



Pergamon

Tetrahedron Letters 41 (2000) 3709–3712

TETRAHEDRON  
LETTERS

# Synthesis and photophysical study of unsymmetrical porphyrin pentamers

M. Ravikanth

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

Received 21 December 1999; accepted 21 March 2000

## Abstract

A dithiaporphyrin building block with an  $N_2S_2$  core is synthesized and coupled with porphyrin building blocks with  $N_4$  cores to obtain an unsymmetrical pentamer. Steady-state fluorescence spectra indicated that there is an efficient energy transfer from an excited  $N_4$  porphyrin unit to an  $N_2S_2$  porphyrin unit. © 2000 Elsevier Science Ltd. All rights reserved.

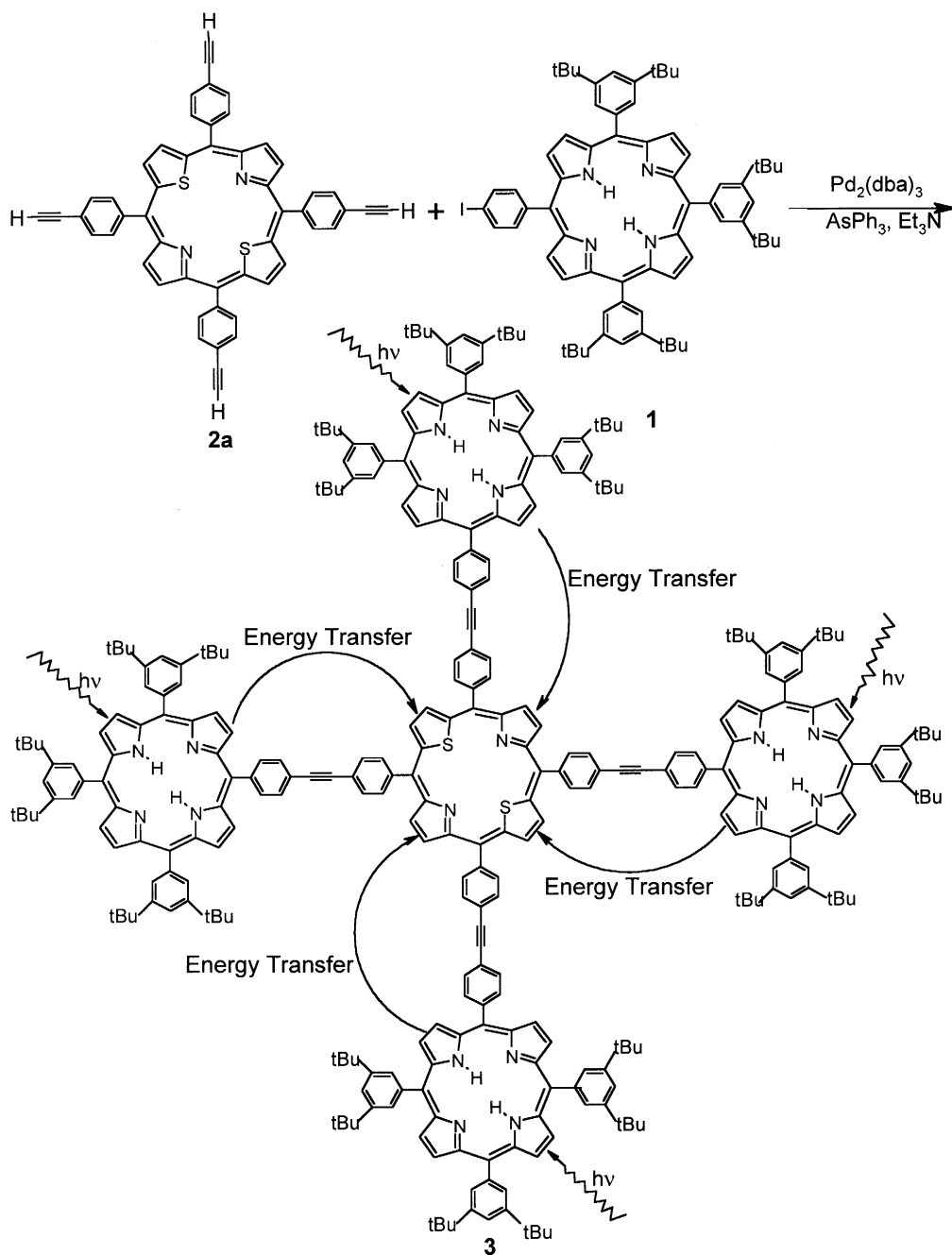
Unsymmetrical porphyrin arrays are suitable models for mimicking energy transfer processes of photosynthesis. Selective excitation of one porphyrin unit and the energy transfer from that unit to another porphyrin unit is feasible in unsymmetrical porphyrin arrays. Recently, several unsymmetrical porphyrin dimers such as porphyrin–chlorin and porphyrin–corrole have been synthesized in order to obtain long lived charge transfer states.<sup>1</sup> Interestingly, there is no report on unsymmetrical arrays containing core modified porphyrins. Core modification of porphyrin rings by introducing thiophene, furan, selenophene, tellurophene, etc. in place of pyrrole leads to novel core modified porphyrins which exhibit interesting properties in terms of both aromatic characters and their ability to stabilize metals in unusual oxidation states.<sup>2</sup> Herein, we report the first synthesis of an unsymmetrical porphyrin pentamer containing a core modified porphyrin with an  $N_2S_2$  core connected to porphyrins with  $N_4$  cores via diaryl ethyne bridging groups.

To construct an unsymmetrical porphyrin pentamer, one needs easy access to porphyrin building blocks.<sup>3</sup> The porphyrin building block 5,10,15-tri(3,5-di-*tert*-butylphenyl)-20-(4-iodophenyl) porphyrin, **1**, was synthesized by following the literature procedure.<sup>4</sup> The other desired core modified porphyrin building block, 5,10,15,20-*tetrakis*-[4-(2-trimethylsilylethynyl)phenyl]-21,23-dithiaporphyrin, **2**, was obtained in 17% yield by reacting 2,5-[4-(2-trimethylsilylethynyl)phenyl hydroxymethyl]thiophene with pyrrole in the presence of a catalytic amount of  $BF_3 \cdot (OEt)_2$  in  $CHCl_3$ . Deprotection with  $K_2CO_3$  in THF/methanol gave 5,10,15,20-*tetrakis*-(4-ethynylphenyl)21,23-dithia porphyrin **2a** in 80% yield. Coupling **1** with **2a** in toluene/triethylamine at 35°C in the presence of  $Pd_2(dba)_3$  and  $AsPh_3$  gave the unsymmetrical porphyrin pentamer **3** in 37% yield (Scheme 1). The crude pentamer was initially passed through a silica gel column to remove unreacted materials and subjected to size exclusion column chromatography (SEC). The pentamer obtained from the SEC column contained small impurities of

0040-4039/00/\$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.

PII: S0040-4039(00)00471-8

higher and lower porphyrin oligomers and was finally purified by preparative HPLC and characterized by  $^1\text{H}$  NMR, MALDI mass, absorption and emission spectroscopies.<sup>5</sup> Zn(II) was introduced into the  $\text{N}_4$  porphyrin core by following the standard  $\text{Zn}(\text{OAc})_2/\text{methanol}$  method.



Scheme 1. Synthetic scheme for the preparation of **3**

The absorption spectra of **1**, **2** and **3** are shown in Fig. 1. It is clear from Fig. 1 that the absorption spectrum of **3** exhibited bands corresponding to both **1** and **2** indicating a weak interaction between the

porphyrin units. The emission spectra of **1**, **2** and **3** recorded at 420 nm are shown as an inset in Fig. 1. The  $N_4$  porphyrin unit absorbs more strongly than the  $N_2S_2$  unit at 420 nm. However, the emission spectrum of the pentamer closely matches the  $N_2S_2$  porphyrin unit and no emission was observed from the  $N_4$  unit. This indicates that selective excitation of the  $N_4$  unit resulted in the energy transfer from the  $N_4$  unit to the  $N_2S_2$  unit. The emission spectrum was recorded at different concentrations to confirm that the observed energy transfer is an intramolecular process. An identical emission spectrum was obtained for **3** at different wavelengths suggesting efficient energy transfer from the  $N_4$  unit to the  $N_2S_2$  unit. Similar observations were made when the Zn porphyrin unit was excited selectively at 550 nm. The Zn porphyrin absorbs about four times as intensively as the free base porphyrin at 550 nm. However, the excitation at 550 nm results in the emission exclusively from the  $N_2S_2$  porphyrin unit. This kind of efficient energy transfer is not possible in free base symmetrical porphyrin pentamers where all the porphyrin units are the same and absorb in the same region. Thus, the unsymmetrical pentamer reported here is unique in the sense that it can be excited selectively and it shows an efficient energy transfer in the free base form. The synthesis and detailed photodynamics of several such unsymmetrical arrays are presently under investigation in our laboratory.

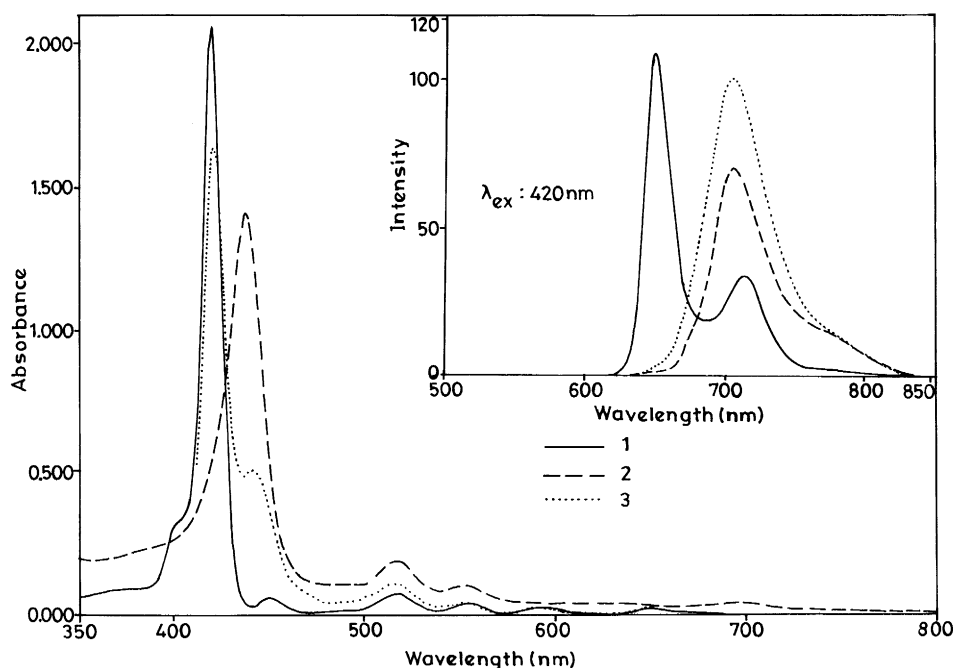


Fig. 1. Absorption and emission (inset) spectra recorded in  $CH_2Cl_2$

## Acknowledgements

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

## References

1. (a) Paolesse, R.; Taglittesta, P.; Boschi, T. *Tetrahedron Lett.* **1996**, 37, 2637. (b) Pandey, R. K.; Forsyth, T. P.; Gerzevske, K. R.; Lin, J. J.; Smith, K. M. *Tetrahedron Lett.* **1992**, 33, 5315. (c) Gust, D.; Moore, T. A.; Moore, A. L.; Krasnovsky Jr., A. A.; Liddell, P. A.; Nicodem, D.; Degraziano, J. M.; Kerrigan, P.; Makings, L. R.; Pessiki, P. J. *J. Am. Chem. Soc.* **1993**, 115, 5684. (d) Bonfantini, E. E.; Officer, D. L. *Tetrahedron Lett.* **1993**, 34, 8531. (e) Arnold, D. P.; Nischinsk, L. J. *Tetrahedron Lett.* **1993**, 34, 693. (f) Paolesse, R.; Pandey, R. K.; Forsyth, T. P.; Jaquinod, L.; Gerzevske, K. R.; Nurco, D. J.; Senge, M. O.; Liocchia, S.; Boschi, T.; Smith, K. M. *J. Am. Chem. Soc.* **1996**, 118, 3869. (g) Kadish, K. M.; Guo, N.; Camelbecke, E. V.; Froio, A.; Paolesse, R.; Monti, D.; Taglittesta, P.; Boschi, T.; Prodi, L.; Bolletta, F.; Zaccheroni, N. *Inorg. Chem.* **1998**, 37, 2358.
2. (a) Ravikanth, M.; Chandrashekar, T. K. *Struc. & Bonding* **1995**, 82, 105, and references cited therein. (b) Grazynski, L.-L.; Olmstead, M. M.; Balch, A. L. *Chem. Eur. J.* **1997**, 3, 268. (c) Gross, Z.; Saltsman, I.; Pandian, R. P.; Barzilay, C. M. *Tetrahedron Lett.* **1997**, 38, 2383.
3. Ravikanth, M.; Strachan, J. P.; Li, F.; Lindsey, J. S. *Tetrahedron* **1998**, 37, 2358.
4. Kawabata, S.; Yamazaki, I.; Nishimura, Y.; Osuka, A. *J. Chem. Soc., Perkin Trans. 2* **1997**, 479.
5. Spectral data for selected compounds: Compound **2**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm) 0.39 (s, 36H,  $\text{CH}_3$ ), 7.92 (AA'BB', 8H, Ar), 8.17 (AA'BB', 8H, Ar), 8.65 (s, 4H,  $\beta$ -pyrrole), 9.65 (s, 4H,  $\beta$ -thiophene). LD-MS  $\text{C}_{64}\text{H}_{60}\text{N}_2\text{S}_2\text{Si}_4$  calcd av. mass: 1033.7; obsd  $m/z$ : 1037.1. UV-vis ( $\lambda_{\text{max}}$ , nm) 439, 516, 551, 632, 698. Compound **2a**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm) 3.33 (s, 4H, CCH), 7.95 (AA'BB', 8H, Ar), 8.20 (AA'BB', 8H, Ar), 8.67 (s, 4H,  $\beta$ -pyrrole), 9.67 (s, 4H,  $\beta$ -thiophene). LD-MS  $\text{C}_{52}\text{H}_{28}\text{N}_2\text{S}_2$  calcd av. mass: 744.9; obsd  $m/z$ : 746.4. UV-vis ( $\lambda_{\text{max}}$ , nm) 439, 516, 552, 633, 698. Compound **3**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm) -2.63 (s, 8H, NH), 1.54 (m, 216H,  $-\text{CH}_3$ ), 7.83 (m, 12H, Ar), 8.05 (m, 24H, Ar), 8.13 (m, 8H, Ar), 8.22 (d, 8H, Ar), 8.34 (d, 8H, Ar), 8.41 (d, 8H, Ar), 8.88–8.97 (m, 36H,  $\beta$ -pyrrole), 9.89 (s, 4H,  $\beta$ -thiophene). LD-MS  $\text{C}_{324}\text{H}_{332}\text{N}_{18}\text{S}_2$  calcd av. mass: 4542.5; obsd  $m/z$ : 4543.9. UV-vis ( $\lambda_{\text{max}}$ , nm) 421, 441, 518, 555, 592, 648, 698.