# Linear fused oligoporphyrins: potential molecular wires with enhanced electronic communication between bridged metal ions

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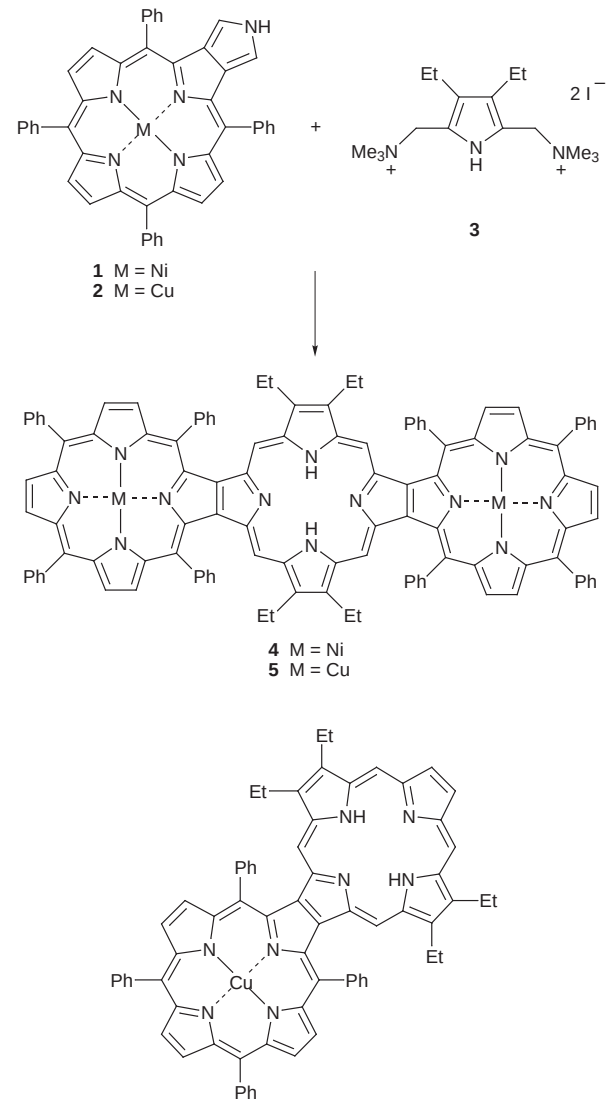
**Syntheses of nanometer scale, directly beta-fused oligoporphyrins sharing an extended π-system are described.**

One-dimensional oligomers containing photoactive and/or redox-active units allow the possibility of long distance delocalization of electron density and metal–metal interactions between multiple metal centres.[1] These appealing architectures may present a range of interesting opportunities based on energy- and electron-transfer processes involving communication along and between these units. Such 'photonic molecular wires' based on side-to-side oligomerization of *meso*-functionalized porphyrins have been studied and have been shown to absorb light at one end of an array of porphyrins and then emit a different photon at the other end.[2] Crossley and Burn outlined criteria which these molecular wires need to meet, and described a synthetic approach to rigid π conjugated porphyrin-based molecular wires.[3] These oligoporphyrins, in which individual porphyrin rings are bridged by coplanar aromatic systems, were synthesized by sequential condensation of porphyrin-2,3-diones and/or porphyrin-2,3,12,13-tetraones with aromatic *ortho*-diamines. The versatility of this methodology was further demonstrated in the recent synthesis of thiophene appended porphyrins[4] and donor bridge-acceptor systems involving porphyrin and phenanthroline.[5] However, the conjugation pathway through bridged oligoporphyrins does not exhibit a large fully-delocalized aromatic network which could possibly give rise to metallic type conduction, and could rather be described as a series of weakly-interacting chromophore conjugation loops.[6] Directly fused oligoporphyrins sharing a common extended π electron system have not been yet synthesized. We now describe their synthesis based on pyrrolo-fused porphyrin building blocks, readily available in three steps from $Ni^{II}$ 5,10,15,20-tetraphenylporphyrin.[7]

Because of the instability of the metal-free fused pyrroloporphyrins,[7b] the oligomerization step was carried out on the more stable nickel or copper complexes, **1** and **2**. Under non-acidic conditions, quaternized 2,5-bis(*N*,*N*-dimethylaminomethyl)-3,4-diethylpyrrole **3**[8] reacted smoothly in refluxing MeOH–THF (1 : 1) with **1** in the presence of 10 equiv. of $K_3Fe(CN)_6$ to afford, after chromatography, an 18% yield of porphyrin trimer **4** [$\lambda_{max}$ 405, 481 (Soret band), 557, 649, 681, 715 nm] (Scheme 1). Pre-quaternisation of the pyrrole with MeI was found to be necessary in order to enhance its reactivity toward the nucleophilic, but sterically congested, fused pyrroloporphyrin **1**. The formation of a new central free base porphyrin was revealed by the NH resonances (−2.55 ppm) in the $^1H$ NMR spectrum. The molecular structure of **4**·$(HCl)_2$ was further confirmed by X-ray crystallography. The central porphyrin appears to possess enhanced basicity since $CHCl_3$ readily caused protonation to give the dication (which was crystallized). This protonation phenomenon apparently facilitated the crystal packing by enabling π–π stacking to occur only between terminal porphyrins, thus giving rise to independent linear rods of fused porphyrins (Fig. 1). Attempts to grow suitable crystals of the non-protonated species failed, which was most likely caused by a random π–π stacking. The inner porphyrin dication adopts a saddle conformation with a mean plane deviation of the 24 core atoms of 0.376 Å. Both of the terminal nickel porphyrins adopt a ruffled conformation with a mean plane deviation of the 24 core atoms of 0.411 and 0.428 Å. The porphyrin trimer has an edge-to-edge span of 27.0 Å and the intermolecular distance between metals is 16.16 Å.

Mixed condensation of **2**, **3** and pyrrole [THF–MeOH/$K_3Fe(CN)_6$/reflux] gave the fused dimer **6** [$\lambda_{max}$ 397, 468 (Soret band), 548, 590, 652 nm], as well as some fused trimer **5** in unoptimized yields of 6 and 5%, respectively (Scheme 1). MALDI-TOF mass spectroscopy confirmed dimer and trimer formation, with ions at *m/z* 1069.5 and 1716.8. Compared with pyrroloporphyrin **1**, the bathochromic shift and hyperchromic effect displayed by the fused porphyrins reflect their extended π-conjugation. The Soret bands of **4**–**6** are significantly red




**Scheme 1**

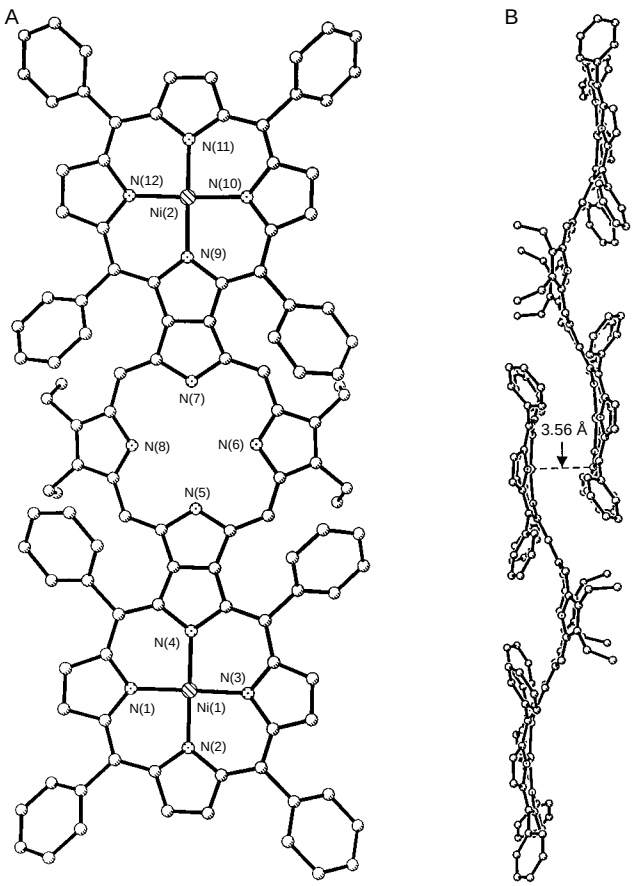



**Fig. 1** Molecular structure of **4**. (A) Top view. (B) Side packing view of two trimer molecules. Hydrogen atoms have been omitted for clarity.

shifted from 430 nm (**1**) to 484 and 468 nm in **5** and **6**, respectively. The most notable feature in the absorption spectra is an intense Q band at 652 (dimer **6**) or 722 nm (trimer **5**), reminiscent of a chlorin or bacteriochlorin type visible spectrum. Metallation of **4** using an excess of $Zn(OAc)_2$ in MeOH–$CHCl_3$ gave quantitatively the $Ni^{II}$–$Zn^{II}$–$Ni^{II}$ species, **7**. The Q band electronic absorption was found at 742 nm and was shifted to 752 nm upon addition of pyridine. Addition of TFA to a brown solution of free base **4** gave a red–pink dication species displaying three split Soret bands at 414, 455 and 516 nm, and a broad Q band at 838 nm. Surprisingly, these fused linear porphyrins are very soluble in a number of organic solvents, including chlorinated solvents; their protonation even enhances their solubilty.

Further synthetic work is aimed at the functionalization of these systems to generate higher fused oligomers, and at development of the chemistry of the dimer and trimer.

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## Notes and References

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‡ *Crystal Data* for **4**, $C_{112}H_{80}N_{12}Ni_2 \cdot 7.33[CHCl_3] \cdot [CH_3OH] \cdot [2[Cl^-]]$: X-ray diffraction data were collected on a Siemens P4 rotating anode diffractometer with a nickel filter monochromator [$\lambda$(Cu K$\alpha$) = 1.54178 Å] at 130(2) K in $\theta/2\theta$ scan mode to $2\theta_{max}$ = 113°. Crystals were grown from slow diffusion of heptane in a mixture of $CHCl_3$ and MeOH. A single parallelepiped crystal was selected with dimensions 0.16 × 0.08 × 0.04 mm. The crystal lattice was monoclinic with a space group of $P2_1/c$. Cell dimensions were $a$ = 38.335(7), $b$ = 16.994(3), $c$ = 19.110(4) Å, $\alpha$, $\gamma$ = 90, $\beta$ = 100.091(14), $V$ = 12257(4) Å3 and $Z$ = 4 ($M$ = 2689.35, $\rho_{calc}$ = 1.456 g cm$^{-3}$, $\mu$ = 5.628 mm$^{-1}$). Of 17 517 reflections measured, 16 228 were independent and 8884 had $I > 2\sigma$ ($R_{int}$ = 0.068); number of parameters = 1455. Final $R$ factors were $R_1$ = 0.1096 (based on observed data) and w$R_2$ = 0.345 (based on all data). The structure was solved by direct methods and refined (based on $F^2$ using all independent data) by full matrix least-squares methods (Siemens SHELXTL V. 5.03). Hydrogen atom positions were located by their idealized geometry and refined using a riding model. An absorption correction was applied using XABS2.[9] CCDC 184/848.

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