



# Synthesis of 21-oxoporphyrin building blocks and energy donor appended systems

D. Kumaresan, Iti Gupta and M. Ravikanth\*

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

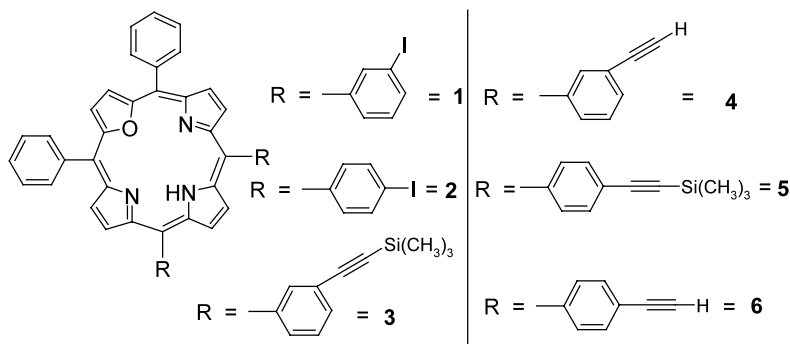
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**Abstract**—A series of 21-oxoporphyrin building blocks bearing iodo- and ethynyl functional groups were synthesized and characterized. A boron–dipyrin unit appended 21-oxoporphyrin was constructed using the building blocks under mild palladium coupling conditions which exhibited efficient energy transfer from boron–dipyrin to 21-oxoporphyrin. © 2001 Published by Elsevier Science Ltd.

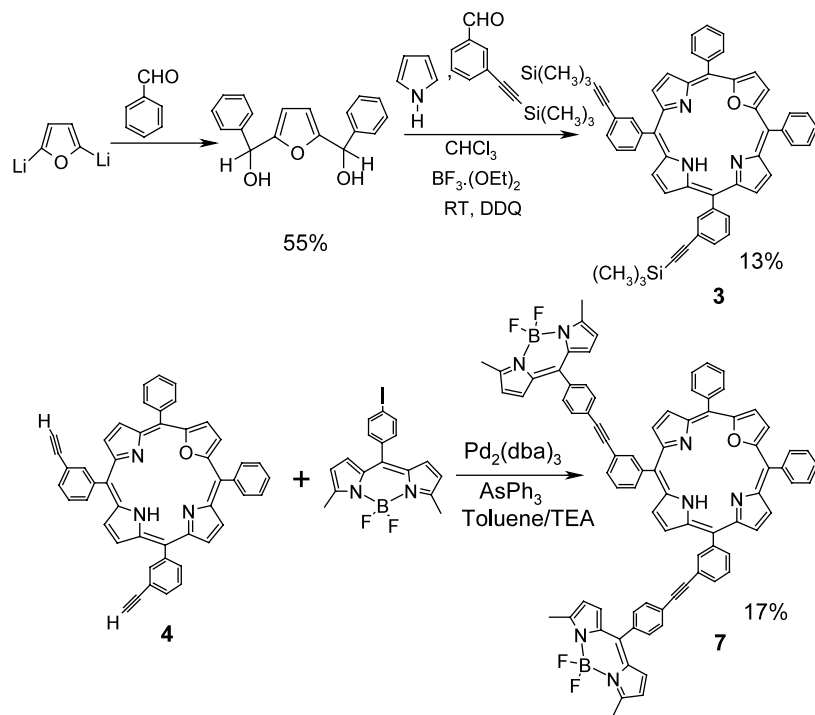
Core modification of the porphyrin ring by introducing thiophene, furan, selenophene and tellurophene in place of pyrrole led to novel hetero-substituted porphyrins which exhibit interesting properties in terms of both aromatic character and their ability to stabilize metals in unusual oxidation states.<sup>1</sup> However, the chemistry of core-modified porphyrins is not very well developed and the main emphasis of reports which are available on core-modified systems are on insertion and stabilization of metals in unusual oxidation states.<sup>2</sup> Reports on oxoporphyrins are scarce even though they exhibit interesting physico-chemical and electrochemical properties.<sup>3</sup> Recently, we have been exploring core modified porphyrin chemistry and we prepared an unsymmetrical porphyrin pentamer<sup>4</sup> containing a dithiaporphyrin (N<sub>2</sub>S<sub>2</sub>) core as the central unit with four peripheral normal porphyrin (N<sub>4</sub>) units, and observed energy transfer from peripheral normal porphyrins to a central dithiaporphyrin core. We have also reported the synthesis of different types of  $\beta$ -substituted thiaporphyrins.<sup>5</sup>

In this paper, we report the synthesis and characterization of a series of 21-oxoporphyrin building blocks bearing iodo- and ethynyl functional groups and their application towards the construction of energy donor appended 21-oxoporphyrin systems.

The 21-oxoporphyrin building blocks bearing iodo- and ethynyl functional groups are synthesized as outlined in Scheme 1. The double alkylation of the dianion of furan with benzaldehyde afforded the 2,5-bis(phenyl hydroxymethyl)furan.<sup>3b</sup> The condensation of 1 equiv. of 2,5-bis(phenyl hydroxymethyl) furan with 2 equiv. of *meta* or *para*-iodobenzaldehyde and 3 equiv. of pyrrole in the presence of BF<sub>3</sub>·OEt<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> gave a mixture of three porphyrins. The crude porphyrin mixture containing three porphyrins was subjected to column chromatography and the desired porphyrin building block **1** or **2** was eluted second with CH<sub>2</sub>Cl<sub>2</sub>/2%CH<sub>3</sub>OH, in 12% yield. Similarly, the condensation of 1 equiv. of 2,5-bis(phenyl hydroxymethyl)furan with 2 equiv. of *meta* or *para*-trimethylsilylethynyl benzaldehyde followed by



\* Corresponding author.



Scheme 1. Synthetic scheme for the preparation of 7.

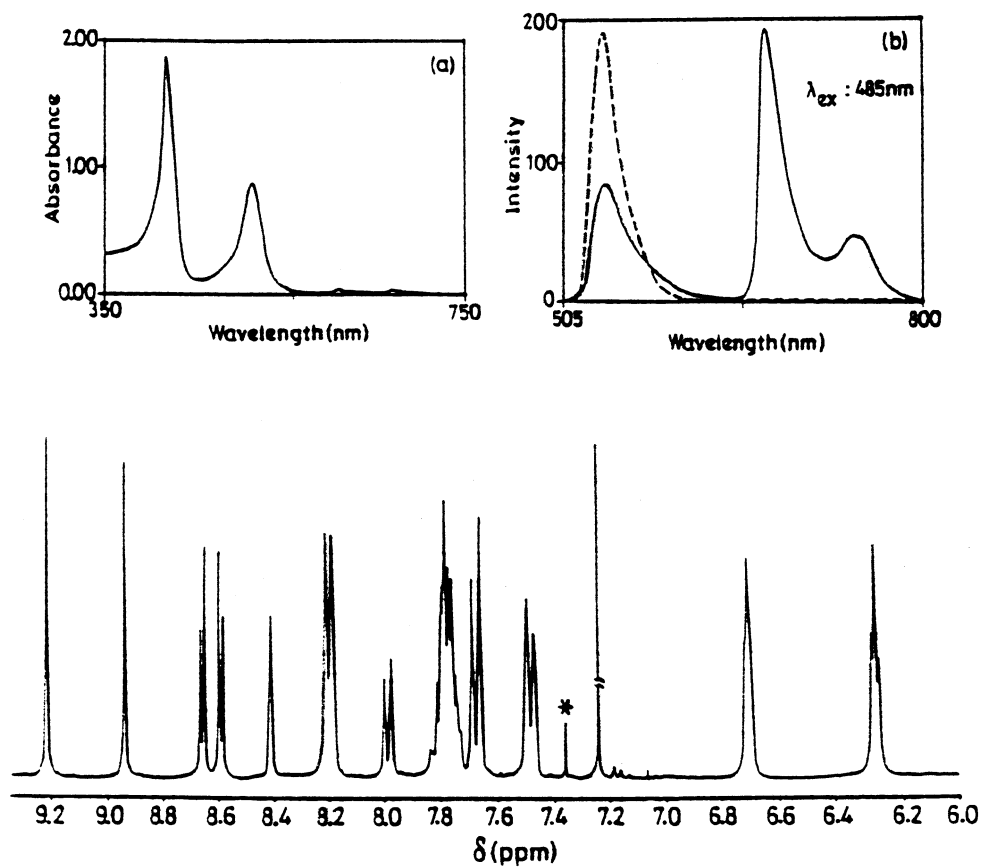


Figure 1.  $^1\text{H}$  NMR spectrum of 7 recorded in  $\text{CDCl}_3$ . (\*) indicates solvent impurity. The absorption spectrum of 7 is shown in inset (a). The emission spectra of 7 (solid line) and 1:2 mixture of 4 and BDPY (dashed line) recorded in toluene is shown in inset (b).

column chromatography yielded porphyrin building blocks **3** or **5**, respectively, in 13% yield. The deprotection of the trimethylsilyl group by treating **3** or **5** with  $K_2CO_3$  in THF–methanol (3:1) gave **4** or **6**, respectively, in 90% yield. All the porphyrin building blocks were characterized by  $^1H$  NMR, FAB mass and absorption and emission spectroscopies.<sup>6</sup> The building blocks with iodo- and ethynyl functional groups are ideal to construct light harvesting systems.<sup>7</sup> Thus, the coupling of **4** with *N,N*-difluoroboryl-1,9-dimethyl-5-(4-iodophenyl)dipyrrin (BDPY-I) in toluene/triethylamine at 35°C in the presence of  $Pd_2(dba)_3$  and  $AsPh_3$  followed by column chromatography on silica gel using  $CH_2Cl_2/15\%$  ethyl acetate gave **7** in 17% yield.<sup>8</sup> The  $^1H$  NMR spectrum of **7** is shown in Fig. 1. The furan protons appeared as a singlet at 9.22 ppm and the three pyrrole rings of the porphyrin appeared as three separate signals indicating the low symmetric nature of the porphyrin ring. The two pyrrole rings of the BDPY group gave multiplets at 6.35 and 6.70 ppm, respectively. The FAB mass spectrum showed a molecular ion peak at 1251 confirming the product. The absorption spectrum of **7** recorded in  $CH_2Cl_2$  is shown as an inset (a) in Fig. 1. It showed three Q-bands and one Soret band. The band at 515 nm, which is mainly due to BDPY units, is very strong compared to the other two Q-bands, which are due to the porphyrin ring. The fluorescence spectra of **7** along with a 1:2 mixture of **4** and BDPY in toluene at an excitation wavelength of 485 nm are presented in Fig. 1 inset (b). As seen from Fig. 1, the mixture of **4** and BDPY recorded at an excitation wavelength of 485 nm showed emission mainly due to BDPY, since at this wavelength the BDPY unit absorbs strongly. When the mixture was excited at 420 nm, where **4** is the strong absorber, emission mainly due to **4** was observed. However, in the case of **7**, strong emission was observed due to the porphyrin unit irrespective of the excitation wavelength. On excitation of **7** at 485 nm where BDPY absorbs strongly, the emission was mainly due to the porphyrin unit (Fig. 1). The emission quantum yield of the BDPY unit in **7** (0.019) was reduced 10 times from the free BDPY unit (0.19), whereas the quantum yield of the porphyrin unit was slightly increased. These results suggest that there is an efficient energy transfer from the BDPY unit to the 21-oxoporphyrin unit in **7**. Recently we reported the BDPY appended 21,23-dithiaporphyrin system in which we failed to observe energy transfer from BDPY to 21,23-dithiaporphyrin.<sup>9</sup> Thus, by changing the heteroatom from sulfur to oxygen in the porphyrin core, the energy transfer dynamics were altered. A detailed photophysical study is needed to understand these observations.

In conclusion, we have synthesized 21-oxoporphyrin building blocks containing iodo- and ethynyl functional groups. We have also shown the use of porphyrin building blocks in the construction of energy donor appended systems. The building blocks reported in this paper are useful for the synthesis of unsymmetrical porphyrin arrays containing 21-oxoporphyrin and normal porphyrin ( $N_4$ ) units and such studies are presently under investigation in our laboratory.

## Acknowledgements

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- Spectral data for selected compounds: **1**:  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  in ppm) 7.58 (t, 2H, Ar), 7.89 (m, 6H, Ar), 8.20–8.39 (m, 8H, Ar), 8.65 (s, 2H, Ar), 8.85 (s, 2H,  $\beta$ -pyrrole), 9.07 (m, 4H,  $\beta$ -pyrrole), 9.64 (s, 2H,  $\beta$ -furan). FAB-MS  $C_{44}H_{27}N_3OI_2$  calcd av. mass 867.5, obsd  $m/z$  868. Anal. calcd: C, 60.9; H, 3.13; N, 4.84. Found: C, 61.1, H, 3.42; N, 4.58. UV–vis ( $\lambda_{max}$ , nm) 421 (119667), 507 (14750), 538 (3434), 613 (2205), 674 (2241). Fluorescence ( $\lambda_{ex}$  = 515 nm, in toluene) 677, 745 ( $\phi$  = 0.0062). **3**:  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  in ppm) 0.39 (s, 18H,  $CH_3$ ), 7.68 (t, 2H, Ar), 7.79 (m, 6H, Ar), 7.89 (d, 2H, Ar), 8.10 (d, 2H, Ar), 8.19 (d, 4H, Ar), 8.31 (s, 2H, Ar), 8.57 (m, 4H,  $\beta$ -pyrrole), 8.85 (s, 2H,  $\beta$ -pyrrole), 9.20 (s, 2H,  $\beta$ -furan). FAB-MS  $C_{54}H_{45}N_3Si_2O$  calcd av. mass, 808.1, obsd  $m/z$  808 ( $M^+$ ). Anal. calcd: C, 80.1; H, 5.61; N, 5.19. Found: C, 79.3, H, 5.90; N, 5.42. UV–vis ( $\lambda_{max}$ , nm) 423 (128567), 444 (46728), 507 (18110), 538 (3687), 612 (2601), 673 (2753). Fluorescence ( $\lambda_{ex}$  = 515 nm, in toluene) 677, 745 ( $\phi$  = 0.037). **4**:  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  in ppm) 3.20 (s, 2H, CCH), 7.75 (m, 8H, Ar), 7.91 (m, 2H, Ar), 8.18 (m, 6H, Ar), 8.32 (s, 2H, Ar), 8.57 (m, 4H,  $\beta$ -pyrrole), 8.86 (m, 2H,  $\beta$ -pyrrole), 9.20 (s, 2H,  $\beta$ -furan). FAB-MS  $C_{48}H_{29}N_3O$  calcd av. mass, 663.7, obsd  $m/z$  664. Anal. calcd: C, 86.8; H, 4.40; N, 6.35. Found: C, 85.9, H, 4.39; N, 6.18. UV–vis ( $\lambda_{max}$ , nm) 421 (171856), 443 (33833), 507 (16747), 538 (4930), 612 (2716), 674 (2456). Fluorescence ( $\lambda_{ex}$  = 485 nm, in toluene) 677, 745 ( $\phi$  = 0.037).

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8. Data for compound **7**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm) 1.25 (s, 12H,  $\text{CH}_3$ ), 6.35 (m, 4H, BDPY pyrrole), 6.70 (m, 4H, BDPY pyrrole), 7.48 (m, 4H, Ar), 7.67 (m, 4H, Ar), 7.78 (m, 8H, Ar), 7.99 (m, 2H, Ar), 8.21 (m, 6H, Ar), 8.42 (s, 2H, Ar), 8.65 (d, 2H,  $\beta$ -pyrrole), 8.93 (s, 2H,  $\beta$ -pyrrole), 9.22 (s, 2H,  $\beta$ -furan).  $^{13}\text{C}$  NMR (77.1 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm) 15.02, 29.79, 119.66, 121.6, 125.1, 127.1, 128.4, 130.3, 130.5, 131.5, 134.4, 137.49, 142.0, 157.9. FAB-MS  $\text{C}_{82}\text{H}_{55}\text{N}_7\text{OB}_2\text{F}_4$  calcd av. mass 1252.2, obsd  $m/z$  1251. Anal. calcd: C, 78.6; H, 4.42; N, 7.86. Found: C, 77.8, H, 4.35; N, 7.78. UV-vis ( $\lambda_{\text{max}}$ , nm) 425 (180539), 443 (34207), 515 (150228), 611 (3896), 673 (3895). Fluorescence ( $\lambda_{\text{ex}} = 485$  nm, in toluene) 542, 678, 746 nm ( $\phi_{\text{BDPY}} = 0.019$ ,  $\phi_{\text{porphyrin}} = 0.038$ ).
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