

## Porphyrins with Appended Phenanthroline Units: a Means by which Porphyrin $\pi$ -Systems can be connected to an External Redox Centre

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Sequential condensation of a variety of porphyrin-2,3-diones with 1,2,4,5-benzenetetramine and 1,10-phenanthroline-5,6-dione generate conjugated phenanthroline-appended porphyrin systems; this chemistry provides a means by which porphyrin  $\pi$ -systems can be connected to external redox centres.

Porphyrins and their derivatives have long attracted interest because of their redox properties and role in electron transfer in biological systems. Previously, we have outlined an approach to porphyrin-based 'molecular wires' that makes use of the fact that porphyrin  $\pi$ - and  $\pi^*$ -systems are redox active and that there is a relatively small energy gap between the HOMOs and the LUMOs.<sup>1-3</sup> Within this approach, there is also a need to generate a 'molecular alligator clip' that allows 'molecular wires' to be connected to metal electrodes and to the functional components of molecular electronic devices.<sup>1</sup> Furthermore, if the redox properties of a number of porphyrin units could be harnessed and used in concert at a single external centre, then there is the prospect of carrying out multi-electron chemistry at that site. A ligand system that attaches porphyrin units in conjugated fashion to an external redox centre is thus desirable. We describe the synthesis of such compounds, **5a-f**, **7** and **12**, which consist of a porphyrin unit attached through a rigid conjugated spacer unit to a 1,10-phenanthroline unit, and report some of the ligation properties of **5a** which give rise to the bis-porphyrins **8-10**.

Free-base phenanthroline-appended porphyrin<sup>+</sup> **5a** was prepared in 91% yield by stepwise condensation in dry pyridine of the porphyrin-2,3-dione<sup>4</sup> **1** with 1,2,4,5-benzenetetramine **3** (1.2 equiv., added as the tetrahydrochloride) and excess 1,10-phenanthroline-5,6-dione **4** (3.4 equiv.) (Scheme 1). The product was easily purified by column chromatography on silica ( $\text{CH}_2\text{Cl}_2$ -MeOH, 19:1).

Nickel(II) porphyrin-2,3-dione **2** was converted in the same way to the phenanthroline-appended nickel(II) porphyrin **5b** in

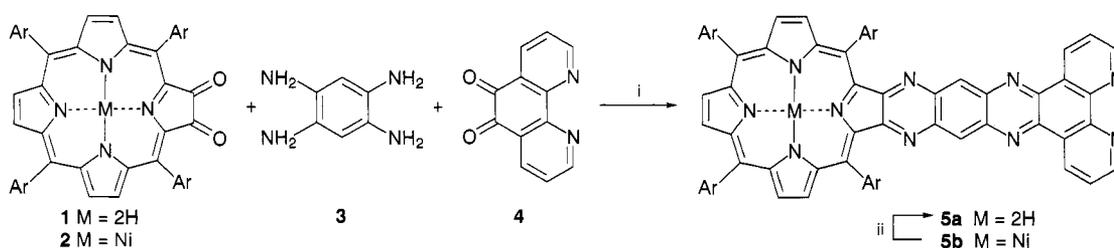
70% yield (Scheme 1), illustrating the reaction is also applicable to metalloporphyrin-2,3-diones. Demetallation ( $\text{H}_2\text{SO}_4$ - $\text{CH}_2\text{Cl}_2$ ) of the nickel(II) porphyrin **5b** followed by neutralization also generated the free-base phenanthroline-appended porphyrin **5a** (55% yield).

In order to illustrate an application to extended oligoporphyrin systems, the bis-porphyrin-dione **6** was converted to the  $\pi$ -conjugated phenanthroline-appended bis-porphyrin **7** in 80% yield (Scheme 2). Thus, **6** was treated with 1,2,4,5-benzenetetramine **3** (1.1 equiv.) in deoxygenated, dry pyridine under nitrogen and after 65 h the solution was transferred by cannula to 1.35 equiv. of 1,10-phenanthroline-5,6-dione **4** and left for 7 days. Work-up afforded **7** which was readily purified by chromatography over silica [ $\text{CH}_2\text{Cl}_2$  eluted a small amount of tetrakisporphyrin and  $\text{CH}_2\text{Cl}_2$ -MeOH (19:1) eluted **7**].

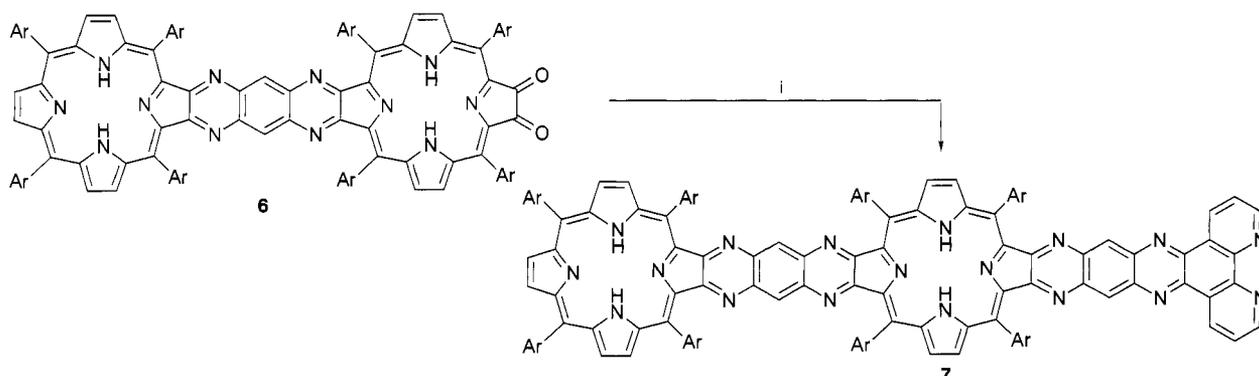
The free-base phenanthroline-appended porphyrin **5a** has two metallation sites, the porphyrin inner periphery and the 1,10-phenanthroline unit. Treatment of **5a** in refluxing dichloromethane with 5.4 equiv. of zinc(II) acetate dihydrate in methanol gave the trizinc complex **8** in 98% yield (Scheme 3). Elemental analysis and the electrospray MS were consistent with the molecular formula  $\text{C}_{192}\text{H}_{202}\text{N}_{20}\text{O}_4\text{Zn}_3$ .

Reaction of the trizinc bis-porphyrin **8** with excess EDTA, in a basic solution of DMF and 3 mol  $\text{dm}^{-3}$  NaOH under reflux for 2 h, sequestered the zinc(II) ion from the phenanthroline unit but left zinc(II) coordinated to the porphyrin inner periphery to yield the zinc(II) porphyrin **5c** (55% yield) (Scheme 3).

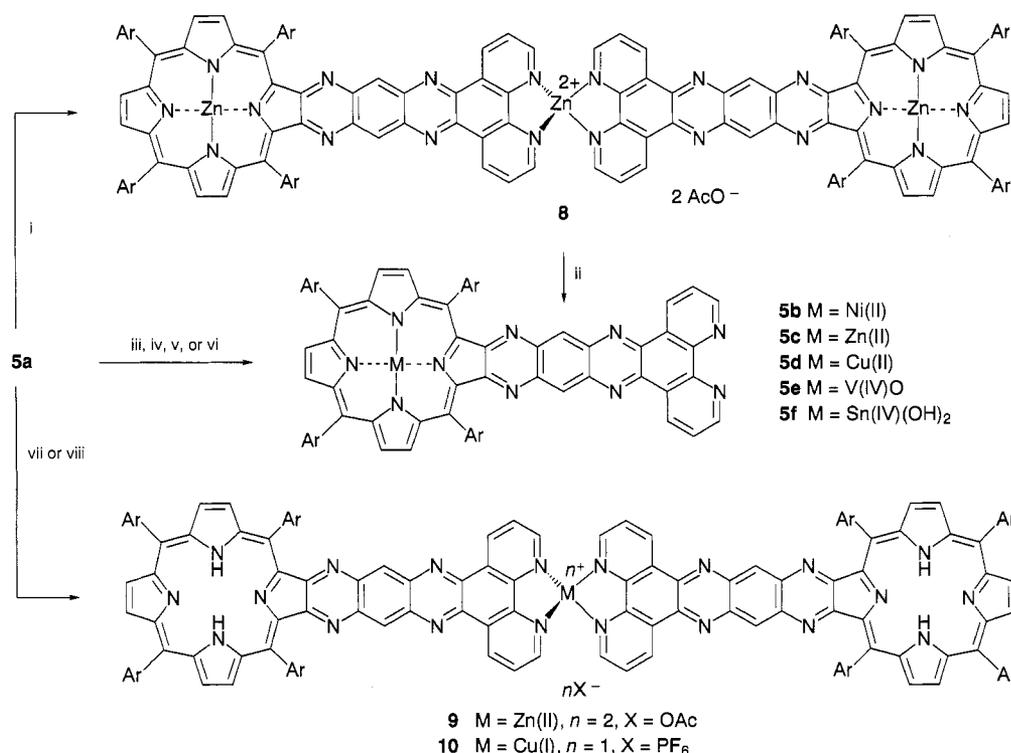
Application of the two-step process of trimetallation and decomplexation at the phenanthroline site was used to synthe-



Scheme 1 Reagents and conditions: i, dione and **3** tetrahydrochloride (1.2 equiv.) dissolved in pyridine under  $\text{N}_2$ , transferred by cannula after 45 h to **4** (3.4 equiv.), workup after 7 days under  $\text{N}_2$ ; ii,  $\text{H}_2\text{SO}_4$ - $\text{CH}_2\text{Cl}_2$ , 10 min, followed by neutralization (Ar = 3,5-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)



Scheme 2 Reagents and conditions: i, see text (Ar = 3,5-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)



**Scheme 3** Reagents and conditions: i, Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (5.4 equiv.) in refluxing CH<sub>2</sub>Cl<sub>2</sub>-MeOH, 2 h, crystallisation; ii, EDTA (20 equiv.) in refluxing DMF for 2 h; iii, Ni(OAc)<sub>2</sub>·2H<sub>2</sub>O (2.1 equiv.) in refluxing DMF, 1 h, then partition between CHCl<sub>3</sub> and 3 mol dm<sup>-3</sup> aq. HCl; iv, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (5 equiv.) in refluxing CHCl<sub>3</sub>-MeOH, 40 min, then EDTA (20 equiv.) in refluxing DMF-3 mol dm<sup>-3</sup> NaOH (7 : 1), 2 h, neutralization; v, VO(SO<sub>4</sub>)·5H<sub>2</sub>O (6 equiv.) in refluxing pyridine-AcOH (1 : 2), 2 days, then EDTA (20 equiv.) in refluxing DMF-3 mol dm<sup>-3</sup> NaOH (7 : 1), 2 h, neutralization; vi, SnCl<sub>2</sub> (75 equiv.) and NaOAc in refluxing AcOH, 2 days, then EDTA (20 equiv.) in refluxing DMF-3 mol dm<sup>-3</sup> NaOH (7 : 1), 2 h, neutralization; vii, Zn(OAc)<sub>2</sub> (0.50 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> under N<sub>2</sub>, 12 h, then gel-permeation chromatography (Sephadex LH-60, CHCl<sub>3</sub>); viii, [Cu(MeCN<sub>4</sub>)]PF<sub>6</sub> (0.50 equiv.) in dry, degassed MeCN under N<sub>2</sub>, 15 h, then gel-permeation chromatography (Sephadex LH-60, CHCl<sub>3</sub>) (Ar = 3,5-Bu<sup>t</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)

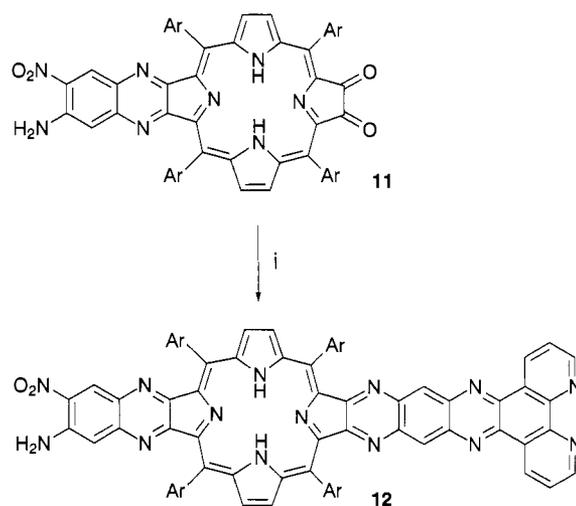
size the corresponding nickel(II), copper(II), oxovanadyl(IV) and dihydroxotin(IV) porphyrins, **5b**, **5d-f**, in 85, 64, 63 and 88% yield, respectively (Scheme 3).

In order to determine which site (porphyrin inner periphery or phenanthroline) is metallated first, compound **5a** was treated with 0.50 equiv. of zinc(II) acetate dihydrate (CH<sub>2</sub>Cl<sub>2</sub>, N<sub>2</sub>, 12 h) and the bis-(free-base)porphyrin zinc(II) complex **9** was obtained in 98% yield as a stable complex. Elemental analysis and the electrospray MS were consistent with the molecular formula C<sub>192</sub>H<sub>206</sub>N<sub>20</sub>O<sub>4</sub>Zn. The <sup>1</sup>H NMR spectrum of **9** showed the presence of a four-proton singlet at δ -2.30, consistent with the free-base nature of the porphyrins. These results indicate that metallation of the 1,10-phenanthroline unit is kinetically much faster than the metallation of the porphyrin inner periphery.

Reaction of free-base phenanthroline-appended porphyrin **5a** with 0.50 equiv. of tetraacetonecopper(I) hexafluorophosphate in dry acetonitrile and purification of the product by passage through Sephadex LH-60 gave the bis-(free-base)-porphyrin copper(I) complex **10** in 98% yield (Scheme 3). Elemental analysis and the electrospray MS (*m/z* 2946 and 2802) were consistent with the molecular formula C<sub>188</sub>H<sub>200</sub>CuF<sub>6</sub>N<sub>20</sub>P.

The methodology for attaching the phenanthroline unit was applied to the aminonitroquinoxalino-porphyrin-dione **11** which was converted to the corresponding substituted porphyrin-phenanthroline **12** in 59% yield (Scheme 4). Reduction of the nitro group of **12** provides a diamino compound that may be used to attach a phenanthroline-appended porphyrin unit as the terminal group to other α-dione containing entities.

Other types of functionality can be appended similarly to porphyrin systems, the only requirement being an α-dione unit in the addend precursor. In this way we have synthesized more elaborate porphyrin-'switch'-'connector' systems, mixed-por-



**Scheme 4** Reagents and conditions: i, dione and **3** tetrahydrochloride (1.1 equiv.) dissolved in pyridine under N<sub>2</sub> and transferred by cannula after 62 h to **4** (1.4 equiv.), workup after 7 days under N<sub>2</sub> (Ar = 3,5-Bu<sup>t</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)

phyrin systems, and oligoporphyrin systems with potential gradients. These studies and studies which have shown that the phenanthroline unit of the compounds **5a**, **5b** and **7** is an effective group for attachment of these compounds to gold in an alignment orthogonal to the surface will be reported in detail shortly.<sup>5</sup>

In summary, a convenient method for attaching an exterior metal complexation site to a porphyrin ring in a π-conjugated, coplanar arrangement has been developed. This may now allow

the rich redox chemistry of porphyrins to be directly utilized at the exterior site.

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### Footnote

† All new porphyrins have been adequately characterised by elemental analysis and MS. *Selected spectroscopic data for 5a*: C<sub>94</sub>H<sub>106</sub>N<sub>10</sub>; IR (CHCl<sub>3</sub>) ν<sub>max</sub> 3353 cm<sup>-1</sup>; VIS (CHCl<sub>3</sub>) λ<sub>max</sub> (log ε) 313 (4.62), 434 (5.70), 503 (4.56), 623 (3.91) and 672 nm (3.72); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ -2.32 (2H, s), 1.54 (36H, s), 1.57 (36H, s), 7.81 (2H, t), 7.88 (2H, dd, J<sub>2',3'</sub> = J<sub>9',8'</sub> 4.45 Hz, J<sub>4',3'</sub> = J<sub>7',8'</sub> 8.0 Hz), 8.05 (4H, d), 8.07 (2H, t), 8.10 (4H, d), 8.77 (2H, s), 8.94 (2H, s), 8.99 and 9.06 (4H, ABq, J<sub>AB</sub> 4.95 Hz), 9.30 (2H, dd, J<sub>4',2'</sub> = J<sub>7',9'</sub> 1.9 Hz, J<sub>3',2'</sub> = J<sub>8',9'</sub> 4.45 Hz), 9.82 (2H, dd, J<sub>2',4'</sub> = J<sub>9',7'</sub> 1.9 Hz, J<sub>3',4'</sub> = J<sub>8',7'</sub> 8.0 Hz). For *5c*: C<sub>94</sub>H<sub>98</sub>N<sub>10</sub>Zn; VIS (CHCl<sub>3</sub>) λ<sub>max</sub> (log ε) 315 (4.47), 442 (5.50), 528 (4.34) and 687 nm (3.79); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.53 (36H, s), 1.56 (36H, s), 7.79 (2H, t), 7.88 (2H, dd, J<sub>2',3'</sub> = J<sub>9',8'</sub> 3.9 Hz, J<sub>4',3'</sub> = J<sub>7',8'</sub> 7.4 Hz), 8.02 (4H, d), 8.06 (2H, t), 8.08 (4H, d), 8.84 (2H, s), 8.96 and 8.98 (4H, ABq, J<sub>AB</sub> 4.0 Hz), 9.01 (2H,

*s*), 9.29 (2H, m), 9.83 (2H, m). For *6*: C<sub>192</sub>H<sub>202</sub>N<sub>20</sub>O<sub>4</sub>Zn<sub>3</sub>; VIS (CHCl<sub>3</sub>) λ<sub>max</sub> (log ε) 319 (4.47), 443 (5.41), 538 (4.30), 625 (3.67) and 711 nm (3.69); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.53 (72H, s), 1.56 (72H, s), 7.80 (4H, t), 8.02 (8H, d), 8.06 (4H, t), 8.08 (8H, d), 8.15 (4H, dd, J<sub>2',3'</sub> = J<sub>9',8'</sub> 4.2 Hz, J<sub>4',3'</sub> = J<sub>7',8'</sub> 8.0 Hz), 8.84 (4H, s), 8.97 and 8.98 (8H, ABq, J<sub>AB</sub> 4.9 Hz), 9.06 (4H, s), 9.34–9.36 (4H, m), 10.02–10.04 (4H, m). For *7*: C<sub>192</sub>H<sub>206</sub>N<sub>20</sub>O<sub>4</sub>Zn; VIS (CHCl<sub>3</sub>) λ<sub>max</sub> (log ε) 314 (4.81), 437 (5.86), 511 (4.72), 589sh (4.04), 632sh (3.99) and 636 nm sh (3.94); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ -2.30 (4H, s), 1.54 (72H, s), 1.56 (72H, s), 7.82 (4H, t), 8.05 (8H, d), 8.07 (4H, t), 8.10 (8H, d), 8.15 (4H, dd, J<sub>2',3'</sub> = J<sub>9',8'</sub> 4.2 Hz, J<sub>4',3'</sub> = J<sub>7',8'</sub> 8.0 Hz), 8.79 (4H, s), 8.99 (4H, s), 9.01 and 9.06 (8H, ABq, J<sub>AB</sub> 5.0 Hz), 9.34–9.36 (4H, m), 10.02–10.04 (4H, m).

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