Synthesis of *meso*-furyl porphyrins

Iti Gupta and M. Ravikanth*

Department of Chemistry, Indian Institute of Technology, Powai, Mumbai 400 076, India

Abstract—Three *meso*-furyl porphyrins with N₄, N₃S and N₂S₂ 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 N₂S₂ core.

Porphyrins serve as a functional group in a wide variety of biological systems, the most common being chlorophyll and the heme proteins.¹ Porphyrins, besides being helpful in understanding crucial biological processes, have enormous potential for applications including those in catalysis of organic reactions,² magnetic resonance imaging² and photodynamic therapy.² Porphyrin macrocycles are very flexible and by introducing substituents selectively at the β- 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*-tetra(thienyl)porphyrins because of their unique energy transfer and electrochemical properties.³ 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(furyl)porphyrins with three different porphyrin cores: N₄ (1), N₃S (2) and N₂S₂ (3). The electronic properties of *meso*-tetra(furyl) porphyrins are very different from tetra-aryl porphyrins and they have the potential to have wide applications in materials chemistry.

The *meso*-tetra(furyl) porphyrin with the N₄ core, 5,10,15,20-tetrakis(2-furyl)porphyrin (H₂TFP), 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 BF₃·OEt₂. The crude compound showing a single spot on TLC was purified by silica gel column chromatography using...
CH₂Cl₂ 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 ¹H NMR spectrum.⁴ To prepare meso-furyl porphyrins with N₃S and N₂S₂ 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 mono-ol 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% yield.⁶

Condensation of 1 equiv. of diol 4 with 2 equiv. of furfural and 3 equiv. of pyrrole in CHCl₃ in the presence of a catalytic amount of BF₃·OEt₂ gave a crude mixture of three porphyrins: 1-3. Purification on silica gel using CH₂Cl₂ gave the desired compound, 5,10,15,20-tetakis(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 ¹H NMR spectrum confirmed the proposed structure and composition.⁷ 5,10,15,20-Tetakis(2-furyl)-21,23-dithiaporphyrin (S₂TFP) 3 was prepared by condensing 1 equiv. of 4 with 1 equiv. of pyrrole in CHCl₃ in the presence of BF₃·OEt₂ (Scheme 1). TLC analysis showed a single spot indicating the formation of 3 as the sole product. Chromatography on silica gel with CH₂Cl₂ gave 3 in 13% yield. The presence of sharp singlet peaks at 8.97 ppm and 10.1 ppm in the ¹H NMR for the pyrrole and thiophene protons, respectively, and a m/z peak at 608.5 in the mass spectrum confirms the N₂S₂ porphyrin 3.⁸

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.](image)

![Figure 1. Q-bands and Soret band (inset) absorption spectra of 1-3 recorded in toluene.](image)
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 N4 to N3S to N3S2 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-tetraphenylporphyrin.3c 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.3d The observed red shifts of the absorption bands of tetra-thiophenyl 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 core1 changes from N4 to N3S to N3S2. 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

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References

4. Compound I: 1H NMR (CDCl3, δ in ppm): 433 (sh), 526 (7579), 571 (6893), 670 (1612).
6. Compound 2: 1H NMR (CDCl3, δ in ppm): 458 (82915), 536 (sh), 575 (7509), 632 (448).
7. Compound 3: 1H NMR (CDCl3, δ in ppm): 2.70 (s, 2H, OH), 5.91 (s, 2H, CH), 6.22 (s, 4H, furan), 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⁻¹.
8. Compound 4: 1H NMR (CDCl3, δ in ppm): 2.41 (s, 1H, β-pyrrole), 3.3 Hz, furan), 8.11 (s, 2H, thiophene). LD-MS C36H22N4O4 calcd: 591.7. UV–vis λmax/nm (ε/mol⁻¹ dm³ cm⁻¹): 433 (127001), 526 (7579), 571 (6893), 670 (1612).
9. Compound 5: 1H NMR (CDCl3, δ in ppm): 7.07 (s, 4H, furan), 7.42 (d, 2H, J = 3.3 Hz, furan), 8.11 (s, 2H, thiophene), 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 C36H21N3SO4 calcd: 591.7. UV–vis λmax/nm (ε/mol⁻¹ dm³ cm⁻¹): 448 (99668), 530 (6827), 575 (7509), 632 (sh), 705 (2298).
10. Compound 6: 1H NMR (CDCl3, δ in ppm): 7.02 (s, 4H, CH), 6.22 (s, 4H, furan), 7.31 (d, 2H, J = 2.6 Hz, furan), 7.42 (d, 2H, J = 3.3 Hz, furan), 8.11 (s, 2H, thiophene), 8.20 (s, 4H, 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 C36H21N3SO4 calcd: 591.7. UV–vis λmax/nm (ε/mol⁻¹ dm³ cm⁻¹): 448 (99668), 530 (6827), 575 (7509), 632 (sh), 705 (2298).