Rational approach to the synthesis of meso–meso (5,5′) linked bis-porphyrins

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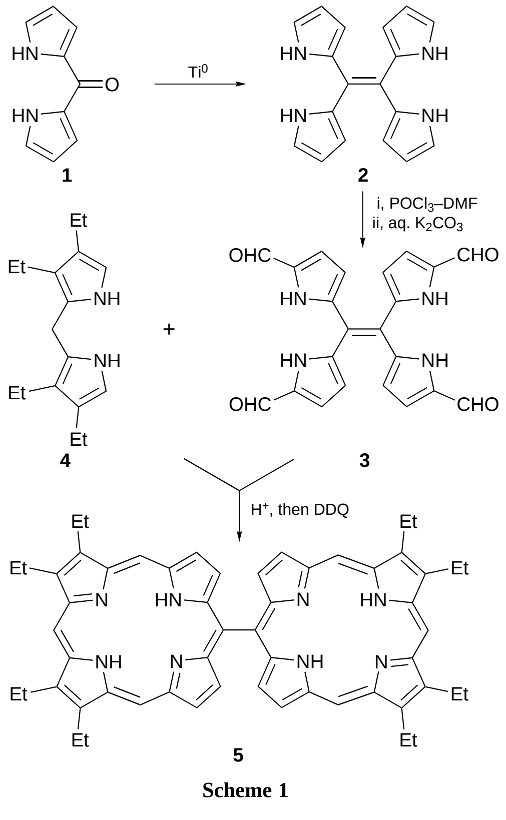
A novel approach for the synthesis of 5,5′-directly linked metal-free bis-porphyrins is reported; McMurry type coupling of dipyrroketones (*e.g.* 1) leads to 1,1,2,2-tetra(2-pyrrolyl)ethene 2, which after tetra-formylation (to give 3) and MacDonald macrocyclization with a 1,9-di-unsubstituted dihydrodipyrrin 4, affords the 5,5′-bis-porphyrin 5.

Publications of structural data on bacterial photosynethetic reaction centres[1] have encouraged interest in the synthesis of oligoporphyrin systems which can act as mimics of reaction centres and antenna systems in photosynthetic bacteria and plants.[2,3] Many porphyrin arrays, including dimers and trimers, have been synthesized for this purpose, and for use in supramolecular photonics.[4] Distance, geometry and orientation have been recognized as important factors for control of the efficiency of energy and electron transfer processes.[5,6] Electronic interaction between porphyrin rings is essential and for this reason we set out to design a number of porphyrin oligomers in which the individual π-systems can interact. A number of dimeric porphyrin arrays, with various spacers, have been synthesized.[7] We surmised that a bis-porphyrin system possessing a direct meso–meso (5,5′) link would be potentially interesting. In the recent publication of Segawa and co-workers[8a] an attempt to prepare a trimeric porphyrin system resulted in serendipitous formation of a bis-porphyrin linked by a single bond between meso positions; this report has caused us to report our rational synthetic approach to this type of bis-porphyrin. After submission of the present paper an additional report of the synthesis of meso–meso bisporphyrins, *via* oxidative coupling of a zinc(II) porphyrin, appeared.[8b]



Scheme 1

2,2′-Dipyrroketone[9] **1** was coupled under McMurry conditions[10,11] in the presence of pyridine at room temperature to afford a 56% yield of the 1,1,2,2-tetra(2-pyrrolyl)ethene **2** (Scheme 1).[12]† As observed with simpler 1,2-di(2-pyrrolyl)ethenes,[13,14] compound **2** was highly fluorescent. In the solid state the 1,1,2,2-tetra(2-pyrrolyl)ethene was stable, but in solution slow decomposition was observed. The molecular structure of **2**‡ was confirmed by X-ray crystallography (Fig. 1).

Attempted MacDonald-type (‘2 + 2’) macrocyclization of the tetrapyrrolylethene **2** with 1,9-diformyl-2,3,7,8-tetraethyldihydrodipyrrin led to a mixture of products. But tetraformylation of **2** using excess $POCl_3$–DMF, followed by treatment with K_2CO_3, afforded the tetra[5-formyl-2-pyrrolyl]ethene **3**§ in 92% yield. Condensation of **3** with 2 equiv. of 2,3,7,8-tetraethyldihydrodipyrrin **4**, followed by oxidation with DDQ and filtration through a plug of silica gel, led to the symmetrical 5,5′-bis-porphyrin **5**¶ in 7% yield. The molecular structure of **5**‡ was confirmed by X-ray crystallography [Fig. 2(*a*)]. Each porphyrin subunit is fairly planar, exhibiting a mean plane

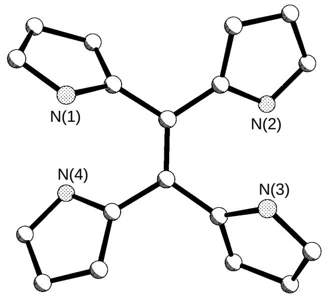


Fig. 1 Molecular structure of the 1,1,2,2-tetra(2-pyrrolyl)ethene **2**. Hydrogen atoms have been omitted for clarity.

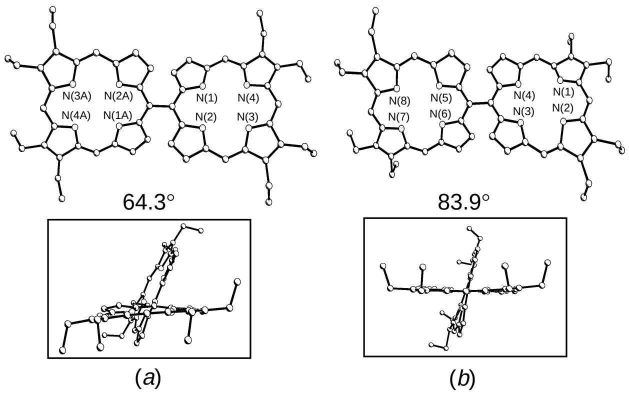


Fig. 2 Molecular structure of the 5,5′-bis-porphyrin **5**. (*a*) The form crystallized from THF–hexane. (*b*) The form crystallized from dichloromethane–methanol. The boxes beneath each structure show side views along the 5,5′-bond. Hydrogen atoms have been omitted for clarity.

deviation of 0.10 Å from the 24 core atoms. A covalent single bond (1.51 Å) links both porphyrin subunits at the meso position. The angle between both porphyrin planes is 65°, and this is almost certainly a feature of lattice packing. When **5** was crystallized from a different solvent system, a second crystal structure‡ was obtained [Fig. 2(*b*)]; this showed the angle between both macrocyclic planes to be 83.9°.

Further work is aimed at synthesis of unsymmetrically substituted 5,5′-bis-porphyrin systems, and higher oligomers.

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Footnotes

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† *Selected data* for **2**: Mp 180–182 °C UV–VIS λ_{max} (CH_2Cl_2) 302 nm (ε 9200), 364 (15 800); δ_H (300 MHz, $CDCl_3$) 6.07 (m, 4 H, β-H), 6.18 (d, 4 H, β-H), 6.69 (d, 4 H, β-H), 7.93 (s, 4 H, NH). HRMS $C_{18}H_{16}N_4$ requires: *m/z* 288.1374, found: 288.1378.

‡ *Crystal data*: The structures were solved by direct methods and refined (based on F^2 using all independent data) by full matrix least-squares methods (Siemens SHELXTL V. 5.02). Hydrogen atom positions were located by their idealized geometry and refined using a riding model. For each structure an absorption correction was applied using XABS2.[15] For **2** ($C_{18}H_{16}N_4$): X-ray diffraction data were collected on a Siemens $P2_1$ diffractometer with a fine-focus sealed tube [λ(Cu Kα) = 1.54178 Å] at 130(2) K in θ/2θ scan mode to $2\theta_{max} = 112°$. Crystals were grown from a mixture of dichloromethane and cyclohexane. A single parallelipeped crystal was selected with dimensions 0.40 × 0.12 × 0.10 mm. The unit cell was triclinic and space group $P\bar{1}$ with cell dimensions: a = 8.231(2), b = 9.335(2), c = 9.671(2) Å, α = 98.64(3), β = 103.22(3), γ = 93.22(3)°, V = 712.0(2) Å^3 and Z = 2 (FW = 288.35, ρ_{calc} = 1.345 g cm^{-3}, μ = 0.652 mm^{-1}). Of 1948 reflections measured (±h, ±k, +l) 1923 were independent and 1431 had $I > 2\sigma$ (R_{int} = 0.012); number of parameters = 199. Final R factors were $R1$ = 0.0524 (based on observed data) and $wR2$ = 0.1304 (based on all data). For **5**: X-ray diffraction data were collected on a Siemens P4 rotating anode diffractometer with a fine-focus sealed tube [λ(Cu Kα) = 1.54178 Å] at 130(2) K in θ/2θ scan mode to $2\theta_{max} = 113°$. First structure [Fig. 2(*a*)]; single crystals of **5** ($C_{56}H_{58}N_8\cdot C_4H_8O\cdot 1.5H_2O$) were grown from a mixture of THF and hexane. A single pyramidal crystal was selected with dimensions 0.18 × 0.12 × 0.10 mm. The unit cell was monoclinic $C2/c$ with cell dimensions: a = 26.068(6), b = 17.644(3), c = 13.842(3) Å, β = 115.99(2)°, V = 5723(2) Å^3, and Z = 4 (FW = 987.25, ρ_{calc} = 0.587 g cm^{-3}, μ = 0.555 mm^{-1}). Of 4086 reflections measured (±h, +k, +l) 3783 were independent and 2594 had $I > 2\sigma$ (R_{int} = 0.117); number of parameters = 343. Final R factors were $R1$ = 0.0921 (based on observed data) and $wR2$ = 0.3064 (based on all data). Second structure [Fig. 2(*b*)]: Crystals of **5** ($C_{56}H_{58}N_8$) were grown from a mixture of dichloromethane and methanol. A single parallelipeped crystal was selected with dimensions 0.34 × 0.14 × 0.06 mm. The unit cell was triclinic and space group $P\bar{1}$ with cell dimensions a = 8.4926(14), b = 12.859(2), c = 21.648(3) Å, α = 96.469(11), β = 97.470(12), γ = 101.096(12)°, V = 2277(6) Å^3 and Z = 2 (FW = 843.10, ρ_{calc} = 1.230 g cm^{-3}, μ = 0.567 mm^{-1}). Of 6700 reflections measured (±h, ±k, +l) 6006 were independent and 4430 had $I > 2\sigma$ (R_{int} = 0.034); number of parameters = 199. Final R factors were $R1$ = 0.0601 (based on observed data) and $wR2$ = 0.1745 (based on all data). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 183/433.

§ *Selected data* for **3**: Mp 190–193 °C; UV–VIS **3**: λ_{max} (CH_2Cl_2) 438 nm (ε 29 900); δ_H (300 MHz, $CDCl_3$): 5.21 (d, 4 H, β-H), 6.11 (d, 4 H, β-H), 8.58 (s, 4 H, CHO), 10.20 (br s, 4 H, NH); MS $C_{22}H_{16}N_4O_4$ requires: *m/z* 400.6, found: 400.11.

¶ *Selected data* for **5**: Mp > 300 °C; UV–VIS λ_{max} (CH_2Cl_2) 400 nm (ε 141 000), 436 (155 000), 508 (41 700), 574 (19 600), 626 (8100); δ_H (300 MHz, $CDCl_3$): −2.95 (br s, 4 H, NH) 2.01 (m, 24 H, CH_2CH_3), 4.18 (m, 16 H, CH_2CH_3), 8.19 (s, 4 H, β-H), 9.06 (s, 4 H, β-H), 10.22 (s, 2 H, meso-H), 10.26 (s, 4 H, meso-H); MS $C_{56}H_{58}N_8$ requires: *m/z* 843.14, Found: 843.38.

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