Bis-porphyrin arrays. Part 2.† The synthesis of asymmetrically substituted bis-porphyrins

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A strategy for the synthesis of asymmetrically substituted tetraazaanthracene linked bis-porphyrins in which the two porphyrin rings contain differences in their peripheral substituents has been developed. The method is illustrated by the preparation of bis-porphyrins with a single *meso*-halophenyl and seven *meso*-3,5-di-*tert*-butylphenyl substituents. The bis-porphyrins were prepared by condensation of a porphyrin-α-dione with benzene-1,2,4,5-tetraamine to form a porphyrin diaminoquinoxaline intermediate which was subsequently condensed with a second different porphyrin-α-dione. The key issue in the synthesis was the separation of the desired asymmetrically substituted bis-porphyrin from the symmetric bis-porphyrin by-products of similar polarities. Enhanced separation of the bis-porphyrin products was achieved by chelation of a metal into one of the porphyrin rings, the metal being introduced at the porphyrin-α-dione stage. Copper was successfully used when chelated into the less polar porphyrin-α-dione but the use of zinc in the more polar porphyrin-α-dione to enhance bis-porphyrin separation was unsuccessful as the pyridinium hydrochloride produced in the reaction was found to demetallate the porphyrins.

Introduction

New covalently linked porphyrin arrays for use in molecular electronics and modelling the photosynthetic process are being continually developed.[1–8] The vast majority of porphyrin arrays are linked through the *meso*-positions.[2,4–8] The alternative and less well studied route for connecting porphyrins is to link them through the β-pyrrolic positions.[1,3,9–11] For the covalently-linked porphyrin arrays reported each of the porphyrins within the array uses only one type of bridging point, *meso*- or β-pyrrolic, and there have been no papers describing porphyrin arrays in which the individual porphyrin rings have links through both the *meso*- and β-pyrrolic positions. The main type of porphyrin array connected by a conjugated bridge through the β-pyrrolic positions uses a tetraazaanthracene linker.[9,10] In these tetraazaanthracene bridged bis-porphyrins the electronic properties of the two porphyrins are modulated[12] so that they may be of interest as charge transport layers in light-emitting diodes or as materials for photovoltaics. We were therefore inter-

ested in developing synthetic routes to bis-porphyrin arrays, as illustrated in Fig. 1, which are linked through the *meso*-positions. Linking of the bis-porphyrins should enhance their solution processability, and by having a conjugated *meso*-diphenylacetylene bridge the electronic properties of the bis-porphyrins may also be modulated. To prepare *meso*-connected bis-porphyrins it is necessary to make bis-porphyrins which have a *meso*-substituent with a linking point. To this end we have reported the synthesis of porphyrin-α-diones which have a single *meso*-halophenyl moiety, to allow coupling to conjugated linkers using palladium catalysis, with the other *meso*-positions carrying the solubilising 3,5-di-*tert*-butylphenyl groups.[13] In this paper we report the strategy for the preparation and purification of asymmetrically substituted bis-porphyrins in which one porphyrin ring contains a single *meso*-linking moiety as the next step towards forming bis-porphyrin arrays.

Results and discussion

The best strategy for the preparation of asymmetrically substituted bis-porphyrins containing tetraazaanthracene bridges is
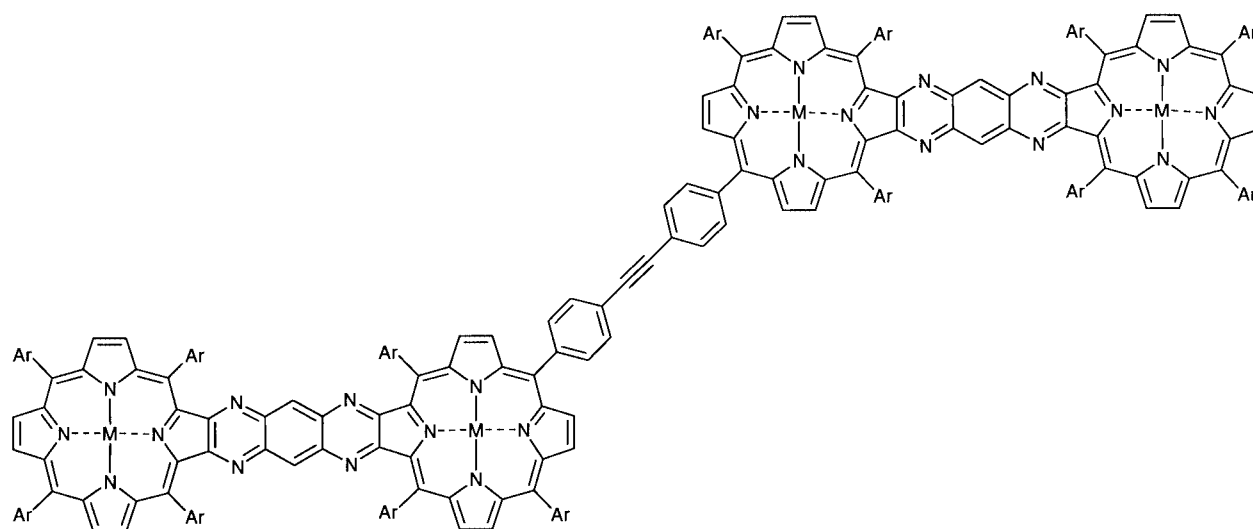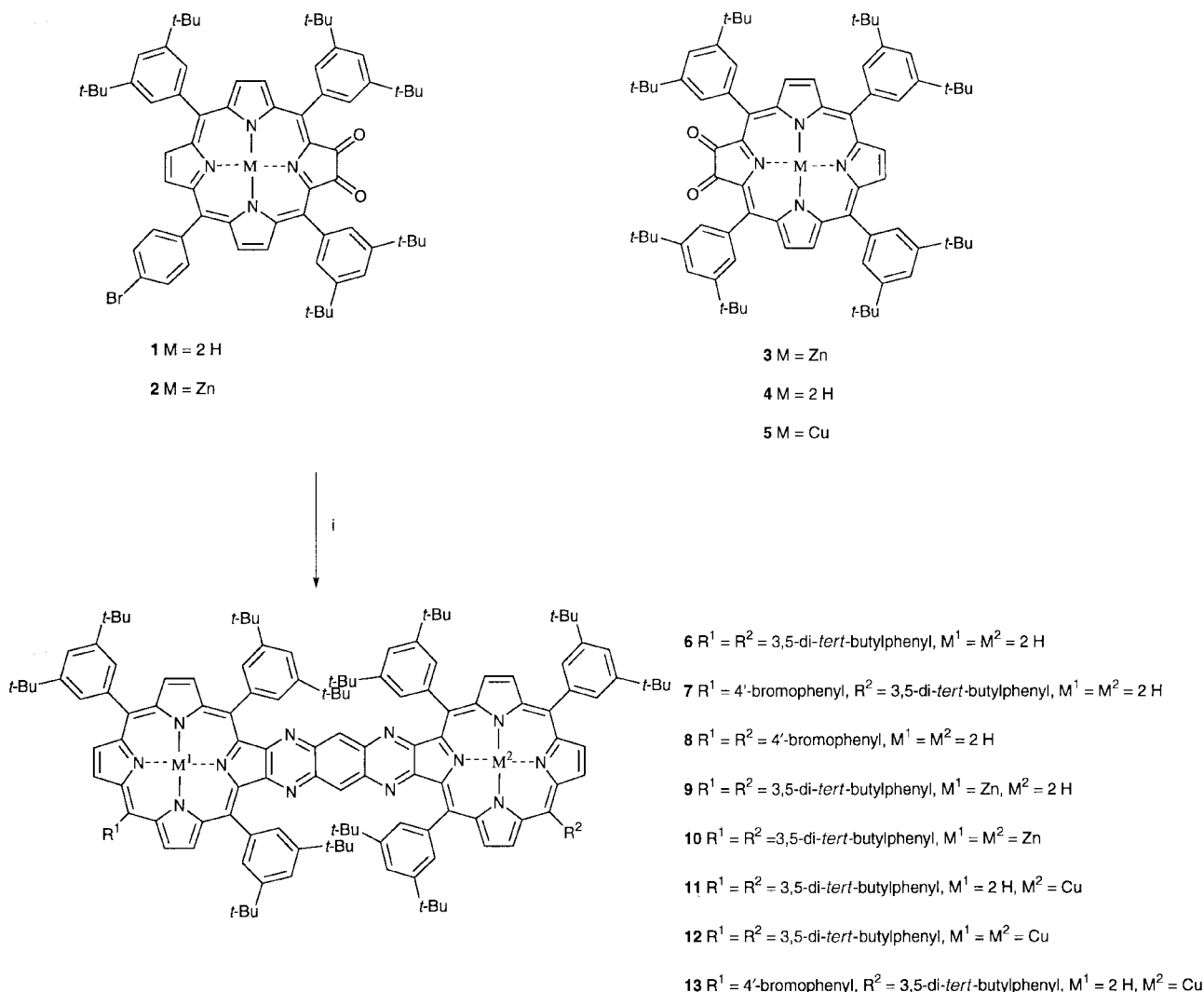
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† For Part 1, see ref. 13.

Fig. 1 A diphenylacetylene linked bis-porphyrin array.

1 M = 2 H

2 M = Zn

3 M = Zn

4 M = 2 H

5 M = Cu

i

6 R^1 = R^2 = 3,5-di-*tert*-butylphenyl, M^1 = M^2 = 2 H

7 R^1 = 4'-bromophenyl, R^2 = 3,5-di-*tert*-butylphenyl, M^1 = M^2 = 2 H

8 R^1 = R^2 = 4'-bromophenyl, M^1 = M^2 = 2 H

9 R^1 = R^2 = 3,5-di-*tert*-butylphenyl, M^1 = Zn, M^2 = 2 H

10 R^1 = R^2 = 3,5-di-*tert*-butylphenyl, M^1 = M^2 = Zn

11 R^1 = R^2 = 3,5-di-*tert*-butylphenyl, M^1 = 2 H, M^2 = Cu

12 R^1 = R^2 = 3,5-di-*tert*-butylphenyl, M^1 = M^2 = Cu

13 R^1 = 4'-bromophenyl, R^2 = 3,5-di-*tert*-butylphenyl, M^1 = 2 H, M^2 = Cu

Scheme 1 *Reagents and conditions*: i, pyridine, benzene-1,2,4,5-tetraamine tetrahydrochloride, Ar, Δ then second porphyrin-α-dione, Ar, Δ.
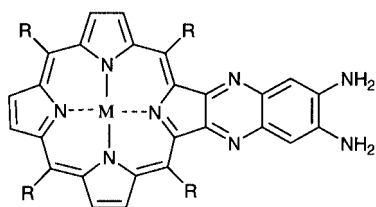

Fig. 2 Porphyrin diaminoquinoxaline intermediate.

to react one equivalent of a porphyrin-α-dione with one equivalent of benzene-1,2,4,5-tetraamine to form a porphyrin diaminoquinoxaline (Fig. 2) which is then condensed with a second porphyrin-α-dione.[14] This procedure works well providing the *meso*-substituents flanking the α-dione of the first porphyrin are sterically demanding and that the two porphyrin components have significantly different properties. The latter is important because in addition to the desired asymmetrically substituted bis-porphyrin there are often small amounts of the undesired symmetric bis-porphyrins which arise from condensation of two equivalents of the same porphyrin-α-dione with the benzene-1,2,4,5-tetraamine. If the polarities of the two porphyrin components used in the synthesis are significantly different then the bis-porphyrin products can be easily separated by column chromatography over silica.[14] However, in our study we require the bis-porphyrins to have only one of the *meso*-phenyls substituted with a halo group (for linking to form the array) with the other seven containing solubilising *tert*-butyl groups (for ease of manipulation). This means that there is the

possibility of forming symmetric bis-porphyrins with eight 3,5-di-*tert*-butylphenyl groups, or with six 3,5-di-*tert*-butylphenyl groups and two halophenyl substituents as well as the desired asymmetrically substituted bis-porphyrin. Given the small changes in outer peripheral substituents the difference in polarity between each of the potential bis-porphyrins might be small and hence separations based on polarity would be difficult. To determine the best method for achieving the synthesis of a mono-*meso*-halophenylbis-porphyrin we chose the more easily accessed mono-*meso*-bromophenylporphyrin-α-dione **1**, although for palladium catalysed couplings to make the desired bis-porphyrin arrays the iodophenyl substituent would be better.

The first experiment was to determine whether the polarities of the free-base (4'-bromophenyl)heptakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin **7** (Scheme 1) and the "symmetric" bis-porphyrin by-products **6** and **8** were sufficiently different to allow easy separation. The (4-bromophenyl)porphyrin-α-dione **1** was reacted with 1.1 equivalents of benzene-1,2,4,5-tetraamine tetrahydrochloride in pyridine heated at reflux. We found that the use of refluxing pyridine was advantageous over the reactions carried out at room temperature as both the first and second condensations occurred much more quickly. After one hour the porphyrin diaminoquinoxaline intermediate was added to an excess of the symmetric porphyrin-α-dione **4** and the reaction mixture heated at reflux overnight. This procedure gave, as expected, a mixture of the three bis-porphyrins and as anticipated they had similar polarities. However, they could be separated with difficulty using chromatotron and column

chromatography over silica and under these conditions the desired (4′-bromophenyl)heptakis(3″,5″-di-*tert*-butylphenyl)-bis-porphyrin **7** was isolated in a 56% yield, with octakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin **6** and bis(4′-bromophenyl)-hexakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin **8** collected in 7% and ~9% yields respectively [**8** was not isolated in a pure form]. Even after careful separation some of the bis-porphyrin material remained as a mixture of **6**, **7**, and **8** (~16% by mass). It is important to note that in the case of bis(4′-bromophenyl)-hexakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin **8** there are two possible isomers, the "*cis*", as illustrated in Scheme 1, and the "*trans*" which has one of the bromophenyl groups in a "top" *meso*-position. We believe that there is no chemical advantage for the formation of one isomer of **8** over the other and therefore a mixture of the two would occur. In addition, the excess symmetric porphyrin-α-dione **4** was recovered. Although the desired bis-porphyrin was the major product, a more efficient method for separating the products was clearly required.

The two strategies that we investigated to improve the separation both involved the chelation of metals to the inner peripheries of the porphyrin-α-diones. It is known that chelation of zinc generally increases the polarity of a porphyrin when compared to the equivalent free-base porphyrin whilst the chelation of copper normally decreases the polarity of the porphyrin. Therefore, the logical approach in our study was to chelate zinc into the more polar porphyrin-α-dione, in this case **1**, or copper into the less polar symmetric porphyrin-α-dione **4**. The zinc (4′-bromophenyl)porphyrin-α-dione **2** was easily made in a 99% isolated yield by reacting **1** with an excess of zinc acetate dihydrate in a dichloromethane–methanol mixture heated at reflux for three hours. However, one of the by-products of the condensation reaction used to form the bis-porphyrins is hydrogen chloride and although the reactions are carried out in pyridine we were concerned that the pyridinium hydrochloride could remove the relatively labile zinc. To test this we carried out a reaction on the more readily available symmetric zinc porphyrin-α-dione **3**[15] to make the dizinc octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin **10**. Two equivalents of the zinc porphyrin-α-dione **3** were reacted with benzene-1,2,4,5-tetraamine tetrahydrochloride in pyridine heated at reflux for 16 hours. We avoided the usual acidic work-up, which is normally used to help remove the pyridine, to avoid demetallation of the zinc bis-porphyrins. Under these conditions the free-base octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin **6** was isolated in a 27% yield, with the zinc octakis-(3′,5′-di-*tert*-butylphenyl)bis-porphyrin **9** isolated in a 33% yield. The desired dizinc octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin **10** was collected in an impure form in a yield of less than 11%. Although the three bis-porphyrins could be separated from each other this reaction clearly showed that zinc was being removed under the reaction conditions and therefore the use of zinc to improve the separation in the preparation of the (4′-bromophenyl)heptakis(3″,5′-di-*tert*-butylphenyl)bis-porphyrin was not viable using these conditions.

In contrast, previous work has shown that a copper porphyrin-α-dione and copper bis-porphyrins are stable to the pyridinium hydrogen chloride produced during the bis-porphyrin preparation when the reaction is carried out at room temperature.[14] However, our synthetic protocol for forming the bis-porphyrins uses pyridine heated at reflux and although copper porphyrins should be stable under these conditions we nevertheless thought it important to confirm their stability by preparing the copper octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin from porphyrin-α-diones **4** and **5**. This was achieved by reacting the free-base porphyrin-α-dione **4** with a small excess of benzene-1,2,4,5-tetraamine tetrahydrochloride in pyridine heated at reflux for 0.5 hours to form the corresponding porphyrin diaminoquinoxaline which was subsequently condensed with an excess of the copper porphyrin-α-dione **5** under the same conditions for 16.5 hours. On purification, the

dicopper octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin **12** was isolated in a 21% yield, the copper octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin **11** was isolated in a 78% yield, and 13% of the copper porphyrin-α-dione **5** was returned. Importantly the bis-porphyrin products were separable by column chromatography. Given the success of using the copper chelated porphyrin-α-dione **5** we reacted the (4′-bromophenyl)-porphyrin-α-dione **1** with a small excess of benzene-1,2,4,5-tetraamine tetrahydrochloride in pyridine heated at reflux for 1 hour. The solution was then added to an excess of the copper porphyrin-α-dione **5** and the reaction mixture heated at reflux for a further 15 hours. On purification the copper (4′-bromo-phenyl)heptakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin **13** was isolated in an 88% yield, and the excess copper diketone **5** was recovered. Only traces of two other bis-porphyrins were observed, which were thought to be the dicopper octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin **12** and the bis(4′-bromo-phenyl)hexakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin **8**, and these were easily removed from the desired bis-porphyrin by chromatography over silica.

The final aspect of this study was to remove the copper from the copper (4′-bromophenyl)heptakis(3″,5″-di-*tert*-butyl-phenyl)bis-porphyrin **13** to give the desired free-base **7**. This was achieved by treating **13** with concentrated sulfuric acid, however, the yields of free-base bis-porphyrin **7** were quite poor (up to 42%). One reason for the low yield during the demetallation procedure may be that protonation of the free-base porphyrin in the bis-porphyrin occurs, causing the bis-porphyrin to precipitate out of the reaction mixture before the metal can be removed.

Conclusion

We have successfully developed a strategy for the synthesis and separation of bis-porphyrins which have similar polarities due to only minor differences in substituents on the porphyrin outer periphery. We have shown that chelation of copper into the less polar porphyrin-α-dione gives enhanced separation of the bis-porphyrins and that the copper is stable under the reaction conditions. In contrast, zinc is an unsuitable metal for this work due to its lability under the reaction conditions caused by the pyridinium hydrochloride in the reaction mixture. Finally we have shown that the copper could be removed from the bis-porphyrin to give the corresponding free-base compound.

Experimental

Measurements

^{1}H NMR spectra were recorded on a Bruker AM-500 (500 MHz) or a Varian Gemini 200 (200 MHz) spectrometer. Infra-red spectra were recorded with either a Perkin-Elmer 781 or Paragon 1000 infrared spectrometer. UV–visible spectra were recorded on Perkin-Elmer UV–visible spectrometers (Lambda 2 or Lambda 14P) in spectrophotometric grade dichloromethane. Fast Atom Bombardment (FAB) mass spectra (*m/z*) were recorded on a VG Autospec spectrometer. MALDI mass spectra were measured on a Micromass TofSpec-2E in the reflectron mode. Samples were run from a Dithranol (1,8,9-trihydroxy-anthracene) matrix using solutions in a chloroform–pyridine mixture (9:1) with a sample concentration of 3–5 pmol μl^{-1}. Due to the combination of metal chelation, halogen substituents, molecular size, and different degrees of protonation the molecular weights observed by mass spectroscopy generally appeared as a complex isotopic cluster around the expected parent ion. We have quoted the mass for the base peak for each compound. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. We found that **2** did not melt but partially decomposed on heating. This was observed by analysis with thin-layer chromatography which

showed the presence of more than one compound after heating. Therefore, the melting point is quoted as decomposition below the highest temperature measured. Microanalyses were performed in the Inorganic Chemistry Laboratory, Oxford. All solvents for recrystallization were distilled before use. Pyridine was dried and stored, after distillation, over potassium hydroxide pellets. Light petroleum refers to the fraction of boiling point 60–80 °C. Thin-layer chromatography was performed on glass micro plates coated with silica GF_{254}, or with Merck aluminium plates coated with silica gel 60 F_{254}. Column chromatography was performed using ACROS Organics silica gel, 0.035–0.07 mm. Where solvent mixtures are used, the proportions are given by volume.

(4′-Bromophenyl)heptakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin 7

Method 1. A solution of (4-bromophenyl)porphyrin-α-dione **1** (73 mg, 0.07 mmol) and benzene-1,2,4,5-tetraamine tetrahydrochloride (23 mg, 0.08 mmol) in dry, deoxygenated, pyridine (1.8 cm³) was heated at reflux under argon for 1 h. The solution was then transferred under argon to porphyrin-α-dione **4**[15] (128 mg, 0.117 mmol). The first reaction flask was rinsed with pyridine (1.4 cm³) and this was transferred to the reaction mixture under argon. The reaction mixture was heated at reflux under argon for 15.6 h and then allowed to cool. Dichloromethane (25 cm³) was added, and the organic solution was washed with dilute hydrochloric acid (2 M, 2 × 15 cm³), aqueous sodium bicarbonate (10%, 20 cm³), and water (20 cm³), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was purified with difficulty by column and chromatotron chromatography over silica using dichloromethane–light petroleum mixtures (3:20 to 2:3) as eluent, and four compounds were isolated. Octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin **6** was isolated as a brown solid (9 mg, 7%), which had an identical ¹H NMR spectrum to that reported.[10] (4′-Bromophenyl)heptakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin **7** was isolated as a brown solid (86 mg, 56%), mp >300 °C (Found: C, 80.74; H, 7.15; N, 7.26. $C_{150}H_{169}N_{12}Br$ requires C, 81.16; H, 7.67; N, 7.57%); ν_{max}(KBr disc)/cm⁻¹ 3350 (N–H); λ_{max}(CH₂Cl₂)/nm (log ε) 426 (5.53), 457 (5.47), 500sh (4.91), 604sh (4.25), 612sh (4.29), 629 (4.32), and 676 (3.84); δ_H(500 MHz; CDCl₃) −2.38 (1 H, s, NH), −2.37 (1 H, s, NH), −2.31 (2 H, s, NH), 1.55–1.60 (126 H, *t*-butyl H), 7.81 (2 H, dd, $J_{2″,4″} = J_{6″,4″} = 2.0$ Hz, C(4″)H), 7.83 (1 H, dd, $J_{2′,4″} = J_{6″,4″} = 2.0$ Hz, C(4″)H), 7.92 and 8.13 (4 H, AA′BB′, C(2′)H, C(3′)H, C(5′)H, and C(6′)H), 8.01 (4 H, m, C(4″)H), 8.10 (14 H, m, C(2″)H and C(6″)H), 8.59 (2 H, s, bridge H), 8.69 and 8.77 (2 H, ABq, $J_{AB} = 4.5$ Hz, C(4)H and C(5)H), 8.77 (2 H, s, C(35)H and C(36)H), and 8.89 and 8.97 (8 H, 2 × m, C(9)H, C(10)H, C(19)H, C(20)H, C(30)H, C(31)H, C(40)H, and C(41)H); *m/z* (FAB) 2221.4 (100%). Bis(4′-bromophenyl)hexakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin **8** was isolated as a brown solid which contained a minor amount of a second porphyrin (~7 mg, ~9%). Selected data for **8**: ν_{max}(KBr disc)/cm⁻¹ 3350 (N–H); δ_H(500 MHz; CDCl₃) −2.39 and −2.37 (4 H, 2 × s, NH), 1.55–1.59 (108 H, *t*-butyl H), 7.83 (2 H, m, C(4″)H), 7.92 and 8.13 (8 H, AA′BB′, C(2′)H, C(3′)H, C(5′)H, and C(6′)H), 8.01 (4 H, m, C(4″)H), 8.09 (12 H, m, C(2″)H and C(6″)H), 8.58 (2 H, s, bridge H), 8.69 and 8.77 (4 H, ABq, $J_{AB} = 4.5$ Hz, C(4)H, C(5)H, C(35)H, C(36)H), 8.87–8.91 (6 H, br m, β-pyrrolic H), and 8.98 (2 H, br 1/2ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H); *m/z* (FAB) 2188.2 (100%). Porphyrin-α-dione **4** was returned as a green solid (32 mg), a sample of which which co-chromatographed with and had an identical ¹H NMR spectrum to an authentic sample. Some material (~19 mg) remained as a mixture of **6**, **7**, and **8**.

Method 2. A mixture of (4′-bromophenyl)octakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin copper(II) **13** (138 mg, 0.060

mmol), dichloromethane (25 cm³), and sulfuric acid (98%, 1.0 cm³) was stirred for 7 min at room temperature. An ice–water mixture (20 cm³) was added carefully, and the ice allowed to melt. The aqueous layer was separated and extracted with dichloromethane (10 cm³). The combined organic layers were washed with aqueous sodium bicarbonate (5%, 20 cm³) and water (20 cm³), dried over anhydrous sodium sulfate, and the solvent completely removed. The residue was purified by column and chromatotron chromatography over silica using dichloromethane–light petroleum mixtures (1:4 to 3:7) as eluent to give (4′-bromophenyl)heptakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin **7** as a brown solid (57 mg, 42%), which co-chromatographed with and had an identical ¹H NMR spectrum to an authentic sample.

[17,18-Dioxo-5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)chlorinato]zinc(II) 2

A mixture of (4-bromophenyl)porphyrin-α-dione **1** (51 mg, 0.048 mmol), zinc(II) acetate dihydrate (31 mg, 0.14 mmol), dichloromethane (20 cm³), and methanol (2 cm³) was heated at reflux for 4.5 h. The solvent was completely removed, and the residue purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:1) as eluent to give **2** as a green solid (52 mg, 98%), mp <300 °C (decomp.) (Found *m/z* 1120.417 (M⁺). $C_{68}H_{73}N_4BrO_2Zn$ requires 1120.421); ν_{max}(KBr disc)/cm⁻¹ 1724 (C=O); λ_{max}(CH₂-Cl₂)/nm (log ε) 414 (5.10), 494 (4.25), 631 (3.65), 723 (3.70); δ_H(500 MHz; CDCl₃) 1.45–1.49 (54 H, 3 × s, *t*-butyl H), 7.63 (4 H, m, C(2″)H and C(6″)H), 7.71 (2 H, m, C(4″)H), 7.76 (1 H, dd, $J_{2′,4″} = J_{6″,4″} = 1.77$ Hz, C(4″)H), 7.84 and 7.94 (4 H, AA′BB′, C(2′)H, C(3′), C(5′)H, and C(6′)H), 7.91 (2 H, d, $J_{4″,2″} = J_{4″,6″} = 2$ Hz, C(2″)H and C(6″)H), 8.35 and 8.53 (2 H, ABq, $J_{AB} = 4.5$ Hz, β-pyrrolic H), 8.36 and 8.62 (2 H, ABq, $J_{AB} = 4.5$ Hz, β-pyrrolic H), and 8.35 and 8.53 (2 H, ABq, $J_{AB} = 5$ Hz, β-pyrrolic H), and 8.45 and 8.54 (2 H, ABq, $J_{AB} = 4.5$ Hz, β-pyrrolic H).

Octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin dizinc(II) 10

A solution of zinc porphyrin-α-dione **3**[15] (45 mg, 0.04 mmol) and benzene-1,2,4,5-tetraamine tetrahydrochloride (6 mg, 0.02 mmol) in dry, deoxygenated, pyridine (0.5 cm³) was heated at reflux under argon in the dark for 16 h. The solution was allowed to cool and then dichloromethane (20 cm³) was added. The organic solution was washed with water (3 × 20 cm³), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:1) as eluent and three bands were collected. Octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin **6** was isolated as a brown solid (12 mg, 27%), which had an identical ¹H NMR spectrum to that reported.[10] Octakis(3′,5′-di-*tert*-butylphenyl)-bis-porphyrin zinc(II) **9** was isolated as a brown solid (15 mg, 33%), which had an identical ¹H NMR spectrum to that reported[14]; δ_H(500 MHz; CDCl₃) −2.25 (2 H, s, NH), 1.60, 1.61, 1.65, and 1.66 (144 H, 4 × s, *t*-butyl H), 7.86 (2 H, dd, $J_{2′,4′} = J_{6′,4′} = 2.0$ Hz, C(4′)H), 7.87 (2 H, dd, $J_{2′,4′} = J_{6′,4′} = 2.0$ Hz, C(4′)H), 8.05 (2 H, dd, $J_{2′,4′} = J_{6′,4′} = 1.5$ Hz, C(4′)H), 8.06 (2 H, dd, $J_{2′,4′} = J_{6′,4′} = 2.0$ Hz, C(4′)H), 8.12 (4 H, d, $J_{4′,6′} = J_{4′,6′} = 1.5$ Hz, C(2′)H and C(6′)H), 8.15 (4 H, d, $J_{4′,6′} = J_{4′,6′} = 1.5$ Hz, C(2′)H and C(6′)H), 8.16 (8 H, br s, C(2′)H and C(6′)H), 8.73 (2 H, s, bridge H), 8.83 and 8.91 (4 H, 2 × s, C(4)H, C(5)H, C(35)H, and C(36)H), 8.89 and 9.03 (4 H, ABq, $J_{AB} = 5$ Hz, C(9)H, C(10)H, C(19)H and C(20)H), and 8.95 and 9.03 (4 H, ABq, $J_{AB} = 5$ Hz, C(30)H, C(31)H, C(40)H and C(41)H); *m/z* (MALDI) 2317.5 (M⁺, 100%). Octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin dizinc(II) **10** was collected as an impure brown solid (5 mg, <11%). The main signals in the ¹H NMR spectrum corresponded to those reported for **10**;[14] δ_H(200 MHz; CDCl₃) 1.54 and 1.59 (144 H, 2 × s, *t*-butyl H),

7.80 (2 H, dd, $J_{2',4'} = J_{6',4'} = 1.5$ Hz, C(4')H), 8.00 (2 H, dd, $J_{2',4'} = J_{6',4'} = 1.5$ Hz, C(4')H), 8.06 (8 H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2')H and C(6')H), 8.09 (8 H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2')H and C(6')H), 8.76 (2 H, s, bridge H), 8.82 and 8.97 (8 H, ABq, $J_{AB} = 5.0$ Hz, C(9)H, C(10)H, C(19)H, C(20)H, C(30)H, C(31)H, C(40)H, and C(41)H), and 8.85 (4 H, s, C(4)H, C(5)H, C(35)H, and C(36)H); m/z (MALDI) 2317.5 (M$^+$, 100%).

Octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin copper(II) 11

A solution of porphyrin-α-dione **4** (29 mg, 0.03 mmol) and benzene-1,2,4,5-tetraamine tetrahydrochloride (9 mg, 0.03 mmol) in dry, deoxygenated, pyridine (0.75 cm³) was heated at reflux under argon for 0.5 h. The reaction mixture was then transferred to copper porphyrin-α-dione **5**[15] (52 mg, 0.045 mmol) under argon. The first flask was rinsed with pyridine (0.5 cm³) which was then transferred to the reaction mixture under argon. The reaction mixture was heated at reflux under argon for 16.5 h and then allowed to cool. Dichloromethane (20 cm³) was added, and the organic solution was washed with dilute hydrochloric acid (3 M, 2 × 10 cm³), aqueous sodium bicarbonate (5%, 20 cm³), and water (20 cm³), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was purified by column and chromatotron chromatography over silica using a dichloromethane–light petroleum mixture (1:4) as eluent and three bands were collected. Octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin dicopper(II) **12** was isolated as a brown solid (11 mg, 21%), which had a UV–visible spectrum corresponding to an authentic sample;[14] λ_{max}(CH₂Cl₂)/nm (log ε) 424 (5.52), 454 (5.39), 517 (4.84), 534 (4.83), and 670 (4.36); m/z (MALDI) 2377.3 (100%). Octakis(3′,5′-di-*tert*-butylphenyl)bis-porphyrin copper(II) **11** was isolated as a brown solid (47 mg, 78%), which had a UV–visible spectrum corresponding to an authentic sample;[14] ν_{max}(CHCl₃)/cm^{-1} 3350 (N–H); λ_{max}(CH₂Cl₂)/nm (log ε) 425 (5.45), 455 (5.30), 507 (4.80), 608sh (4.19), 642 (4.26), and 687sh (4.04); m/z (MALDI) 2316.3 (100%). Copper porphyrin-α-dione **5** was isolated as a green solid (7 mg), a sample of which co-chromatographed with and had an identical infrared spectrum to an authentic sample.

4′-Bromophenyl heptakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin copper(II) 13

A solution of 4′-bromophenyl porphyrin-α-dione **1** (89 mg, 0.084 mmol) and benzene-1,2,4,5-tetraamine tetrahydrochloride (29 mg, 0.10 mmol) in dry, deoxygenated, pyridine (2.3 cm³) was heated at reflux under argon for 1 h. The reaction mixture was transferred under argon to copper porphyrin-α-dione **5** (165 mg, 0.143 mmol). The original flask was rinsed

with pyridine (1.2 cm³) and this was then transferred to the reaction mixture. The reaction mixture was heated at reflux under argon for 15 h and then allowed to cool. Dichloromethane (20 cm³) was added, and the organic solution was washed with water (3 × 20 cm³), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was purified by column chromatography over silica using dichloromethane–light petroleum mixtures (1:4–2:3) as eluent and two bands were collected. (4′-Bromophenyl)heptakis(3″,5″-di-*tert*-butylphenyl)bis-porphyrin copper(II) **13** was isolated as a brown solid (169 mg, 88%), mp >300 °C (Found: C, 78.46; H, 7.50; N, 7.08. C₁₅₀H₁₆₇N₁₂BrCu requires C, 78.97; H, 7.38; N, 7.37%); ν_{max}(CHCl₃)/cm^{-1} 3350 (N–H); λ_{max}(CH₂Cl₂)/nm (log ε) 425 (5.51), 454 (5.34), 505 (4.83), 641 (4.30), and 680sh (4.13); m/z (FAB) 2281.7 (100%). Copper porphyrin-α-dione **5** was isolated as a green solid (55 mg, 33%), a sample of which co-chromatographed with and had an identical infrared spectrum to an authentic sample.

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Paper a907059a