

# Octatetrayne-linked porphyrins: 'stretched' cyclic dimers and trimers with very spacious cavities

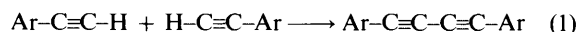
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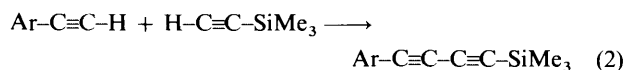
Syntheses are described for two octatetrayne-linked cyclic porphyrin oligomers with extremely spacious cavities. These hosts bind strongly to complementary multidentate guests. Thus, the octatetrayne-linked dimer binds bifunctional ligand bis(4-pyridyl)ethyne with an affinity of  $7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}$ , and the trimer binds the new 'stretched' trifunctional ligand 1,3,5-tris[(4-pyridyl)ethynyl]benzene with an affinity of  $2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$  in  $\text{C}_2\text{H}_2\text{Cl}_4$  at  $30^\circ\text{C}$ .

## Introduction

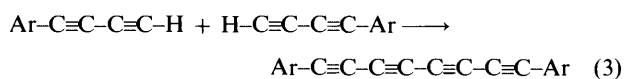
The first paper in this series set out a general design for enzyme mimics based on porphyrins;<sup>1</sup> it was an important part of our strategy that we should create a series of receptors of the same shape but with a range of cavity sizes, and preferably using the same diarylporphyrin monomer as a building block. In the first instance we used butadiyne linkers generated by Glaser-Hay coupling of a terminal alkyne:



Our first attempt at creating larger cavities used a platinum linker between the monomer units, but the resulting oligomers were not sufficiently stable for extended catalytic studies.<sup>2</sup> We describe here a further elaboration of the same porphyrin monomer, **Zn-Mon1b** to give a butadiyne-terminated monomer **Zn-Mon3b** [eqn. (2)] and hence octatetrayne-linked

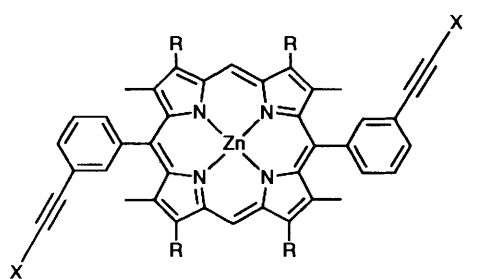


cyclic porphyrin dimer **Zn<sub>2</sub>-c-Dim3b** and trimer **Zn<sub>3</sub>-c-Tri3b** [eqn. (3)]:



The mixed coupling in eqn. (2) was developed in this laboratory for the synthesis of linear conjugated porphyrin oligomers and polymers<sup>3</sup> and has proved a reliable method for chain extension. Octatetraynes occur in some pharmacologically active natural products<sup>4</sup> and are also of interest for their electronic properties,<sup>4,5</sup> but they have rarely been used previously as simple spacers.<sup>6</sup>

Inspection of models reveals that the Zn-Zn distance in the octatetrayne-linked dimer **Zn<sub>2</sub>-c-Dim3b** is around 15 Å, almost the same as in the butadiyne-linked trimer, while the angle between Zn-ligand bonds is  $180^\circ$  rather than  $120^\circ$ . The potential for carrying out interesting bimolecular chemistry within the cavity of this 'stretched' dimer therefore seems higher than for the smaller butadiyne-linked dimer, and indeed this new dimer is effective at accelerating a Diels-Alder reaction isomeric to that accelerated by **Zn<sub>3</sub>-c-Tri1b**.<sup>7</sup> As in the

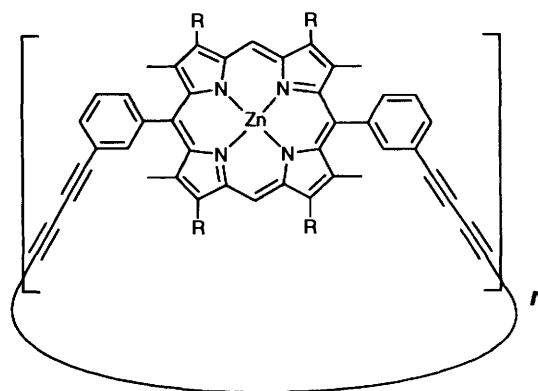


**Zn-Mon1b**                      X = H

**Zn-Mon3b(SiMe<sub>3</sub>)<sub>2</sub>**        X = C≡C-SiMe<sub>3</sub>

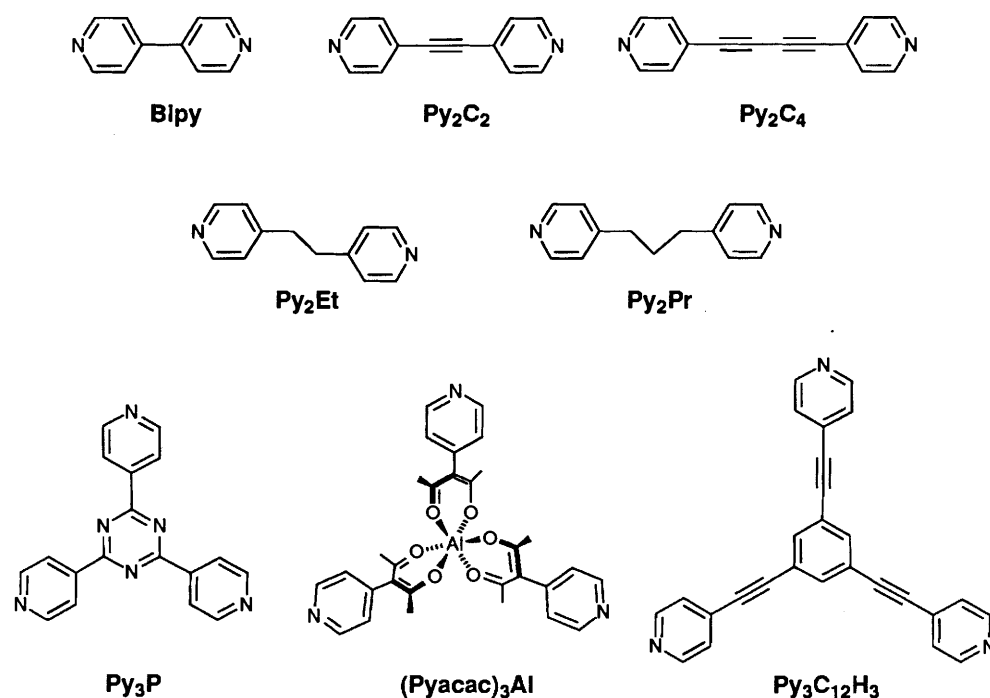
R = CH<sub>2</sub>CH<sub>2</sub>Y

Y = (b) CO<sub>2</sub>Me, (c) CO<sub>2</sub>-[CH<sub>2</sub>]<sub>6</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>3</sub>  
or (d) CO<sub>2</sub>CH<sub>2</sub>Ph



**Zn<sub>2</sub>-c-Dim3b, c, d**        n = 2

**Zn<sub>3</sub>-c-Tri3b**                      n = 3



platinum-linked case discussed in the preceding paper, structure confirmation and the probing of cavity size were aided by the use of complementary ligands, including the new extended tripyridyl ligand  $\text{Py}_3\text{C}_{12}\text{H}_3$  which was designed and synthesised specially for this purpose.

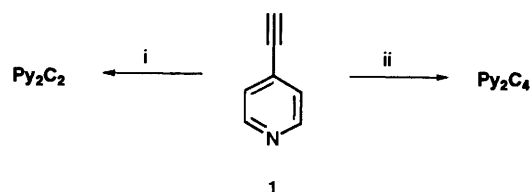
## Results and discussion

### Synthesis

Extension of **Zn-Mon1b** by mixed Glaser–Hay coupling with trimethylsilylacetylene yielded the new extended monomer **Zn-Mon3b**( $\text{SiMe}_3$ )<sub>2</sub>. This reaction was carried out using a 10-fold excess of trimethylsilylacetylene to minimise homo-coupling of **Zn-Mon1b**. Although cross-coupling using an excess of one acetylene is less elegant than the use of a specific cross-coupling reaction,<sup>8</sup> it is an efficient procedure in this case because trimethylsilylacetylene has a low molecular weight and is cheap compared with **Zn-Mon3b**, and because the two types of acetylenes have similar reactivity.

The deprotected extended monomer with terminal butadiyne groups **Zn-Mon3b** was rather unstable so it was immediately subjected to Glaser–Hay coupling with an excess of copper(I) chloride. The stretched dimer **Zn<sub>2</sub>-c-Dim3b** and trimer **Zn<sub>3</sub>-c-Tri3b** were isolated by chromatography in 28 and 27% yield, respectively. The octatetrayne link is surprisingly robust chemically, being much easier to handle than the platinum linker in these systems, and it appears to be remarkably rigid. This rigidity presumably contributes to the relative insolubility; millimolar concentrations of the dimer could only be obtained by transesterification to the benzyl or isodecyl ester using the same method as previously.<sup>3</sup> Several attempts were made to template the synthesis of the stretched dimer and trimer using the strongly binding ligands described below, but without convincing success.

The binding and recognition properties of these new 'extended' super-macrocycles were probed using the ligands **Bipy**, **Py<sub>2</sub>C<sub>2</sub>**, **Py<sub>2</sub>C<sub>4</sub>**, **Py<sub>2</sub>Et**, **Py<sub>2</sub>Pr**, **Py<sub>3</sub>T**, **(Pyacac)<sub>3</sub>Al** and **Py<sub>3</sub>C<sub>12</sub>H<sub>3</sub>**. Bis(4-pyridyl)butadiyne **Py<sub>2</sub>C<sub>4</sub>** was prepared using the published procedure.<sup>9</sup> Bis(4-pyridyl)ethyne **Py<sub>2</sub>C<sub>2</sub>** was prepared from 4-ethynylpyridine **1** and 4-bromopyridine



**Scheme 1** i, 4-bromopyridine, CuI,  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ ,  $\text{NHET}_2$ ; ii, CuCl, pyridine

as shown in Scheme 1; we used this route rather than that of Tanner and Ludi<sup>10</sup> [from *trans*-1,2-di(4-pyridyl)ethene] because it uses materials we had in hand. The new tridentate ligand, 1,3,5-tris[(4-pyridyl)ethynyl]benzene **Py<sub>3</sub>C<sub>12</sub>H<sub>3</sub>** was prepared as shown in Scheme 2,<sup>†</sup> a route derived from the work of Huynh and Linstrumelle.<sup>12</sup>

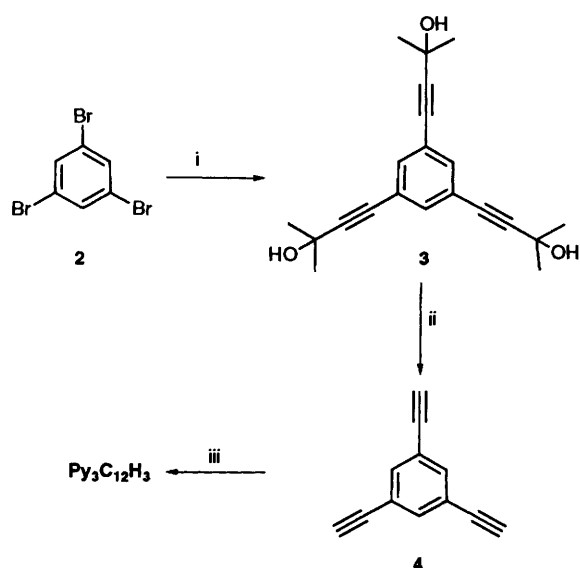
### Binding properties

Binding constants were measured using electronic spectroscopy as before.<sup>13</sup> Because the dimer was being assayed for its ability to accelerate the Diels–Alder reaction, all the binding constants gathered in Tables 1 and 2 were obtained in  $\text{C}_2\text{H}_2\text{Cl}_4$  solution at 30 °C; to aid comparison, some of the binding constants reported in ref. 2 were re-measured under these same conditions.<sup>‡</sup>

The data in Table 1 show that the long bidentate ligands **Py<sub>2</sub>C<sub>2</sub>**, **Py<sub>2</sub>C<sub>4</sub>**, **Py<sub>2</sub>Et** and **Py<sub>2</sub>Pr** are all more complementary to the larger dimer **Zn<sub>2</sub>-c-Dim3d** than to **Zn<sub>2</sub>-c-Dim1b**; this is hardly surprising, given the rigidity of the smaller cyclic dimer. However, even the best ligands for the larger dimer have binding constants of only  $10^6$ – $10^7$  rather than the  $10^8$ – $10^9$  which would have been expected for a good fit. Since the larger dimer has linkages which are longer by one butadiyne

<sup>†</sup> The same ligand has been independently prepared by Ward.<sup>11</sup>

<sup>‡</sup> In general, the strength of binding decreases in the order  $\text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{C}_2\text{H}_2\text{Cl}_4$ . Use of a less polar solvent such as cyclohexane would undoubtedly increase binding affinities<sup>14</sup> but at the expense of solubility problems.



**Scheme 2** i, 2-methylbut-3-yn-2-ol, CuI, [Pd(PPh<sub>3</sub>)<sub>4</sub>], NEt<sub>3</sub>, 85 °C; ii, aq. KOH, cyclohexane, TBAI, reflux; iii, 4-bromopyridine, CuI, [Pd(PPh<sub>3</sub>)<sub>4</sub>], NEt<sub>3</sub>, 85 °C

**Table 1** Binding constants to bidentate ligands<sup>a</sup>

| Ligand                         | Zn <sub>2</sub> -c-Dim1b | Zn <sub>2</sub> -c-Dim3d |
|--------------------------------|--------------------------|--------------------------|
| Bipy                           | 1 × 10 <sup>8</sup>      | 1 × 10 <sup>4</sup>      |
| Py <sub>2</sub> C <sub>2</sub> | 0.4 × 10 <sup>3</sup>    | 7 × 10 <sup>6</sup>      |
| Py <sub>2</sub> C <sub>4</sub> | 0.6 × 10 <sup>3</sup>    | 1 × 10 <sup>6</sup>      |
| Py <sub>2</sub> Et             | 1 × 10 <sup>5</sup>      | 7 × 10 <sup>6</sup>      |
| Py <sub>2</sub> Pr             | 2 × 10 <sup>4</sup>      | 1 × 10 <sup>6</sup>      |

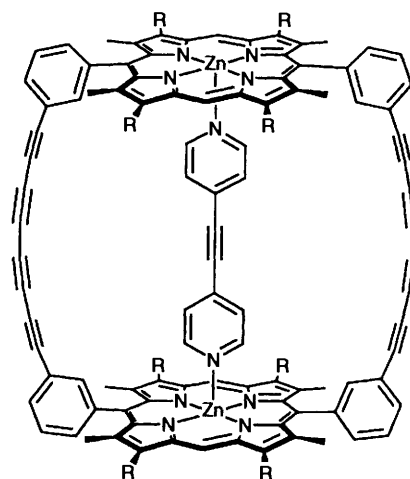
<sup>a</sup> Determined in C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> solution at 30 °C using UV-VIS spectroscopy.

(-C≡C-C≡C-) unit, we had expected that ligands with 4-carbon atom links would be optimal. In fact, the shorter Py<sub>2</sub>C<sub>2</sub> appears to be the best ligand (Fig. 1). This may be rationalised if the Zn-Zn distance is less than expected: evidence was presented in an earlier paper<sup>13</sup> that the porphyrin units in the small dimer Zn<sub>2</sub>-c-Dim1b are domed, presumably because the butadiyne units are too short to accommodate significant distortion. However, the longer octatetrayne linker may be able to bend more, leading to less porphyrin doming and a smaller Zn-Zn distance.

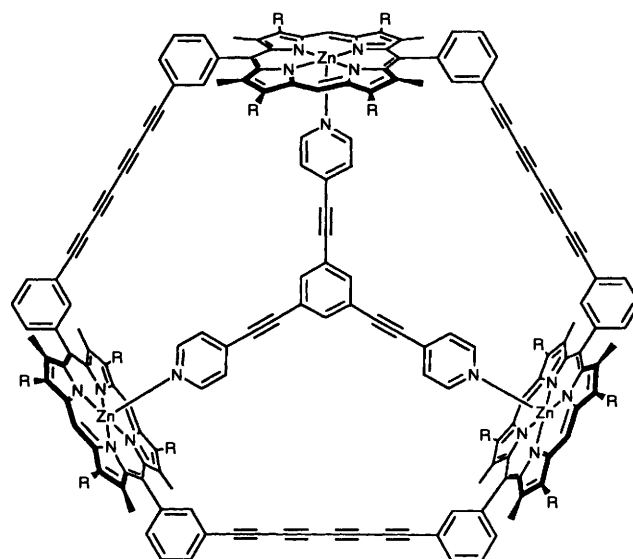
The results in Table 2 show that Py<sub>3</sub>T and (Pyacac)<sub>3</sub>Al can achieve two-point binding within the stretched trimer, the latter with rather less strain. The lack of significant three-point binding for (Pyacac)<sub>3</sub>Al implies that, although the host is remarkably flexible, it cannot support excessive distortion. However, Py<sub>3</sub>C<sub>12</sub>H<sub>3</sub> is large enough to achieve three-point binding to Zn<sub>3</sub>-c-Tri3b, giving the complex shown in Fig. 2. The observed binding constant of 2 × 10<sup>8</sup> dm<sup>3</sup> mol<sup>-1</sup> is significantly less than that for the smaller trimers and their complementary guests; while this may reflect imperfect fit, it is probably more a measure of the very large entropic costs involved in organising such a large cavity.

### Conclusions

A key question in the search for biomimetic host molecules that are capable of recognition and catalysis is how to create and characterise spacious cavities; given the difficulty of characterising these 2–5 kDa molecules crystallographically,<sup>15</sup> convincing evidence on the nature of the cavity often rests on finding a complementary guest that will bind strongly. Thus, in creating



**Fig. 1** Structure of the Py<sub>2</sub>C<sub>2</sub> complex with stretched dimer



**Fig. 2** Structure of the Py<sub>3</sub>C<sub>12</sub>H<sub>3</sub> complex with stretched trimer

the trimer series with increasing linker length from -C≡C-C≡C- to -C≡C-PtR<sub>2</sub>-C≡C- to -C≡C-C≡C-C≡C-C≡C-, we have also prepared a series of ligands, each of which will only bind strongly to its complementary partner. In the case of these stretched oligomers, the complementary ligands bind strongly despite the very large organisational costs which must be involved. Unfortunately, in neither the platinum<sup>2</sup> nor the octatetrayne cases is ligand binding strong enough to template cyclisation with a useful effective molarity; given the marginal effective molarities found for the smaller butadiyne systems<sup>16</sup> this is perhaps not surprising. However, recent improvements in templating using stronger metal-ligand interactions<sup>17,§</sup> and the development of stepwise construction methods<sup>18</sup> show that we can efficiently construct a much wider range of molecular architectures than appeared plausible at the outset<sup>1</sup> of this project.

<sup>§</sup> Note added in proof. The use of a *meso*-dinitro substituted stretched monomer does increase template-porphyrin binding sufficiently that Py<sub>3</sub>C<sub>13</sub>H<sub>3</sub> significantly increases the yield of cyclic trimer (D. W. J. McCallien and J. K. M. Sanders, unpublished work). However the efficiency of templating is still much less than observed in the smaller butadiyne-linked series using electronically substituted porphyrins.<sup>17</sup>

**Table 2** Binding constants to tridentate ligands<sup>a</sup>

| Ligand   | Zn <sub>3</sub> -c-Tri1b | Zn <sub>3</sub> -c-Tri3b |
|--|--------------------------|--------------------------|
| Py <sub>3</sub> T                              | 1 × 10 <sup>9</sup>      | 2 × 10 <sup>5</sup>      |
| (Pyacac) <sub>3</sub> Al                       | 1 × 10 <sup>6</sup>      | 3 × 10 <sup>6</sup>      |
| Py <sub>3</sub> C <sub>12</sub> H <sub>3</sub> | 2 × 10 <sup>5</sup>      | 2 × 10 <sup>8</sup>      |

<sup>a</sup> Determined in C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> solution at 30 °C using UV-VIS spectroscopy.

### Experimental

General directions are as before.<sup>1</sup>

#### Di(4-pyridyl)ethyne Py<sub>2</sub>C<sub>2</sub>

To a suspension of 4-bromopyridine hydrochloride (500 mg, 3 mmol) in diethylamine (50 cm<sup>3</sup>; freshly distilled) were added 2-methylbut-3-yn-ol (625 mm<sup>3</sup>, 6.5 mmol), copper(I) iodide (49 mg, 0.3 mmol) and bis(triphenylphosphine)palladium(II) chloride (54 mg, 80 μmol). After three freeze-thaw cycles the reaction mixture was stirred under argon for 15 h at room temperature. The reaction mixture was washed with water (50 cm<sup>3</sup>; distilled) and extracted into chloroform. Washing a second time with water (50 cm<sup>3</sup>; distilled) yielded the crude 2-methyl-4-(4-pyridyl)but-3-yn-2-ol which was purified by column chromatography (eluting with 2% methanol in chloroform) and used without characterisation.

To a solution of 2-methyl-4-(4-pyridyl)but-3-yn-2-ol (580 mg, 4 mmol) in toluene (40 cm<sup>3</sup>; distilled ex. CaH<sub>2</sub>) was added potassium hydroxide (200 mg, 4 mmol). After being flushed with argon, the reaction mixture was heated under reflux under argon for 45 min and then filtered to remove the insoluble potassium salts. To the filtrate, a toluene solution of (4-pyridyl)acetylene, were added diethylamine (30 cm<sup>3</sup>; freshly distilled), 4-bromopyridine hydrochloride (500 mg, 3 mmol), copper(I) iodide (49 mg, 0.3 mmol) and bis(triphenylphosphine)palladium(II) chloride (54 mg, 80 μmol). After three freeze-thaw cycles the reaction mixture was stirred under argon at room temperature for 15 h and then warmed with dilute acid (pH 5–6) and subjected to preparative plate chromatography (1% methanol in chloroform) to give the crude product. This was purified by extraction into dilute hydrochloric acid (1 mol dm<sup>-3</sup>) followed by neutralisation (potassium carbonate) and extraction back into chloroform; yield 25 mg (5%); δ<sub>H</sub>(250 MHz, CDCl<sub>3</sub>) 7.40 (d, 4 H, *J* 6) and 8.64 (d, 4 H, *J* 6) [Found: *m/z* (EI) 180.0685. C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> requires 180.0688].

#### 1,3,5-Tris(2-hydroxy-2-methylbut-3-ynyl)benzene 3

2-Methylbut-3-yn-2-ol (8.41 g, 0.10 mol) and copper(I) iodide (0.46 g, 2.4 mmol) were added at 60 °C to a stirred suspension of tetrakis(triphenylphosphine)palladium(0) (1.38 g, 1.2 mmol) and 1,3,5-tribromobenzene 2 (6.30 g, 0.02 mol) in dry triethylamine (freshly distilled from CaH<sub>2</sub>). The mixture was degassed (three freeze-thaw cycles) and then stirred at 60 °C under dry argon for 5 h. The mixture was then concentrated by solvent removal, diluted with saturated aqueous ammonium chloride (60 cm<sup>3</sup>), and extracted with ether (6 × 50 cm<sup>3</sup>); the combined extracts were dried (MgSO<sub>4</sub>) and evaporated and the product recrystallised from di-isopropyl ether and a few drops of methanol, after hot filtration of the solution through Celite, to yield a pale yellow powder (4.9 g, 76%), mp 170–172 °C; ν<sub>max</sub>/(cm<sup>-1</sup>) 3350 and 2225; δ<sub>H</sub>(CDCl<sub>3</sub>) 1.6 (18 H, s), 2.0 (3 H, s, OH) and 7.4 (3 H, s, ArH); δ<sub>C</sub>(CDCl<sub>3</sub>) 22 (CH<sub>3</sub>), 65 (quaternary), 81 and 95 (alkyne C), 123 (Ar) and 134 (ArH); *m/z* 324 (M<sup>+</sup>).

#### 1,3,5-Triethynylbenzene 4

Aqueous NaOH (5 mol dm<sup>-3</sup>; 15 cm<sup>3</sup>) was added to a stirred

mixture of compound 3 (1.62 g, 0.005 mol) and tetrabutylammonium iodide (0.37 g, 0.001 mol) in cyclohexane (25 cm<sup>3</sup>). After the mixture had been heated under reflux at 85 °C for 4 days, the organic layer was separated and the aqueous layer was extracted with ether (4 × 50 cm<sup>3</sup>). The combined organic layer and extracts were washed with water (3 × 50 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), filtered and evaporated to leave an orange solid which was subjected to chromatography (1 : 1 chloroform–hexane). The product was recrystallised from hexane to yield bright yellow crystals (273 mg, 36%), mp 94–96 °C (lit.,<sup>19</sup> 96–97); ν<sub>max</sub>/cm<sup>-1</sup> 3280 and 2108; δ<sub>H</sub>(CDCl<sub>3</sub>) 3.1 (3 H, s) and 7.6 (3 H, s, ArH); δ<sub>C</sub>(CDCl<sub>3</sub>) 79 (alkyne CH), 81 (alkyne C), 123 (ArH) and 135 (Ar); *m/z* 150 (M<sup>+</sup>).

#### 1,3,5-Tris(4-pyridylethynyl)benzene Py<sub>3</sub>C<sub>12</sub>H<sub>3</sub>

A mixture of 1,3,5-triethynylbenzene 4 (0.296 g, 1.97 mmol), 4-bromopyridine (1.91 g, 9.82 mmol), copper(I) iodide (49 mg, 0.252 mmol), tetrakis(triphenylphosphine)palladium(0) (147 mg, 0.126 mmol) and freshly distilled triethylamine (100 cm<sup>3</sup>) was degassed (three freeze-thaw cycles) and stirred under argon at 80 °C for 2 days. The mixture was then evaporated, washed with saturated aqueous NH<sub>4</sub>Cl (60 cm<sup>3</sup>) and extracted with ethyl acetate (3 × 150 cm<sup>3</sup>). The combined extracts were washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. Recrystallisation of the residue from ethanol–water (1 : 1) yielded the pure product (526 mg, 70%) as a yellow–orange solid, mp > 200 °C (decomp.); ν<sub>max</sub>/cm<sup>-1</sup> 3035 and 2215; δ<sub>H</sub>(CDCl<sub>3</sub>) 7.38 (6 H, d, *J* 5.8 Py-β), 7.73 (3 H, s, Ar) and 8.61 (6 H, d, *J* 5.8, Py-α); δ<sub>C</sub>(CDCl<sub>3</sub>) 88 and 92 (alkyne C), 123 (Ar), 126 (ArH), 131 (Py-γ), 135 (Py-β) and 150 (Py-α) (Found: *m/z* 381.1269. C<sub>27</sub>H<sub>15</sub>N<sub>3</sub> requires 381.1266).

#### Zn-Mon3b(SiMe<sub>3</sub>)<sub>2</sub>

To a solution of Zn-Mon1b (230 mg, 309 μmol) in dichloromethane (500 cm<sup>3</sup>; freshly distilled ex. CaH<sub>2</sub>) were added TMS acetylene (1 cm<sup>3</sup>, 7 mmol), copper(I) chloride (3.7 g, 38 mmol) and TMEDA (5.4 cm<sup>3</sup>, 34 mmol). The reaction mixture was stirred vigorously under dry air whilst portions of TMS acetylene (0.5 cm<sup>3</sup>, 3.5 mmol) were added to it every 30 min until the reaction was judged by TLC to have gone to completion. After this the mixture was washed with water (4 × 300 cm<sup>3</sup>) and concentrated by removal of solvent under reduced pressure. The resulting product was purified by column chromatography (eluting with 15% chloroform in dichloromethane) and recrystallised from chloroform–methanol; yield 200 mg (73%); δ<sub>H</sub>(250 MHz, CDCl<sub>3</sub>) 0.21 (s, 18 H), 2.43 (s, 12 H), 3.11 (t, 8 H), 3.67 (s, 12 H), 4.26 (t, 8 H), 7.71 (t, 2 H), 7.94 (d, 2 H), 7.99 (d, 2 H), 8.20 (s, 2 H) and 10.13 (s, 2 H); δ<sub>C</sub>(100 MHz, CDCl<sub>3</sub>) -0.4 (SiMe<sub>3</sub>), 15.6 (Me), 21.8 (CH<sub>2</sub>-CH<sub>2</sub>CO<sub>2</sub>Me), 36.9 (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Me), 51.7 (MeO), 74.7, 87.7 and 91.1 (C≡C–C≡C–SiMe<sub>3</sub>), 97.5 (*meso*-H), 118.2 (*meso*-aryl), 120.9 (aryl–C≡C), 127.8, 132.6, 133.9 and 136.9 (aryl-H), 138.8, 141.6, 146.0 and 147.5 (pyrrole), 143.6 (aryl-porph) and 173.5 (CO<sub>2</sub>Me) [Found: *m/z* (FAB) 1165.394 50 (MH<sup>+</sup>). C<sub>66</sub>H<sub>69</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>2</sub>Zn requires 1165.394 46]; λ<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/nm 268, 284, 302, 334, 413, 540 and 575 (log ε 4.5, 4.6, 4.6, 4.4, 5.7, 4.3 and 4.0).

#### Zn<sub>2</sub>-c-Dim3b and Zn<sub>3</sub>-c-Tri3b

To a solution of Zn-Mon3b(SiMe<sub>3</sub>)<sub>2</sub> (580 mg in 40 cm<sup>3</sup> dichloromethane) was added tetrabutylammonium fluoride in THF (1 mol dm<sup>-3</sup> solution; 1.25 cm<sup>3</sup>, 1.25 mmol); the mixture was stirred under argon until TLC showed the absence of starting material (30 min). Calcium chloride (2 spatulas full) was added to the mixture after which it was stirred for 5 min and then washed with water (2 × 100 cm<sup>3</sup>) and evaporated. Layered addition of MeOH onto a solution of the residue in the minimum amount of chloroform gave crystalline zinc-5,15

bis[3-(buta-1,3-diyne)phenyl]-2,8,12,18-tetra(2-methoxycarbonylethyl)-3,7,13,17-tetramethylporphyrin (**Zn-Mon3b**) (78%);  $\delta_{\text{H}}$ (250 MHz) 2.45 (s, 12 H, Me), 2.48 (s, 2 H, CCH), 3.13 (br t, 8 H,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 3.67 (s, 12 H, MeO), 4.30 (br t, 8 H,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 7.73 (t, *J* 8, 2 H, 5-H Ar), 7.97 (d, *J* 8, 2 H) and 8.08 (*J* 8, 2 H) corresponding to 4-H Ar and 6-H Ar, 8.23 (s, 2 H, 2-H Ar) and 10.19 (s, 2 H, *meso*);  $\delta_{\text{C}}$ (100 MHz,  $\text{CDCl}_3$ ) 15.7 (Me), 21.9 ( $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 36.9 ( $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 51.7 (MeO), 68.1, 74.0 and 75.4 ( $\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$ ), 71.5 ( $\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$ ), 97.6 (*meso*-C), 118.2 (*meso*-aryl), 120.6 (*aryl*- $\text{C}\equiv\text{C}$ ), 127.9, 132.8, 134.2 and 137.1 (*aryl*-H), 138.9, 141.7, 146.1 and 147.5 (pyrrole), 143.7 (*aryl*-porph) and 173.5 ( $\text{CO}_2\text{Me}$ ) [Found: *m/z* (FAB) 1021.3202 ( $\text{MH}^+$ ).  $\text{C}_{60}\text{H}_{53}\text{N}_4\text{O}_8\text{Zn}$  requires 1021.3154];  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  253, 273, 292, 313, 334, 413, 540 and 575 ( $\log \epsilon$  4.4, 4.5, 4.4, 4.3, 4.4, 5.6, 4.3 and 4.0).

To a solution of freshly prepared **Zn-Mon3b** (180 mg, 0.176 mmol) in dichloromethane (400  $\text{cm}^3$ , freshly distilled ex.  $\text{CaH}_2$ ) was added copper(I) chloride (1.20 g, 12.15 mmol) and *N,N,N',N'*-tetramethylethylenediamine (1.84  $\text{cm}^3$ , 1.41 g, 12.15 mmol). The reaction mixture was stirred vigorously under dry air for 90 min, after which it was washed with water (3  $\times$  500  $\text{cm}^3$ ), treated with trifluoroacetic acid (2  $\times$  100  $\text{cm}^3$  of 10% trifluoroacetic acid in methanol and 300  $\text{cm}^3$  of water) and lastly washed again with water (4  $\times$  500  $\text{cm}^3$ ). The mixture was then concentrated by solvent removal and the residue dried *in vacuo* and purified by column chromatography (dry-packed column, eluting with 40% chloroform in dichloromethane). Stretched dimer was obtained as a first, rather insoluble, fraction (28% yield). Metallation and transesterification, using the standard procedure,<sup>3</sup> gave the more soluble benzyl and isodecyl ester substituted 'stretched' dimer. For the benzyl molecule  $\delta_{\text{H}}$ (250 MHz,  $\text{CDCl}_3$ ) 2.36 (s, 24 H), 3.01 (m, 16 H), 4.20 (t, 16 H), 4.83 (s, 16 H), 6.7–6.9 (m, 40 H), 7.51 (s, 4 H), 7.76 (m, 8 H), 8.43 (d, 4 H) and 10.05 (s, 4 H) [Found: *m/z* (FAB) 1325 ( $\text{M}^{2+}$ ) and 2651 ( $\text{M} + \text{H}$ ).  $\text{C}_{168}\text{H}_{132}\text{N}_8\text{O}_{16}\text{Zn}_2$  requires 2650];  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  273, 289, 325, 348, 375, 413, 541 and 577.

Further elution with the same eluent yielded **H<sub>6</sub>-c-Tri3b** (27%);  $\delta_{\text{H}}$ (400 MHz) –2.57 (br s, exchangeable with  $\text{D}_2\text{O}$ , 6 H, NH), 2.46 (br s, 36 H, Me), 3.11 (t, *J* 7, 24 H,  $\text{CH}_2\text{-CH}_2\text{CO}_2\text{Me}$ ), 3.60 (s, 36 H, MeO), 4.31 (br s, 24 H,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 7.74–8.16 (m, 24 H, Ar) and 10.24 (br s, 6 H, *meso*);  $\delta$ (100 MHz) 14.97 (Me), 21.97 ( $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 36.9 ( $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 51.58 (MeO), 63.71, 67.49 and 75.13 ( $\text{C}^{\text{sp}}$ ), 97.19 (*meso*-C), 116.73 (*meso*-Ar), 120.47 (Ar-CC), 128.09, 133.15, 134.30, 134.36, 136.95, 137.39, 141.43, 141.79, 142.66 and 145.05 (pyrrole + Ar) and 173.27 ( $\text{C}=\text{O}$ ).

#### Zn<sub>3</sub>-c-Tri3b

To a solution of **H<sub>6</sub>-c-Tri3b** (25 mg, 0.087 mmol) in dichloromethane (50  $\text{cm}^3$ ) were added zinc acetate dihydrate (0.114 mmol) and methanol (0.5  $\text{cm}^3$ ). The mixture was stirred under reflux until TLC indicated the absence of starting material (35 min). The mixture was then filtered and worked up. Layered addition of methanol onto a solution of the product in the minimum amount of chloroform gave **Zn<sub>3</sub>-c-Tri3b**; yield 90%;  $\delta_{\text{H}}$ (400 MHz) 2.37 (br s, 36 H, Me), 2.92 (br s, 24 H,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 3.51 (s, 36 H, MeO), 4.09 (br s, 24 H,

$\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 7.72–8.13 (m, 24 H, Ar), 9.94 (br s, 6 H, *meso*-H);  $\delta_{\text{C}}$ (100 MHz) 14.97 (Me), 21.26 ( $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 36.45 ( $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ), 50.90 (MeO), 63.71, 116.72 (*meso*-Ar), 118.87 (Ar-CC), 127.28, 137.55, 140.72, 145.16, 146.48 (pyrrole + Ar) and 172.65 ( $\text{C}=\text{O}$ );  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  289 (5.41), 324 (5.10), 346 (5.13), 374 (5.14), 413 (6.01), 540 (4.77) and 575 (4.52) [Found: *m/z* (FAB) 1531 ( $\text{M}^{2+}$ ) and 3061 ( $\text{M} + \text{H}$ ).  $\text{C}_{180}\text{H}_{150}\text{N}_{12}\text{O}_{24}\text{Zn}_3$  requires 3061].

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