Rigid, Laterally-bridged Bis-porphyrin Systems

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The synthesis of novel bis-porphyrin systems in which the porphyrins are rigidly constrained in a coplanar arrangement is reported.

We report the first synthesis of a bis-porphyrin system in which the macrocycles are rigidly constrained in a coplanar arrangement. Such compounds are of interest as chemical models for physiological electron-transfer systems.[1] Our strategy for the synthesis of rigidly bridged bis-porphyrin systems involves the 2 : 1 condensation of an α-dione (17,18-dioxochlorin) with a tetra-amine; the α-diones being accessible by an efficient route which we developed in earlier work.[2]

Treatment of 17,18-dioxo-5,10,15,20-tetraphenylchlorin (**1**)[2] (3 equiv.) with 1,2,4,5-benzenetetramine tetrahydrochloride (**3**) in pyridine for 27 h, followed by chromatography to remove unreacted dione, afforded a 71% yield of the bis-porphyrin (**4**)† [$\lambda_{max.}$ (log ε) ($CHCl_3$): 423(5.56), 456(5.51), 609(4.31), 629(4.32), 676 nm (3.96); *m/z* 1354] (Scheme 1). The origin of the two, very intense, absorption maxima in the Soret region of the visible spectrum of (**4**) is under investigation; this spectral feature is common to all the bis-porphyrins prepared in this study, and is not observed in the spectra of model linear compounds which lack the second porphyrin ring. The D_{2h} symmetry of (**4**) is apparent from the relatively simple ^1H n.m.r. spectrum: δ ($CDCl_3$): −2.39 (s, 4H, NH), 7.81 (m, 12H, $H_{m,p}$ at $C_{4,7,17,20}$), 7.97 (t, *J* 7.5 Hz, 8H, H_m at $C_{1,10,14,23}$), 8.15 (t, *J* 7.5 Hz, 4H, H_p at $C_{1,10,14,23}$), 8.25 (m, 16H, H_o), 8.56 (s, 2H, $H_{12,25}$), 8.71 (s, 4H, $H_{5,6,18,19}$), 8.96 and 9.04 (ABq, J_{AB} 5 Hz, 8H, $H_{2,3,8,9,15,16,21,22}$).

The porphyrin units in compound (**4**) are coplanar and project pyrrolic rings towards each other at an interporphyrin separation of 7.5 Å (from examination of a Dreiding model). This spatial arrangement of porphyrins is very similar to that of the central haems in the cytochrome unit of the photosynthetic reaction centre from *Rhodopseudomonas viridis* in which the porphyrins are nearly coplanar and are aligned in such a way that they project pyrrolic rings towards each other at an interporphyrin separation of 7.5—8.5 Å (iron–iron distance: *ca.* 16 Å).[3] A similar spatial arrangement of two porphyrins has also been proposed to be important in electron-transfer steps in several other biological systems.[4]

As compound (**4**) has low solubility in most solvents, we were prompted to synthesize the much more lipophilic hexadeca t-butyl analogue (**5**). The starting dione, 17,18-dioxo-5,10,15,20-tetrakis(3,5-di-t-butylphenyl)chlorin (**2**), was prepared in 53% overall yield in six steps from 5,10,15,20-tetrakis(3,5-di-t-butylphenyl)porphyrin, following our earlier route.[2,5]

Treatment of the dione (**2**) with the salt (**3**) (2.8 equiv.) in pyridine for 9 days gave an 89% yield of (**5**) [$\lambda_{max.}$ (log ε) ($CHCl_3$): 426(5.54), 458(5.51), 498sh(4.96), 604sh(4.27), 614sh(4.30), 630(4.34), 677 nm(3.87); ^1H n.m.r. ($CDCl_3$): δ −2.31 (s, 4H), 1.54 (s, 36H, t-butyl), 1.59 (s, 36H, t-butyl), 7.81 (t, *J* 2 Hz, 4H), 8.00 (t, *J* 2 Hz, 4H), 8.10 (m, 16H), 8.59 (s, 2H), 8.76 (s, 4H), 8.89 and 8.96 (ABq, J_{AB} 5 Hz, 8H).

When 1,2,4,5-tetra-aminobenzene was used directly in the preparation of (**4**), the reaction rate was faster by at least an order of magnitude but the yield (10—60%) of bis-porphyrin was lower, apparently because of the susceptibility of reaction intermediates to oxidation.

The electronic properties of the bis-porphyrin systems were modified by metal ion chelation. The bis-porphyrin (**5**) was readily metallated in boiling dichloromethane–methanol by treatment with an excess of zinc acetate to yield the bis-zinc

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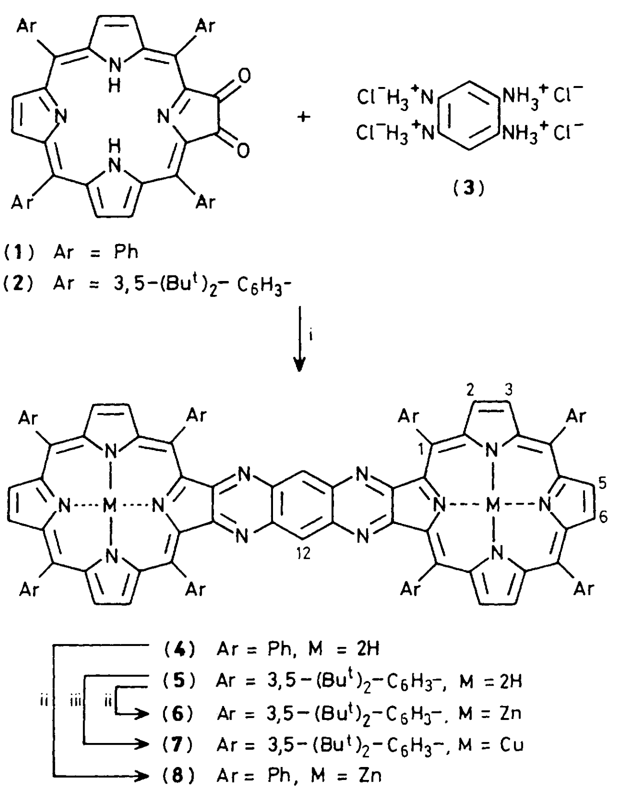
† All new porphyrins have been characterised by analytical and/or spectroscopic means.



Scheme 1. i, see text, reaction at room temperature under nitrogen in dark; ii, $Zn(OAc)_2 \cdot 2H_2O$ (10 equiv.) in boiling CH_2Cl_2–MeOH (25:2), 1 h, then H_2O wash and filtration through silica; iii, $Cu(OAc)_2 \cdot H_2O$ (10 equiv.) in boiling CH_2Cl_2–MeOH (25:2), 1 h, then H_2O wash and filtration through silica.

compound (**6**) [$\lambda_{max.}$ (log ε) ($CHCl_3$): 430(5.54), 463(5.52), 524(4.85), 667(4.33), 705sh(4.30); ^{1}H n.m.r. spectrum consistent with D_{2h} symmetry] in 84% yield, and with copper acetate to yield the bis-copper compound (**7**) [$\lambda_{max.}$ (log ε) ($CHCl_3$): 424(5.50), 454(5.40), 515(4.84), 537(4.84), 671(4.40)] in 91% yield. Similar treatment of the bis-porphyrin (**4**) with an excess of zinc acetate gave the bis-zinc compound (**8**) in 72% yield.

Preliminary cyclic voltammetry studies on bis-porphyrins (**4**) [$E_{\frac{1}{2}}$ *vs.* Ag/$AgNO_3$ in CH_2Cl_2 (0.1 M $Bu_4N^+PF_6^-$), Pt disc electrode: −1.11, −1.28, −1.53, −1.73 V], (**5**), and (**8**) have shown that each compound undergoes a progression of four reversible one-electron reductions to form the corresponding tetra(π-anion). This observation requires that the porphyrin rings are in communication otherwise two two-electron reductions [to a bis(π-anion-radical) then to a bis(π-dianion)] would have been observed; these results will be reported fully elsewhere.[6] Work directed towards disruption of the conjugation in the bridging structure of these bis-porphyrins by the use of Diels–Alder reactions is underway.

Extension of the synthetic strategy outlined in this communication to the synthesis of other bridged systems, whereby the interporphyrin distance, the degree of bond saturation, and the angle between the macrocycle planes is systematically varied, is under active investigation in our laboratories.

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