 (m, 2H, furan), 7.06 (m, 2H, furan), 7.31 (d, 2H, J=2.6 Hz, furan), 7.42 (d, 2H, J=3.3 Hz, furan), 8.11 (s, 2H, furan), 8.20 (s, 2H, furan), 8.85 (d, 2H, J=4.7 Hz, β-pyrrole), 9.01 (d, 2H, J=4.4 Hz, β-pyrrole), 9.22 (s, 2H, β-pyrrole), 10.21 (s, 2H, β-thiophene). LD-MS C<sub>36</sub>H<sub>21</sub>N<sub>3</sub>SO<sub>4</sub> calcd av, mass: 591.6; obsd m/z: 591.7. UV-vis  $\lambda_{max}/nm$  ( $\varepsilon/mol^{-1}$  dm<sup>3</sup> cm<sup>-1</sup>): 448 (99668), 530 (6827), 575 (7509), 632 (sh), 705 (2298).
- 8. Compound 3: <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): 7.07 (m, 4H, furan), 7.42 (m, 4H, furan), 8.20 (m, 4H, furan), 8.97 (s, 4H,  $\beta$ -pyrrole), 10.05 (s, 4H,  $\beta$ -thiophene). LD-MS C<sub>36</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>O<sub>4</sub> calcd av, mass: 608.5; obsd *m/z*: 608.5. UV–vis  $\lambda_{max}/nm$  ( $\epsilon/mol^{-1}$  dm<sup>3</sup> cm<sup>-1</sup>): 458 (82915), 536 (sh), 585 (6206), 740 (1368).