

An Approach to Porphyrin-based Molecular Wires: Synthesis of a Bis(porphyrin)tetraone and its Conversion to a Linearly Conjugated Tetrakisporphyrin System

Maxwell J. Crossley* and Paul L. Burn

Department of Organic Chemistry, The University of Sydney, NSW 2006, Australia

An approach to molecular wires based on quasi-one-dimensional linearly conjugated poly-porphyrin systems is outlined and a rationally designed synthesis of the tetrakisporphyrin **9**, a strand some 65 Å in length, *via* the bis(porphyrin)tetraone **2** is described.

The development of an effective 'molecular wire' will be a key element in the realization of molecular electronic devices. A molecule that meets the functional requirements for such a 'wire' needs to satisfy the following criteria: it must be electron conducting; have a defined length capable of spanning a supporting element such as a monolayer or bilayer lipid membrane; have termini that can be connected to the functional components of the system; allow redox reactions at its termini; and the interior of the 'wire' should be insulated from the surroundings to prevent indiscriminate electron transfer. In this communication, we outline an approach to such 'molecular wires' based on porphyrins and we describe the synthesis of the quasi-one-dimensional, fully conjugated tetrakisporphyrin **9** by way of the bis(porphyrin)tetraone **2**. The tetrakisporphyrin **9** is about 65 Å long and has a sheath of *tert*-butyl groups along the backbone that insulate the conjugated core from the surroundings as well as providing the molecule with good solubility in a number of organic solvents.

Poly-porphyrin systems, in which individual porphyrin rings are either directly fused or are bridged by coplanar aromatic systems, are expected to meet the criteria for electrical conductivity. Porphyrins can be readily oxidized to π -cation radicals and then to π -dications; similarly, they can be reduced readily to π -anion radicals and π -dianions. The highest-occupied and lowest-unoccupied molecular orbitals (HOMO

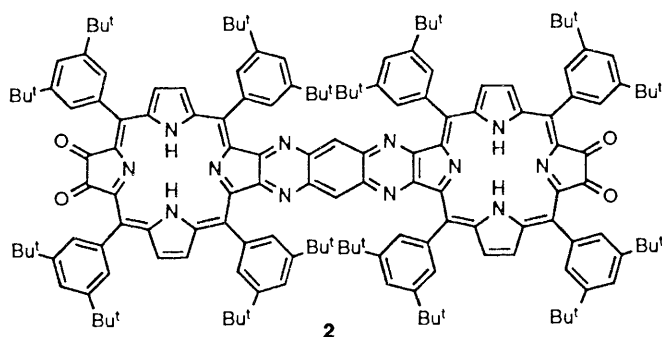
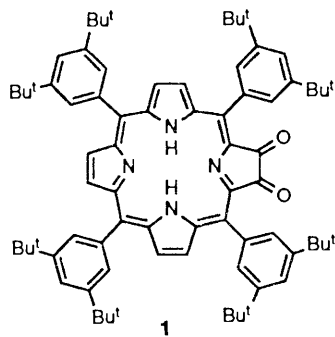
and LUMO, respectively) of porphyrins are generally separated by only 2 eV; this gap has to be narrowed only slightly to bring it into the range in which useful electrical properties can be expected. Furthermore, metal chelation at the porphyrin inner periphery allows considerable control of the redox properties of such systems, given that some 56 different metals are known to form complexes with porphyrins. The free positions on the outer periphery of the porphyrin rings could be substituted with appropriate solubility-controlling groups or functionalities.

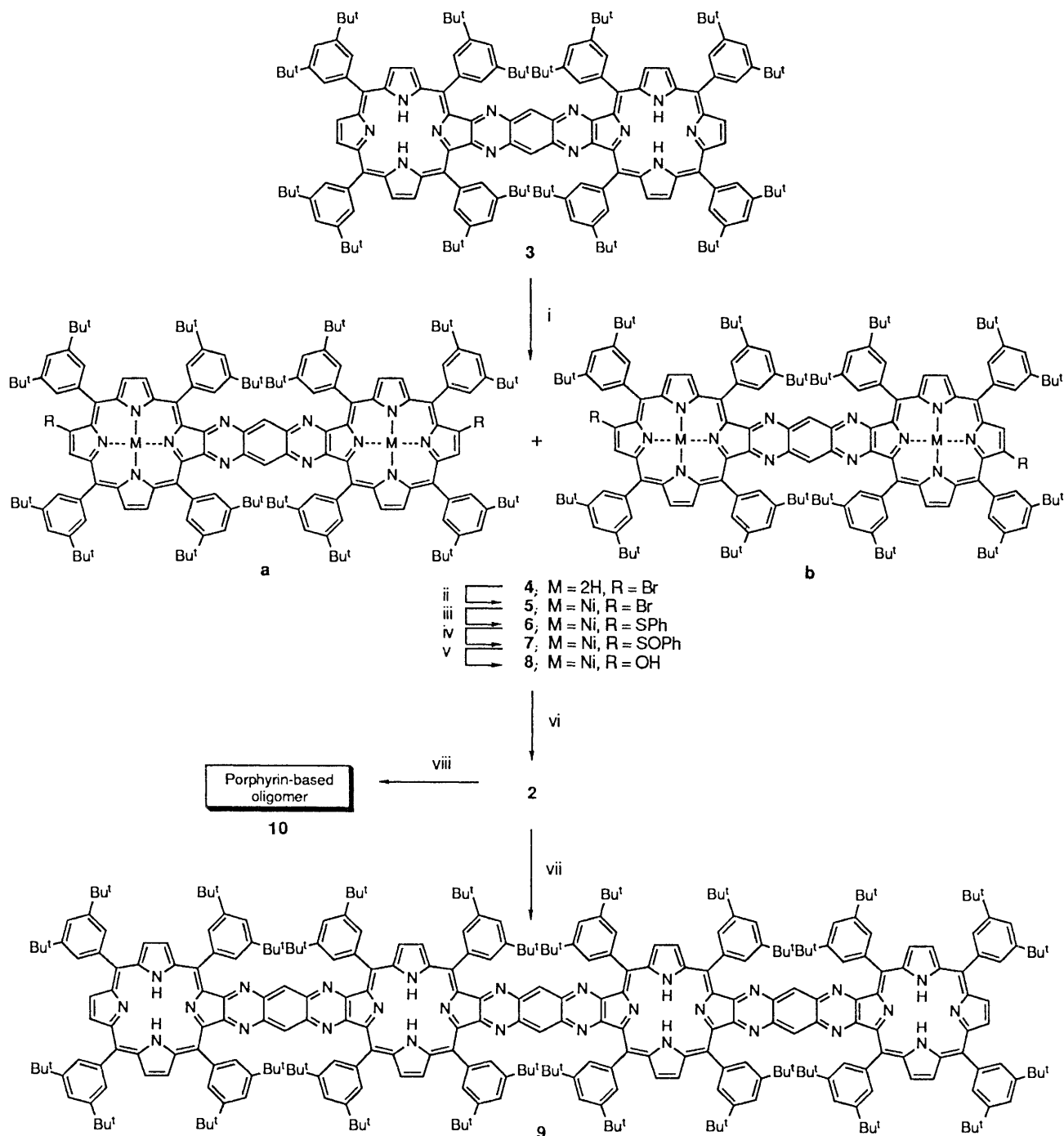
The strategy for the synthesis of extended porphyrin systems exploits advances in porphyrin chemistry, which we have developed recently, and involves the condensation of a porphyrin- α -dione (bis- α -dione for the synthesis of polymers) with a bis- α -diamine. In earlier work, we reported the synthesis of the lipophilic, planar, laterally bridged, rigid bisporphyrin system **3** by the condensation of dione **1** with benzenetetramine.¹ Electrochemical studies have shown that bisporphyrin **3** and its di-zinc(II) and di-copper(II) chelates are substantially delocalized systems and each compound shows four reversible one-electron reductions;² compared with the corresponding porphyrins, these bisporphyrin systems have significantly narrowed HOMO-LUMO energy gaps (by 0.4–0.5 eV).

The synthesis of the extended porphyrin system **9** involved a seven-step sequence (Scheme 1). The approach required a porphyrin system which has α -dione units at β -pyrrolic positions on antipodal rings. A regiospecific route has been established to the key precursor **2** and is based on new advances in porphyrin chemistry described in the preceding two communications.^{3,4}

The key step is the regiospecific bromination of the $\Delta^{7,8}$ and $\Delta^{7',8'}$ double bonds of the bisporphyrin **3**; in the free-base form, these double bonds are the only positions on the molecule with full double-bond character.³ Treatment of **3** with *N*-bromosuccinimide (NBS) (2.2 equiv.) gave a 1:1 mixture of the regioisomers, 7,7'- and 7,8'-dibromobisporphyrin **4a** and **b**, together with a very small amount of the 7,8-dibromo derivative. When 4.3 equiv. of NBS were used in the reaction the corresponding 7,7',8,8'-tetrabromobisporphyrin was obtained pure in 75% yield by crystallization of the crude reaction product.

The dibromobisporphyrins **4** were transformed into the tetraone **2** by the process developed on simple porphyrins described in the preceding communication.⁴ Metallation of **4** using an excess of nickel(II) acetate dihydrate in *N,N*-dimethylformamide (DMF) at reflux for 1.75 h gave the di-nickel(II) bisporphyrins **5**, which on treatment with an excess of benzenethiolate ion under nitrogen in DMF at 117 °C for 70 h afforded the di-nickel di(phenylthio)bisporphyrins **6**, after work-up and chromatography over silica (solvent CH₂Cl₂: light petroleum, 1:6), in 58% yield from **3**. Peracetic acid oxidation of **6** in dry toluene at 25 °C for 20 min gave the di-nickel di(phenylsulphonyl)bisporphyrin **7** in 68% yield and some of the monooxidized compound; longer reaction times led to extensive destruction of the bisporphyrin. Treatment of **7** with the anion of *E*-benzaldoxime in Me₂SO at 128–144 °C for 2.75 h gave the dihydroxybisporphyrins **8** in 60% yield. Demetallation of **8** (H₂SO₄-CH₂Cl₂) followed by oxidation





Scheme 1 Reagents and conditions: i, NBS (2.2 equiv.) in refluxing CHCl_3 , 2 h; ii, $\text{Ni}(\text{OAc})_2$ in DMF; iii, excess PhSH-LiOH in DMF; iv, excess MeCO_3H in dry toluene; v, *E*-benzaloxime-NaH (20 equiv.) in Me_2SO ; vi, $\text{H}_2\text{SO}_4\text{-CH}_2\text{Cl}_2$, 15 min, followed by neutralization, then SeO_2 (10 equiv.) in dioxane; vii, 1,2,4,5-benzenetetramine tetrahydrochloride (2.2 equiv.) in dry deoxygenated pyridine, then dione **1** (3.5 equiv.); viii, 1,2,4,5-benzenetetramine tetrahydrochloride (1.0 equiv.) in dry deoxygenated pyridine for 37 days, then *o*-phenylenediamine (20 equiv.)

with SeO_2 in refluxing dioxane for 20 min afforded the tetraone **2**,[†] in 29% yield.

The tetrakisporphyrin **9**[‡] was obtained by treatment of the bis(porphyrin)tetraone **2** with 2.2 equiv. of 1,2,4,5-benzenetetramine tetrahydrochloride in pyridine as solvent and base

for 2.5 h at 84 °C and then addition of this mixture to excess porphyrin-dione **1** (to end-cap the system) and holding the reaction mixture at 70–88 °C for a further 40 h. The pure tetrakisporphyrin **9**[‡] was obtained in 10% overall yield by

[†] Selected spectroscopic data: **2** $\text{C}_{158}\text{H}_{182}\text{N}_{12}\text{O}_4$. IR (CHCl_3) ν_{max} 1724 cm^{-1} . VIS (CHCl_3) λ_{max} (log ϵ) 406sh (5.30), 419 (5.34), 442sh (5.23), 494sh (5.01), 563sh (4.45), 642 (4.12), 704 (4.17), and 751 nm (4.10). ^1H NMR (400 MHz, CDCl_3) δ -1.92 (br s, 4H), 1.548 and 1.554 (each s, 144H), 7.74 (d, 8H), 7.77 (t, 4H), 7.97 (t, 4H), 8.00 (d, 8H), 8.52 (s, 2H), 8.62 and 8.71 (d of ABq, J_{AB} 5.00, $^4J_{\text{NH,A}}$ 1.85, $^4J_{\text{NH,B}}$ 1.85 Hz).

[‡] **9**: VIS (CHCl_3) λ_{max} (log ϵ) 426 (5.63), 466 (5.51), 527sh (5.27), 574 sh (4.98), 611sh (4.60), 641sh (4.48), 664 (4.49), 722 (4.26), and 786 nm (2.88). ^1H NMR (400 MHz, CDCl_3) δ -2.31 (br s, 4H), -2.14 (br s, 4H), 1.54, 1.60, 1.613, 1.617 (each s, 288H), 7.81 (t, 4H), 8.00 (br t, 12H), 8.10–8.13 (32H), 8.60 (s, 2H, central bridge H), 8.61 (s, 4H, side bridge H), 8.76 (s, 4H, end β -pyrrolic H), 8.88–8.90, (12 H, side β -pyrrolic H), 8.96 (B part of ABq, 4H, side β -pyrrolic H). FAB-MS (3-nitrobenzyl alcohol- CH_2Cl_2 matrix) m/z 4627 \pm 5.

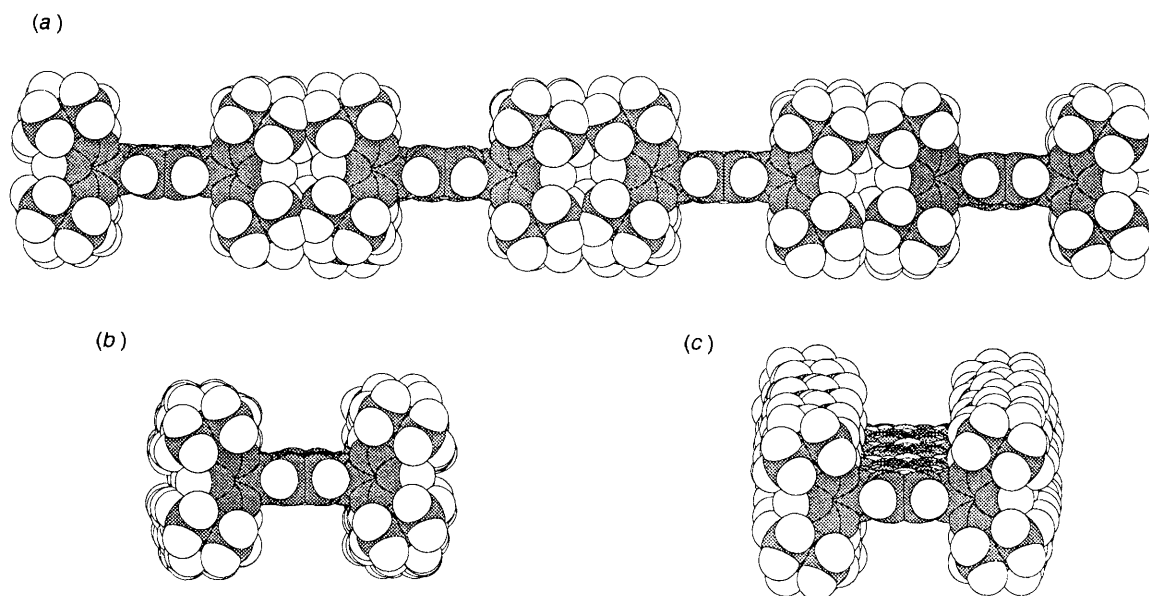


Fig. 1 A space-filling model of the tetrakisporphyrin **9**: (a) side view; (b) end view; (c) end view from 3° elevation

gel-permeation chromatography over Sephadex LH-60 (CHCl_3) which readily separated it from the slower running bisporphyrin by-product **3** (29%). The tetrakisporphyrin **9** ($\text{C}_{322}\text{H}_{370}\text{N}_{28}$; M_r 4632.653) is soluble in a number of organic solvents, including chlorinated hydrocarbons, and was able to be chromatographed in hexane- CH_2Cl_2 mixtures; indeed, it is relatively non-polar and runs ahead of the bisporphyrin **3** in these solvents on silica. Model building§ indicated that the tetrakisporphyrin **9** is about 65 Å in length with a fully conjugated essentially planar polyporphyrin backbone (Fig. 1). The *tert*-butyl groups provide a sheath of lipophilic character to the molecule, which in some ways resembles an insulated wire.

For good conduction properties in 'organic metals' it is desirable to have a system which has a linear (planar) array of overlapping (sp^2) orbitals and which can also be easily oxidized or reduced; such a system should also have only a small band (HOMO-LUMO) gap.^{5,6} One dimensional tight-binding band theory, an extension of Hückel theory, has become the accepted model for understanding charge-transport properties of these materials.^{7,8} It follows from this model that as a conjugated system is extended, the band gap decreases. Preliminary spectroscopic studies on the tetrakisporphyrin **9** indicate that the HOMO-LUMO gap has narrowed significantly (by *ca.* 0.8 eV) compared with the same gap in simple porphyrins.

Although the route to extended porphyrin systems still requires optimization of a number of steps, the overall reaction sequence is applicable to both small and multi-gram scale preparations and the route is sufficiently flexible to allow the incorporation of other porphyrin and metalloporphyrin units. Work on the properties of the tetrakisporphyrin **9**, and its metal chelates, is continuing and is a major theme in our laboratory.

Finally, condensation of equimolar amounts of bis(porphyrin)tetraone **2** and 1,2,4,5-benzenetetramine in pyridine for

up to 37 days followed by end-capping of the products by reaction with *o*-phenylenediamine has given rise to oligometric-porphyrins **10** (Scheme 1) of molecular weights well in excess of 5000 units. These materials are presently under investigation.

These materials are designed to have substantial alignment and overlap of atomic orbitals in both solution and the solid state and to overcome difficulties (solubility, tractability, control of redox properties and processability) of existing 'organic metals.' Rational and specific syntheses of tris-, pentakis-, and octakisporphyrin analogues of the tetrakisporphyrin **9** are also underway, as is extension of the work to incorporate 'connectors' at the terminal porphyrins of the chain.

We thank the Australian Research Council and the University of Sydney for research grants to M. J. C. and the Australian Government for a Post-graduate Research Award to P. L. B.

Received, 10th July 1991; Com. 1/03495B

References

- M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1987, 39.
- P. L. Burn, M. J. Crossley and P. A. Lay, in *Electrochemistry-Current and Potential Applications* ed. T. Tran and M. Skyllas-Kazacos, Royal Australian Chemical Institute, Electrochemistry Division, Kensington, 1988, pp. 245-247.
- M. J. Crossley, P. L. Burn, S. S. Chew, F. B. Cuttance and I. A. Newsom, *J. Chem. Soc., Chem. Commun.*, 1991, 1564.
- M. J. Crossley, P. L. Burn, S. J. Langford, S. M. Pyke and A. G. Stark, *J. Chem. Soc., Chem. Commun.*, preceding Communication.
- J. Heinze, *Top. Curr. Chem.*, 1990, **152**, 1.
- R. H. Baughman, J. L. Brédas, R. R. Chance, R. L. Elsenbaumer and L. W. Shacklette, *Chem. Rev.*, 1982, **82**, 209.
- R. E. Peierls, *Quantum Theory of Solids*, OUP, London, 1955.
- E. Cliberto, K. A. Doris, W. J. Pietro, G. M. Reisner, D. E. Ellis, I. Fragala, F. H. Herbstein, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 7748.

§ The program CHEM 3D PLUS™ (Version 3.0, 1991) from Cambridge Scientific Computing, Inc, Cambridge MA, USA was used on a Macintosh IIfx.