

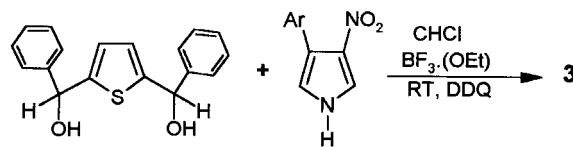
## Synthesis of $\beta$ -Substituted 21,23-Dithiaporphyrins

M. Ravikanth

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

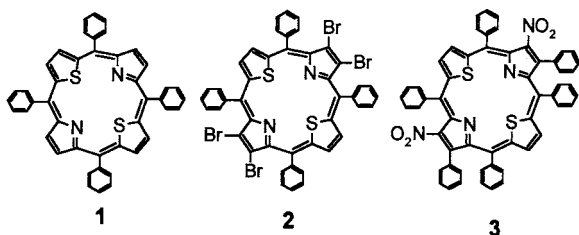
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Synthesis and characterization of  $\beta$ -substituted 5,10,15,20-tetraphenyl-21,23-dithiaporphyrins are reported. The absorption and emission spectra exhibited large bathochromic shifts due to nonplanarity of porphyrin ring which is induced on  $\beta$ -substitution.



Scheme 1 Synthetic scheme for **3**

Core modification of porphyrin ring by introducing thiophene, furan, selenophene, tellurophene etc, in place of pyrrole lead to novel heterosubstituted porphyrins which exhibit interesting properties in terms of both aromatic character and their ability to stabilize metals in unusual oxidation states.<sup>1</sup> Porphyrins bearing electron withdrawing substituents such as  $-\text{Br}$ ,  $-\text{NO}_2$  at  $\beta$ -pyrrole carbons have considerable potential as catalysts for epoxidation of alkenes and hydroxylation of alkanes.<sup>2</sup> Although there is extensive literature on  $\beta$ -substitution of normal porphyrins, there is no report on  $\beta$ -substituted core modified porphyrins. Herein we report the synthesis and characterization of few  $\beta$ -substituted core modified porphyrins and the proposed strategy can be further extended to synthesize several other  $\beta$ -substituted core modified porphyrins.



Initially we were interested in introducing bromines at  $\beta$ -positions of pyrrole and then use them as precursors for the synthesis of other  $\beta$ -substituted dithiaporphyrins via Suzuki coupling. Thus we investigated the possibility to tetra brominate the 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin, **1** ( $\text{S}_2\text{TPP}$ ). Treatment of **1** with 5 equivalents of *N*-bromosuccinimide in chloroform gave  $(\beta\text{-Br}_4)\text{S}_2\text{TPP}$ , **2**, in 70% yield. **2** was purified by silica gel column using dichloromethane and characterized with  $^1\text{H}$  NMR, MALDI mass, absorption and emission spectroscopies.<sup>3</sup> The absence of pyrrole signal in  $^1\text{H}$  NMR indicated that the hydrogens were replaced by bromines at  $\beta$ -positions of two pyrrole rings. MALDI mass showed characteristic  $\text{M}^+$  and  $\text{M} - \text{Br}_n$  ( $n = 1-4$ ) peaks. Reaction of **2** with substituted phenylboronic acids under Suzuki coupling conditions resulted in complicated mixture of products and no attempts were made to separate and identify the products. While the work was in progress in our laboratory, Ono et al. reported an easy and faster method for the synthesis of 3,4-disubstituted pyrroles and their conversion to  $\beta$ -substituted porphyrins.<sup>4</sup> Thus, we prepared 3-phenyl-4-nitropyrrole by following their method and condensed with 2,5-bis( $\alpha$ -hydroxyphenylmethyl)thiophene in the presence of  $\text{BF}_3 \cdot (\text{OEt})_2$  in chloroform to obtain  $(\beta\text{-Ph})(\beta\text{-NO}_2)_2\text{S}_2\text{TPP}$ , **3**, in 4.8% yield (Scheme 1). Ono et al. reported that 3-phenyl-4-nitropyrrole is not reactive to form porphyrins with aromatic aldehydes hence they formylated and reduced it to hydroxymethyl group and tetramerized under acidic conditions to form porphyrins. However, in present case the 3-phenyl-4-nitropyrrole is reacted easily since 2,5-bis( $\alpha$ -hydroxyphenylmethyl)thiophene has reactive functionality and formed dithiaporphyrin under normal porphyrin forming conditions. The crude dithiaporphyrin was purified by silica gel column chromatography using dichloromethane as an eluent.  $^1\text{H}$  NMR spectrum of **3** varied with the concentration since porphyrins with electron withdrawing substituents have high tendency to aggregate and MALDI showed  $\text{M}^+$  ion peak.<sup>5</sup>

Similarly  $(\beta\text{-Ph})_4\text{S}_2\text{TPP}$ , **4**, (structure not shown) was prepared in 25% yield by condensing 3,4-diphenyl pyrrole with 2,5-bis( $\alpha$ -hydroxyphenylmethyl)thiophene using  $\text{BF}_3 \cdot (\text{OEt})_2$  in chloroform. The compound was purified by silica gel column chromatography using dichloromethane as an eluent and characterized by  $^1\text{H}$  NMR, MALDI and absorption spectroscopies.<sup>6</sup>

The absorption spectra of compounds recorded at very dilute concentration are presented in Figure 1. Introduction of substituents at  $\beta$ -pyrrole carbons resulted in broadening and large red shifts of absorption bands. The maximum effects were observed for **3**. The presence of bulky substituents at the  $\beta$ -pyrrole carbons induced nonplanarity in the porphyrin ring and reduced energy gap between HOMO and LUMO resulted in large red shifts in absorption peak maxima.<sup>1a</sup> The maximum

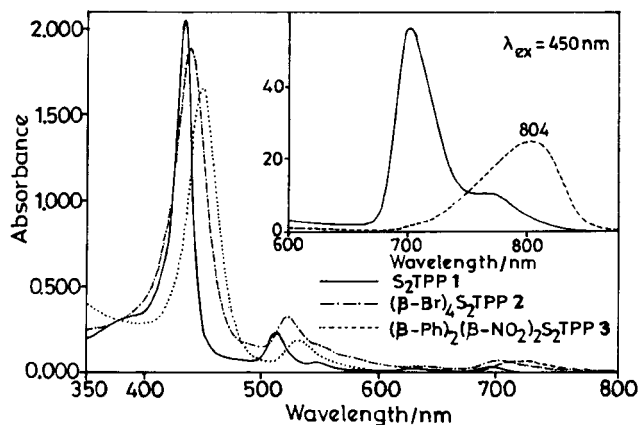


Figure 1 Absorption and emission (inset) spectra of dithiaporphyrins recorded in  $\text{CH}_2\text{Cl}_2$ .

red shifts observed for **3** indicates that it is more nonplanar because of steric crowding at the dithiaporphyrin periphery. The emission spectra of **1** and **3** are shown as an inset in figure 1. The emission bands in **3** are very broad and experienced large red shifts compared to **1**. Compound **2** also exhibited similar red shifts and broadening but lesser in magnitude compared to **3**. Both **2** and **3** are weakly fluorescent because of combined effects of heavy halogens and nonplanarity in the dithiaporphyrin ring.<sup>7</sup>

In summary, we prepared the first  $\beta$ -substituted 21,23-dithiaporphyrins under mild conditions. The synthetic strategy can be extended to prepare several hetero substituted porphyrins. Synthesis and their study on nonlinear optical properties<sup>8</sup> of several  $\beta$ -substituted core modified porphyrins are underway and reported in due course of time.

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### References and Notes

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- 3 Spectral data for **2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  in ppm) 7.80 (m, 12H, Ar), 8.06 (m, 8H, Ar), 9.39 (s, 4H,  $\beta$ -thiophene). LD-MS C<sub>44</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub>Br<sub>4</sub> calcd av mass 964.4, obsd *m/z* 964.7 (M<sup>+</sup>), 885.7 (M-1Br), 805.9 (M-2Br), 725.2 (M-3Br), 645.0 (M-4Br). UV-vis ( $\lambda_{\text{max}}$ /nm,  $\epsilon/10^4$  dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>) 440 (19.2), 521 (1.9), 633 (0.15), 698 (0.22).
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- 5 Spectral data for **3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  in ppm) 7.10-7.30 (m, 30H, Ar), 7.50, 7.70 (m, 4H,  $\beta$ -thiophene). LD-MS C<sub>56</sub>H<sub>34</sub>N<sub>4</sub>S<sub>2</sub>O<sub>4</sub> calcd av mass 891.0, obsd *m/z* 892.7. UV-vis ( $\lambda_{\text{max}}$ /nm,  $\epsilon/10^4$  dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>) 449 (18.1), 530 (1.7), 649 (0.18), 717 (0.23).
- 6 Spectral data for **4**: <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  in ppm) 6.90 (m, 8H, Ar), 7.06 (m, 4H, Ar), 7.21 (m, 8H, Ar), 7.52 (m, 8H, Ar), 7.71 (m, 8H, Ar), 7.80 (m, 4H, Ar), 9.23 (m, 4H,  $\beta$ -thiophene). LD-MS C<sub>68</sub>H<sub>44</sub>N<sub>2</sub>S<sub>2</sub> calcd av mass 953.2, obsd *m/z* 953.9. UV-vis ( $\lambda_{\text{max}}$ /nm,  $\epsilon/10^4$  dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>) 440 (21.2), 519 (1.9), 637 (0.22), 700 (0.31).
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