



## Synthesis of *meso*-furyl porphyrins

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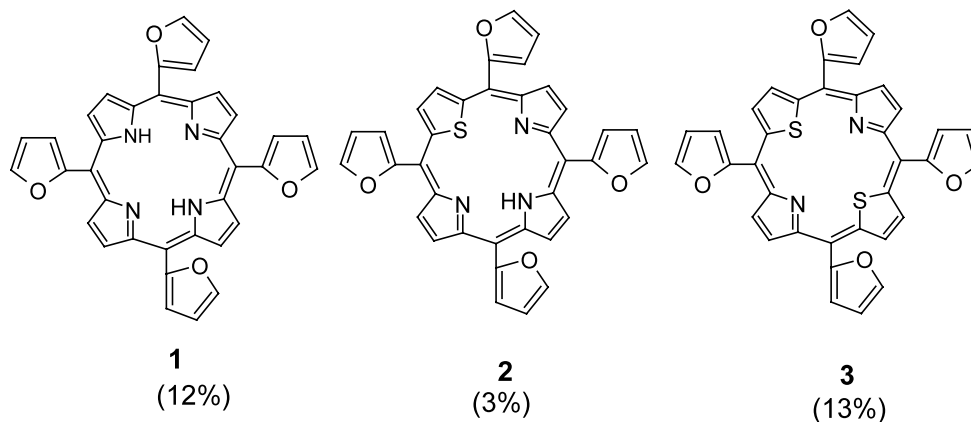
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**Abstract**—Three *meso*-furyl porphyrins with  $N_4$ ,  $N_3S$  and  $N_2S_2$  porphyrin cores were synthesized and characterized. The absorption bands of *meso*-furyl porphyrins experienced large red shifts compared to *meso*-aryl porphyrins and 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*-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  $N_4$  core, 5,10,15,20-tetrakis(2-furyl)porphyrin ( $H_2TFP$ ), **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  $BF_3 \cdot OEt_2$ . The crude compound showing a single spot on TLC was purified by silica gel column chromatography using



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band unlike tetraaryl 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<sub>4</sub> to N<sub>3</sub>S to N<sub>2</sub>S<sub>2</sub> 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.<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.<sup>3c</sup> The observed red shifts of the absorption bands of tetra-thienyl 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<sub>4</sub> to N<sub>3</sub>S to N<sub>2</sub>S<sub>2</sub>. 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.

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- 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).
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- 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>.
- 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>O<sub>4</sub> calcd av, mass: 591.6; obsd *m/z*: 591.7. UV-vis λ<sub>max</sub>/nm (ε/mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>): 448 (99668), 530 (6827), 575 (7509), 632 (sh), 705 (2298).
- Compound **3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): 7.07 (m, 4H, furan), 7.42 (m, 4H, furan), 8.20 (m, 4H, furan), 8.97 (s, 4H, β-pyrrole), 10.05 (s, 4H, β-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 λ<sub>max</sub>/nm (ε/mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>): 458 (82915), 536 (sh), 585 (6206), 740 (1368).