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Tripodaphyrins, a New Class of Porphine Derivatives Designed for Nanofabrication

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Abstract : Tripodaphyrins are tetrahedral or pyramidal assemblies in which a porphyrin macrocycle, situated on the top of the molecule, is "supported" by three "legs" consisting of linear arrays of rigid constitutive elements. The present work describes the synthesis of two representative examples (**1** and **2**) of this novel class of molecules.

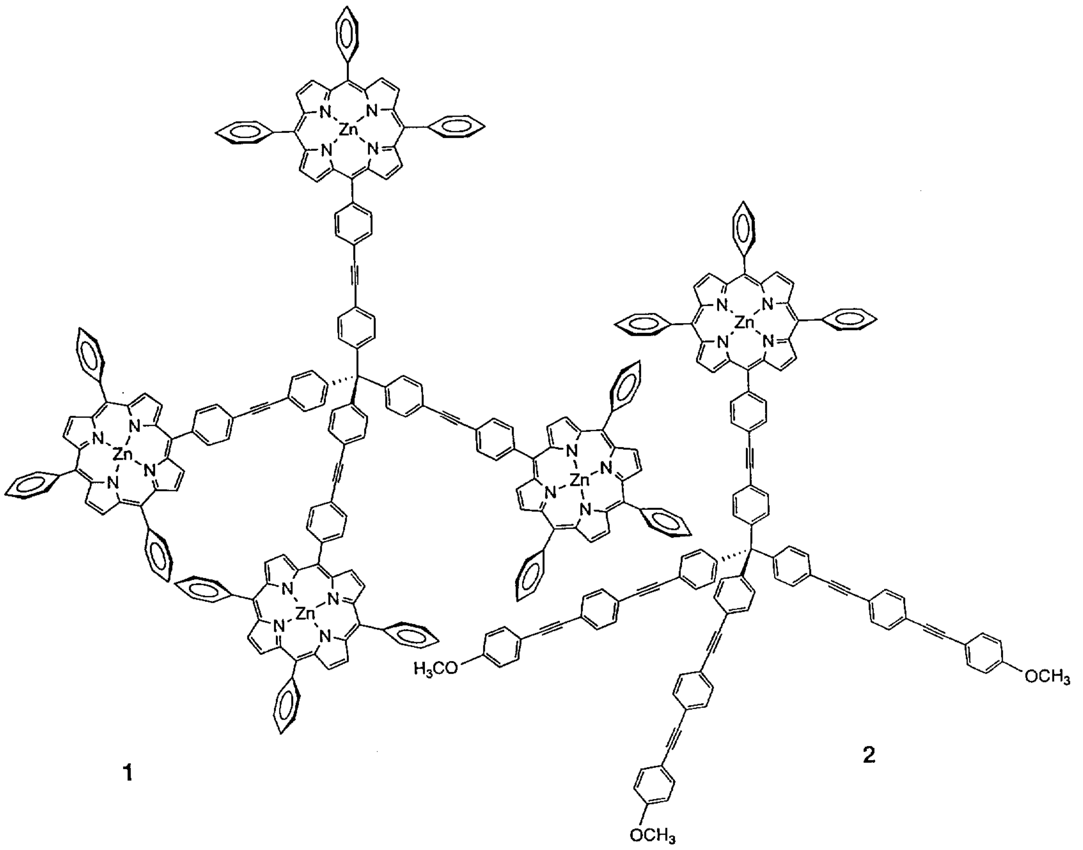
Introduction. Owing to the diversity of their particular properties (chemical stability, colour, fluorescence, formation of metal chelates, etc.) the study of porphyrins seems to be an inexhaustible source of new research fields in organic chemistry.[1,2] Indeed, porphyrin derivatives play an important role not only in living organisms as prosthetic groups of functional proteins like haemoglobin, myoglobin, cytochromes, catalases and peroxydases, chlorophylls, etc., but also as versatile synthetic pigments. Among the latter number different catalysts,[3,4] oxygen-carrying molecules,[5] and electron-transfer systems.[6] Moreover, for some time past porphyrin derivatives attract growing interest in medical research both as photosensitizers in Photodynamic Therapy (PDT)[7] and as vectors in Boron Neutron Capture Therapy (BNCT)[8,9] of cancer.

In the course of these investigations a large number of both "stacked" (so-called cofacial) porphyrin dimers[10] and laterally bridged "flat" or "gable" porphyrin dimers[11-13], as well as some pillared cofacial trimers,[14,15] and toroid-shaped tetramers[16,17] have been synthesised in relation to the important roles of porphyrin aggregates with restricted geometries in haemoproteins and photosynthetic pigments. Also straight linear oligomers (trimers[18] and tetramers[19]) as well as pentamers in which four *meso*-tetraphenylporphine units are radially arranged around a central macrocycle[20,21] have been synthesised, in which the porphyrin units are joined at their *meso*-positions by phenyl rings either directly or through ethynyl groups. Until now, however, no oligomeric structures are known, in which the monomeric subunits point into the three directions of the space.

The recent report on the positioning of a *meso*-tetraphenylporphine derivative under the scanning tunnelling microscope (STM)[22] prompted us to communicate our synthesis of a *meso*-tetraphenylporphine tetramer **1** which owing to its molecular geometry seems to be predestinate for nanofabrication experiments. Actually, as the synthesis of **1** starts from a tetraphenylmethane core, to which four porphyrin macrocycles are covalently linked, the "legs" of the tetrahedral-shaped molecule can be prolonged as it may be required, enabling therefore the construction of molecules with quite long base edges. Thus, in *tripodaphyrins*[23] **1** and **2** the longest distances between the vertices of the molecule measure approximately 420 and 315 pm, respectively, so that such kind of molecules should firmly stand when adsorbed on a surface. Owing to the presence of the porphyrin macrocycle, the positioned molecules should render service on the different fields of application outlined above. These conjectures are presently investigated in our laboratory.

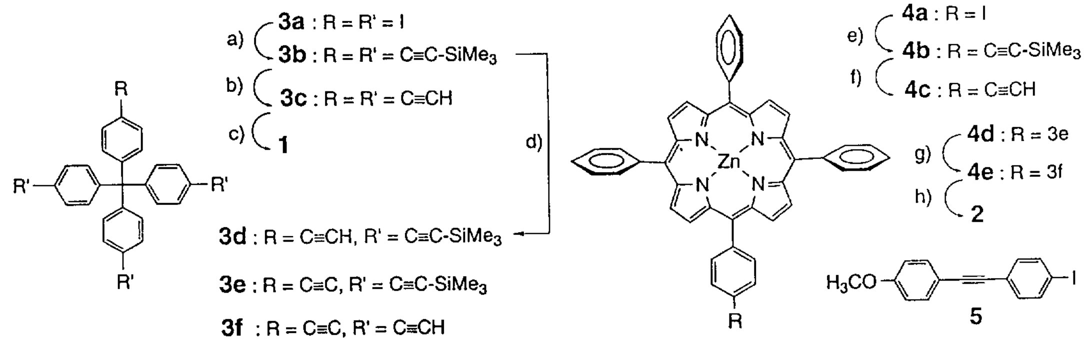
Experimental. To synthesize **1**, 5-(4-iodophenyl)-10,15,20-triphenylporphine[24] was transformed in 97% yield into the corresponding zinc chelate (**4a**) under standard conditions (Zn(II) acetate, $CHCl_3$/MeOH (9:1), reflux, 1h) and thereafter reacted with tetrakis(4-ethynylphenyl)methane (**3c**), which was prepared as outlined in *Scheme 1.* A better overall yield (76 *vs.* 51%) was obtained reacting tetrakis(4-iodophenyl)methane (**3a**)[25] with

6 eq. of [5-(4-ethynylphenyl)-10,15,20-triphenylporphinato]zinc(II) (**4c**) under the same conditions as in c) (*Scheme 1*). As expected from the distance between the porphyrin chromophores (about 270 pm) and their mutual geometrical orientation (*cf.*[26]), both the UV/VIS (Fig. 1) and fluorescence spectrum (Fig. 2) of **1**[27] does not reveal the presence of significant excitonic interaction between them.



1

2



Scheme 1 : a) HC≡C-SiMe$_3$, Pd(PPh$_3$)$_2$Cl$_2$, CuI, DMF/NEt$_3$ (9:1), 35 °C, 15h (95%). b) 1N NaOH, THF, 20 °C, 2h (93%). c) **4a** (4 eq.), Pd(PPh$_3$)$_4$, DMF/NEt$_3$ (5:1), 40°C, 15h (58%). d) TBAF (0.5 eq.), CHCl$_3$, 20°C (30%). e) same cond. as in a) (93%). f) 0.5 N NaOH, THF, 20 °C, 2h (92%). g) 0.5 N NaOH, THF, 20 °C, 3h (99%). h) **5** (3 eq.), Pd(PPh$_3$)$_4$, DMF/NEt$_3$ (5:1), 45°C, 20h (88%).

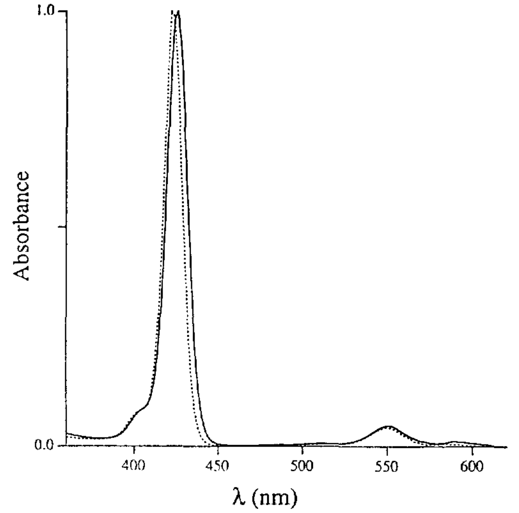


Figure 1 : Superposed UV/VIS spectra of **1** (—) and [*meso*-tetraphenylporphinato] Zn(II) (----) 5.5 x 10^{-7} M and 1.8 x 10^{-6} M, respectively, in benzene

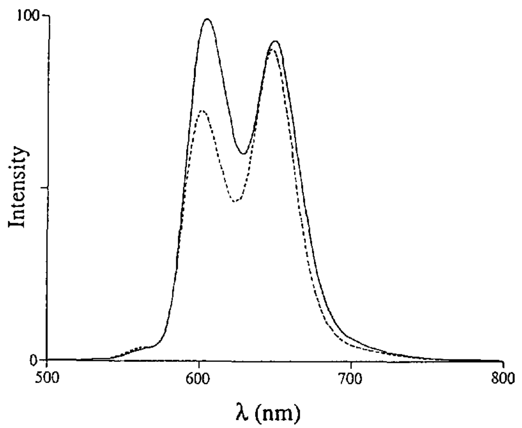


Figure 2 : Superposed fluorescence spectra of **1** (—) and [*meso*-tetraphenylporphinato] Zn(II) (----) 2.1 x 10^{-8} M and 6.9 x 10^{-8} M, respectively, in benzene

The synthesis of **2** started as well from **4a**, which was treated with 1 eq. of (4-ethynylphenyl)tris{[4-[(trimethylsilyl)ethynyl]phenyl]}methane (**3d**) under the conditions c) given in *Scheme 1* to afford the corresponding tripodaphyrin **4d** in 80% yield, the "legs" of which were elongated, after cleavage of the ethynyl protecting groups, by $Pd[P(C_6H_5)_3]_4$ catalysed condensation with 1-iodo-4-[(4-methoxyphenyl)ethynyl]benzene (**5**). The latter was prepared in 65% yield reacting 4-methoxyphenylacetylene[29] with 3 eq. of p-diiodobenzene under analogous conditions as those used for the synthesis of **3b** ($Pd(PPh_3)_4$, CuI, toluene/NEt_3 (5:1), 40°C, 15h). The analytical data of **2**[30] confirm the structure assigned to this compound.

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References and Notes

1. Dolphin, D. (Ed.) *The Porphyrins*; Academic Press, Inc., New York **1979**, Vols 1-7.
2. Falk, J. E. (Ed.) *Porphyrins and Metalloporphyrins*; Elsevier Science Pub. Co., Inc., Amsterdam **1975**.
3. Sheldon, R. A.(Ed.) *Metalloporphyrins in Catalytic Oxidations*; M. Dekker, Inc., New York, **1994**.
4. Montanari, F.; Casella, L. (Eds.) *Metalloporphyrins Catalysed Oxidations*; Vol 17 in the series *Catalysis by Metal Complexes*, Kluver Academic Publ. Dordrecht, **1994**.
5. Momenteau, M.; Reed, C. A. *Chem. Rev.* **1994**, *94*, 659-698.
6. Kurreck, H.; Huber, M. *Angew. Chem.* **1995**, *107*, 929-947. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 849-866.
7. For a recent review see : Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19-33.
8. Hawthorne, M. F. *Angew. Chem.* **1993**, *105*, 997-1033; *Angew. Chem. Int. Ed. Engl.* **1993**,*32*, 950.
9. Phadke, A. S.; Morgan, A. R. *Tetrahedron Lett.* **1993**, *34*, 1725-1728, and references given therein.

10. Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E. *Angew. Chem*, **1994**, *106*, 1620-1639; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1537, and references given therein.
11. Sessler, J. L.; Johnson, M. R.; Creager, S. E.; Fettinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9310-9329, and references given therein.
12. Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 6227-6238.
13. Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941-8968.
14. Abdalmuhdi, I.; Chang, C. K. *J. Org. Chem.* **1985**, *50*, 411-413.
15. Osuka, A.; Kobayashi, F.; Maruyama, K. *Chem. Lett.* **1990**, 1521-1524.
16. Dubowchik, G. M.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.*, **1987**, 293-295.
17. Anderson, S.; Anderson, H, L.; Sanders, J. K. M. *Angew. Chem*, **1992**, *104*, 921-924; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 907.
18. Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266-5273.
19. Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759-9760.
20. Wennerström, O.; Ericsson, H.; Raston, I.; Svensson, S.; Pimlott, W. *Tetrahedron Lett.*, **1989**, *30*, 1129-1132.
21. Prathapan, S.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7519-7520
22. Jung, T. A.; Schlitter, R. R.; Gimzewski, J. K.; Tang, H.; Joachim, C. *Science* **1996**, *271*, 181-184.
23. Suggested trivial name which results from the contraction of τρίποδος (tripod) and πορφυροῦς (purple, *i. e.* porphyrin).
24. Syrbu, S. A.; Semeikin, A. S.; Berezin, B. D. *Khim. Geterotsikl. Soedin.* **1990**, *11*, 1507-1509.
25. Simard, M.; Su, D.; Wuest, J. D *J. Am. Chem. Soc.* **1991**, *113*, 4696-4698.
26. Osuka, A.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Tamai, N. *J. Am. Chem. Soc.* **1990**, *112*, 4958-4959.
27. **Analytical data of compound 1**: UV/VIS (CH_2Cl_2) : λ_{max} (log ε) : 300 (5.28), 422 (6.33), 548 (5.10), 588 nm (4.49); UV/VIS (benzene) : 300 (5.15), 426 (6.26), 550 (4.93), 590 nm (4.34). $\Phi = 0.04$. relative to Zn(II) *meso*-tetraphenylporphine ($\Phi = 0.033$ in benzene[28]). ^{1}H-NMR ($CDCl_3$, 500 MHz), δ : 7.47 and 7.73 (2 × apparent *d*, $J = 8.4$ Hz, 16H, H-phenylene on central C), 7.73-7.79 (m, 36H, m-H and p-H-phenyl), 7.98 and 8.26 (2 × apparent *d*, $J = 8.2$ Hz, 16H, H-phenylene on porphine), 8.21-8.25 (*m*, 24H, o-H-phenyl), 8.96 (s, 16H, β-H on porphine), 8.98 and 9.00 (2 × d, $J = 4.7$ Hz, 16H, β-H on porphine). MALDI-MS: 3120.3 (calc. avg. mass for $C_{209}H_{124}N_{16}Zn_4$: 3120.91) 2344.5 (calc. for M^+-$C_{52}H_{31}N_4Zn$: 2343.7), 776.6 ((calc. for $[C_{52}H_{31}N_4Zn]^+$: 777.22). ES$^+$-MS (in HCO_2H) : m/z 1434 ($[MH_2]^{2+}$), 957 ($[MH_3]^{3+}$), 718 ($[MH_4]^{4+}$), 574 ($[MH_5]^{5+}$) (calc. for $C_{209}H_{132}N_{16}$: 2867).
28. Quimby, D. J,; Longo, F. R. *J. Am. Chem. Soc.* **1975**, *97*, 5111-5117.
29. Allen, A. D.; Cook, C. D. *Can. J. Chem.* **1963**, *41*, 1084-1087.
30. **Analytical data of compound 2**: UV/VIS (CH_2Cl_2) : λ_{max} (log ε) : 334 (5.33), 421 (5.71), 548 (4.40), 590 nm (3.88). ^{1}H-NMR (CDCl3, 500 MHz), δ : 3.83 (s, 9H, OCH3), 6.89 and 7.48 (2 × apparent *d*, $J = 8.7$ Hz, 12H, H-methoxyphenylene), 7.29 and 7.51 (2 × apparent *d*, $J = 8.4$ Hz, 12H, H-phenylene on central C), 7.31 and 7.63 (2 × apparent *d*, $J = 8.4$ Hz, 4H, H-phenylene on central C), 7.50 (s, 12H, H-centralphenylene of the *legs*), 7.73-7.80 (m, 9H, m-H and p-H-phenyl), 7.93 (apparent *d*, $J = 8.1$ Hz, 2H, H-phenylene on porphine), 8.20-8.26 (m, 8H, 2 H-phenylene on porphine and 6 o-H-phenyl), 8.96 (s, 4H, β-H on porphine), 8.98 (s, 4H, β-H on porphine). FAB-MS: 1711.6 (calc. avg. mass for $C_{122}H_{76}N_4O_3Zn$: 1711.36).

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