Bis-porphyrin arrays. Part 1. The synthesis of *meso*-halophenyl porphyrin-α-diones

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Received (in Cambridge) 7th December 1998, Accepted 21st January 1999

meso-Functionalised porphyrin-α-diones have been prepared as the basic building blocks for bis-porphyrin arrays. *meso*-Halophenyl porphyrins **4** and **7** were prepared by condensation of 3,5-di-*tert*-butylbenzaldehyde with dipyrromethanes **1**, **2**, and **3**. Conversion of **4** and **7** to the corresponding *meso*-halophenylporphyrin-α-diones was achieved in five steps in overall yields of up to 58%. The reaction sequence consisted of chelation of the porphyrin with copper(II), nitration, hydroxylation with the benzaldoximate anion, demetallation, followed by oxidation with the Dess–Martin periodinane. The key hydroxylation step was found to proceed chemoselectively, displacing the β-pyrrolic nitro group whilst leaving the *meso*-halophenyl group intact.

Introduction

There is continuing interest in the development of porphyrin arrays for modelling photosynthesis,[1–10] and for use in molecular electronics.[9–13] Porphyrin arrays generally consist of two or more porphyrin rings joined covalently at their peripheral positions either directly or through conjugated bridges and this gives rise to well-defined geometries. Most covalently-linked porphyrin arrays use only one bridging point for all the porphyrins within the array, these being either the β-pyrrolic[12,14] or *meso* positions.[1,2,3,11,15,16] Of these two types of linkage the *meso* connected arrays have been studied more extensively. There have been no reports of porphyrin arrays in which the individual porphyrin rings have links through both the *meso* and β-pyrrolic positions, although there are examples of arrays in which the *meso* position of one ring is linked to the β-pyrrolic position of another.[13] β-Pyrrolic tetraazaanthracene linked bis-porphyrins are potential materials for charge transport layers in light-emitting diodes and, because their UV–visible absorption edge is approximately 1.8 eV, as materials for photovoltaic devices. We are therefore interested in developing synthetic routes to bis-porphyrin arrays, for example, Fig. 1, which are linked through the *meso* positions to enhance their processibility and modulate their electronic properties. For this study we have chosen a *meso*-diphenylacetylene bridge to link the bis-porphyrins as such a link has been successfully used to prepare models for photosynthetic antenna complexes.[1] As the tetraazaanthracene linked bis-porphyrins are prepared by the condensation of porphyrin-α-diones with benzene-1,2,4,5-tetramine[14] this requires the preparation of a porphyrin-α-dione with a reactive *meso* substituent. In this paper, we describe the strategy and methodology for the preparation of two isomeric porphyrin-α-diones from mono-*meso*-bromo- and -iodo-phenylporphyrins, **4** and **7**, which can be used as building blocks for *meso* linked bis-porphyrin arrays.

Results and discussion

The most straightforward strategy for the synthesis of mono-*meso*-halophenylporphyrin-α-diones is to first construct the porphyrin ring incorporating the halophenyl group at one *meso* position and then functionalise the β-pyrrolic position. For our work we have chosen 3,5-di-*tert*-butylphenyl substituents for the three other *meso* positions to give good solubility to the porphyrins. The two main methods for making *meso*-arylporphyrins with different aryl substituents involve either reacting a stoichiometric amount of each of the benzaldehydes with pyrrole or condensing two dipyrromethanes with two equivalents of an appropriate benzaldehyde. The advantage of the latter method is that providing scrambling of the dipyrro-

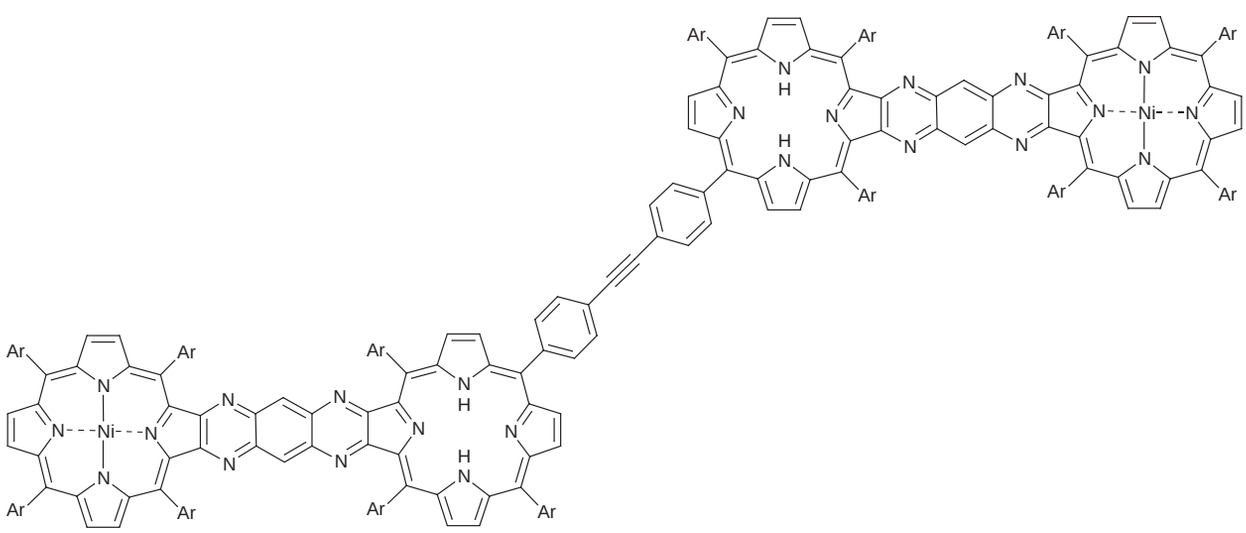
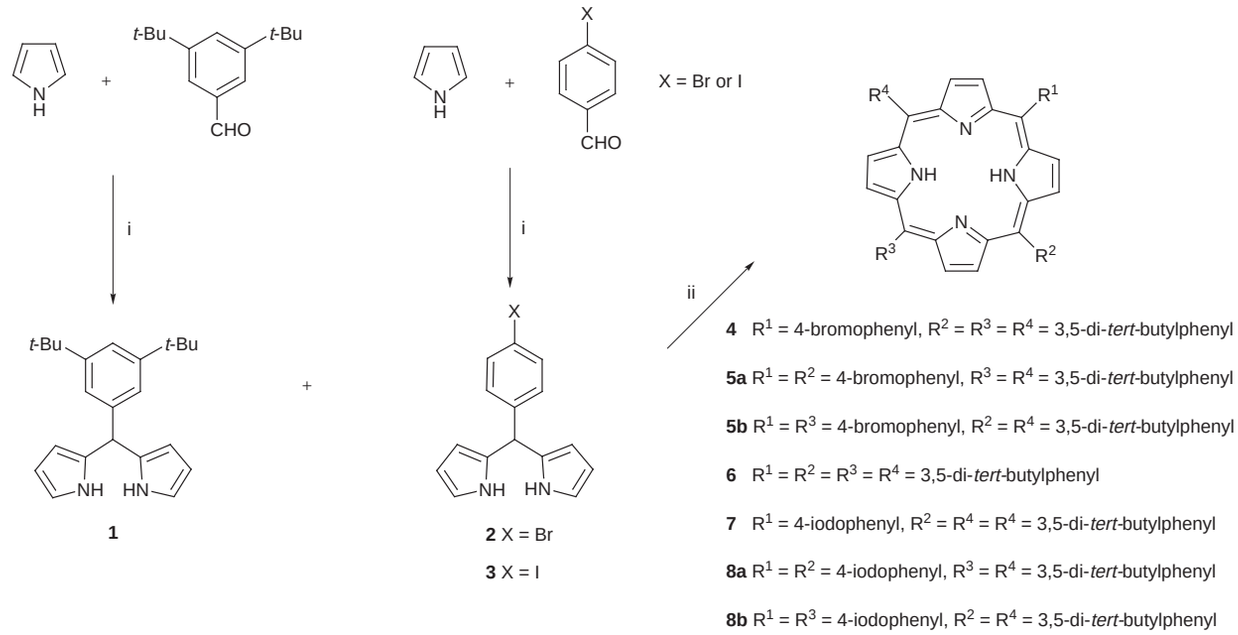


Fig. 1 An acetylene linked bis-porphyrin array.



Scheme 1 *Reagents and conditions*: i, trifluoroacetic acid; ii, trifluoroacetic acid, DCM, and 3,5-di-*tert*-butyl benzaldehyde, room temp. then DDQ.

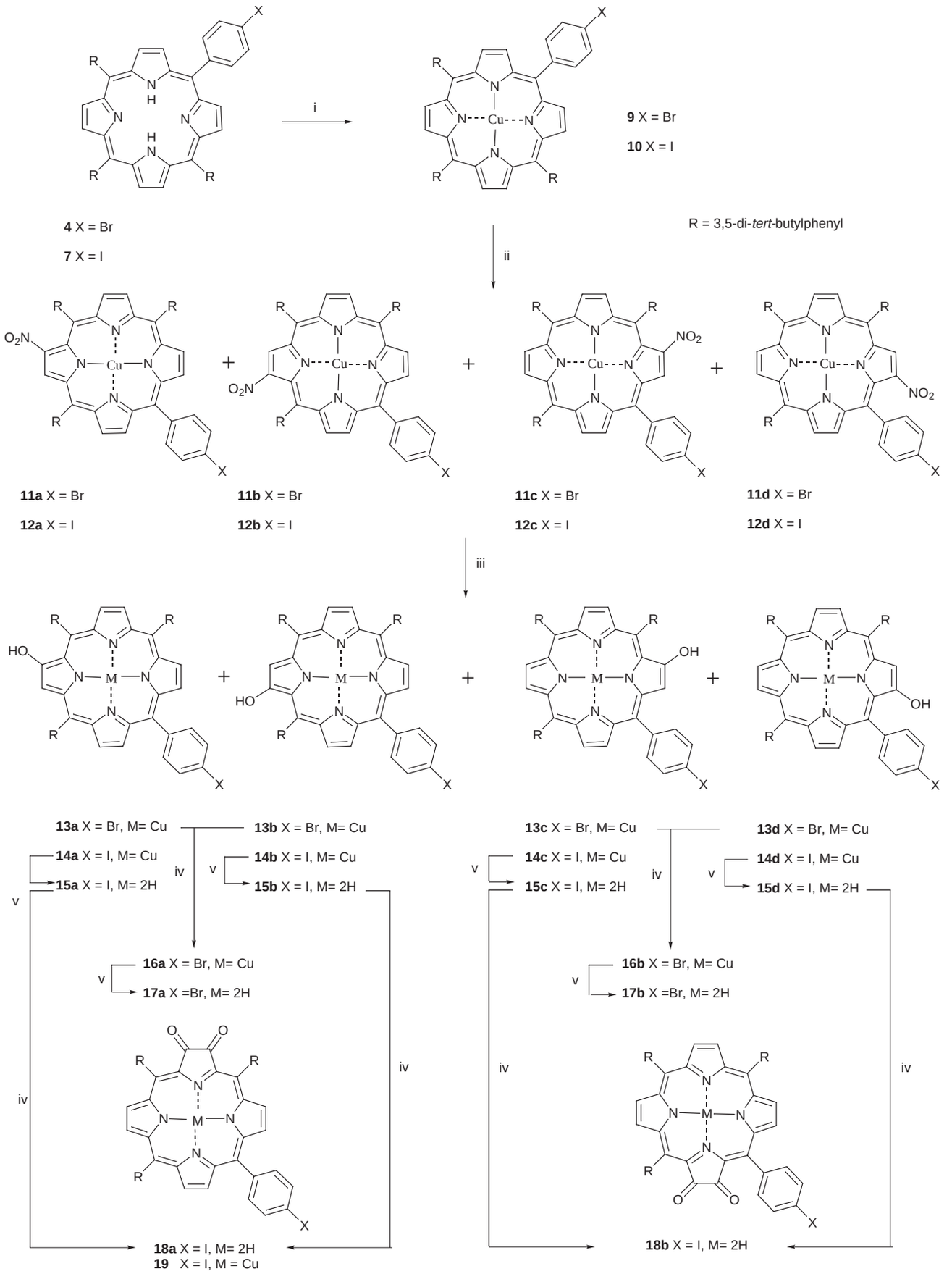
methanes does not occur higher yields of the desired porphyrin should be attainable as the former route can give rise to a mixture of six porphyrins. Therefore, to prepare the monohalophenylporphyrins **4** and **7** we synthesised the halophenyldipyrromethanes **2**[17] and **3**[17] and *meso*-(3,5-di-*tert*-butylphenyl)-dipyrromethane **1**. *meso*-(3,5-Di-*tert*-butylphenyl)dipyrromethane **1** was made by the same method as **2** and **3**, but proved more difficult to purify. Whereas **2** and **3** could be purified by recrystallisation, **1** required partial purification by chromatography over silica using a mixture of light petroleum and ethyl acetate, with 1% triethylamine to prevent decomposition of the dipyrromethane on the mildly acidic silica before recrystallisation from light petroleum. When these conditions were used, dipyrromethane **1** could be isolated as a white crystalline solid in a 55% yield. A second product of slightly higher R_f, which could not be completely purified by chromatography on silica from dipyrromethane **1** was determined to be bis-*meso*-(3,5-di-*tert*-butylphenyl)tripyrromethane from its ^{1}H NMR and mass spectra. The tripyrromethane was formed in yields of approximately 10%.

Following a reported procedure[18] for the formation of porphyrins from dipyrromethanes we condensed one equivalent of **1** with equimolar amounts of **2** or **3** and two equivalents of 3,5-di-*tert*-butylbenzaldehyde[19] to make the required halophenylporphyrins **4** and **7** (Scheme 1). We found that the optimum conditions for the formation of bromophenylporphyrin **4** required the initial concentration of 3,5-di-*tert*-butylbenzaldehyde to be 0.08 M and the trifluoroacetic acid catalyst to be one equivalent with respect to the aldehyde. The oxidation of the tetrapyrrole to the porphyrin in the final stage was straightforward and three equivalents of 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone was usually sufficient for complete oxidation. Purification of the crude reaction mixture was also generally straightforward. On larger scales the crude product was passed through a plug of silica to remove black baseline material which is thought to be polymeric by-products. The black material which did not adsorb onto the silica, eluted before the porphyrin and so could be almost completely removed at this stage. The porphyrin mixture was then separated by further column chromatography over silica. On small to medium scales (<3 mmol) complete separation was achieved on a single silica column. As well as the desired mono-bromophenylporphyrin **4**, isolated in an 11% yield, several other porphyrins were formed. The symmetric 5,10,15,20-tetrakis(di-*tert*-butylphenyl)porphyrin **6** was produced in yields of up to 10% and we also isolated two inseparable isomers, *cis*-**5a** and *trans*-**5b**, of bis(bromophenyl)porphyrin in combined yields of up to 9%. Finally, trace amounts of 5,10,15-tris(4′-bromophenyl)-20-(3″,5″-di-*tert*-butylphenyl)porphyrin were also observed in some experiments. The latter three porphyrins show that the bromophenylpyrromethane link is unstable towards scrambling under the acid catalysis used in the reaction.

Utilising the optimum conditions for the formation of **4**, iodophenylporphyrin **7** was formed in a 10% isolated yield from the condensation of **1**, **3**, and two equivalents of 3,5-di-*tert*-butylbenzaldehyde. In addition, the symmetric tetrakis(di-*tert*-butylphenyl)porphyrin **6** was formed in a 6% yield, and there was also an inseparable mixture of the *cis* and *trans* isomers of the bis(iodophenyl)porphyrins, **8a** and **8b**, which were isolated in a total yield of 7%. In this case the the major product was the *cis* isomer **8a** with only trace amounts of the *trans* isomer **8b** being observed in the ^{1}H NMR.

With the desired mono-halophenylporphyrins in hand the next part of the reaction sequence was their conversion into the desired diketones. The reported routes for this transformation involve a copper 2-nitroporphyrin as the common intermediate. The copper 2-nitroporphyrin is prepared in two steps; first the porphyrin is metallated with copper which then directs the subsequent nitration with nitrogen dioxide to the β-pyrrolic positions.[20] In the case of the asymmetric halophenylporphyrins **4** and **7** there are four isomers which can be formed on nitration which, following further elaboration, will lead to two regiosomers of the halophenylporphyrin-α-diones. Both **4** and **7** were metallated with excess copper(II) acetate in a dichloromethane–methanol mixture heated at reflux to give both of the corresponding copper chelated porphyrins **9** and **10** in isolated yields of 99% (Scheme 2).

Copper porphyrins **9** and **10** were then nitrated by treatment with a solution of nitrogen dioxide in light petroleum.[20] The nitrogen dioxide solution was added in aliquots and the progress of the reactions monitored by thin layer chromatography. When all the starting material had been consumed the reaction mixtures were immediately filtered through a plug of silica to remove excess nitrogen dioxide and prevent over-nitration. Under these conditions the copper bromophenylporphyrin **9** gave the expected four nitrated products which could only be partially separated by chromatography on silica. The less polar nitro-bromophenylporphyrin isomers **11a** and **11b** co-



Scheme 2 *Reagents and conditions*: i, $Cu(OAc)_2 \cdot H_2O$, DCM–MeOH; ii, NO_2, light petroleum, DCM, room temp.; iii, sodium benzaldoximate, DMSO–THF, Δ, N_2; iv, Dess–Martin periodinane, DCM; v, H_2SO_4, DCM, room temp.

chromatographed, and were isolated as a mixture in a 51% yield. However, the more polar isomers **11c** and **11d** could be separated, but only with difficulty, in yields of 18 and 22% respectively. Some 7% of the material still remained as a mixture of **11c** and **11d**. Therefore the total yield for the nitration of **9** to form **11a**–**d** was 98%. Similarly, nitration of copper

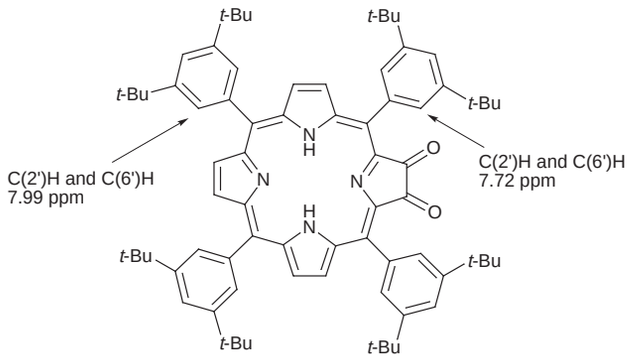


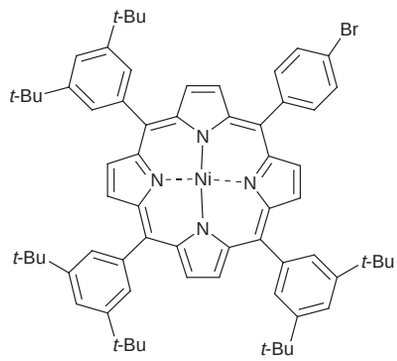
Fig. 2 ^{1}H NMR chemical shifts for C(2^1)H and C(6^1)H in a symmetric porphyrin-α-dione.

iodophenylporphyrin **10** gave an inseparable mixture of nitro-iodophenylporphyrins **12a** and **12b** in a 55% yield, and **12c** and **12d** in yields of 21 and 24% respectively.

The regiochemistry of the four nitroporphyrin isomers has been deduced by considering the relative polarities of the isomers and the structures of the subsequent porphyrin-α-diones. When the copper nitroporphyrins were separately converted to the porphyrin-α-diones, the inseparable mixtures of both **11a**,**b** and **12a**,**b** gave the single porphyrin-α-dione isomers **17a** and **18a** respectively. Similarly, when the individual isomers **11c** or **11d** and **12c** or **12d** were converted to porphyrin-α-diones they were found to give the alternate isomers **17b** and **18b** respectively. The structures of **17a**, **18a**, **17b**, and **18b** were confirmed by comparison of their ^{1}H NMR spectra with that of the symmetric porphyrin-α-dione, 17,18-dioxo-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrin (Fig. 2). In the symmetric porphyrin-α-dione (Fig. 2), the ^{1}H NMR signals corresponding to the phenyl protons C(2′)H and C(6′)H next to the dione are a doublet found at 7.72 ppm. Porphyrin-α-diones **17a** and **18a** have two flanking di-*tert*-butylphenyl groups in different environments and two doublets were observed near 7.72 ppm confirming the position of the dione. In contrast, both **17b** and **18b** which are flanked on one side by the halophenyl moiety and the other by a di-*tert*-butylphenyl group were found to have, as expected, only one doublet in the region of 7.72 ppm. The confirmation of the pairings of isomers fits well with the relative polarities of the nitroporphyrins. The *meso* groups adjacent to the β-pyrrolic position to which the nitro moiety is attached affect the polarities of the nitroporphyrins by how well they shield the polar nitro group. The 3,5-di-*tert*-butylphenyl group shields the polar nitro group more effectively than does the halophenyl group, and so isomers **11a**,**b** and **12a**,**b** (which give **17a** and **18a** respectively, with two flanking 3,5-di-*tert*-butylphenyl groups) are less polar than **11c**,**d** and **12c**,**d** (which give **17b** and **18b** respectively, with one flanking 3,5-di-*tert*-butylphenyl group). A similar argument would indicate that **11c** and **12c** should be less polar than **11d** and **12d** respectively as the former pair have the nitro moiety adjacent to the 3,5-di-*tert*-butylphenyl group, and hence we have assigned them in this order.

Hydroxylation of the nitrated porphyrins was achieved with sodium benzaldoximate using our recently reported improved procedure.[21] Solutions of excess sodium benzaldoximate in dimethyl sulfoxide were added to solutions of the copper nitroporphyrins in equal volumes of tetrahydrofuran. The reaction mixtures were heated at reflux before work-up and purification by column chromatography over silica. Under these conditions **11a**,**b**, **11c**, **11d**, **12a**,**b**, **12c**, and **12d** gave the corresponding hydroxyporphyrins **13a**,**b**, **13c**, **13d**, **14a**,**b**, **14c**, and **14d** in yields of 79, 98, 51, 74, 80 and 58%. We also found that in addition to the desired hydroxyporphyrins we sometimes observed some of the corresponding porphyrin-α-diones. Therefore, it is important when purifying hydroxyporphyrins to ascertain whether any of the corresponding porphyrin-α-dione has been formed on the silica column to maximise the overall yield of the reaction sequence. For example, on hydroxylation of **12a**,**b** not only was **14a**,**b** isolated in a good 74% yield, but the corresponding porphyrin-α-dione **19** was also formed in a 17% yield.

It is interesting to note that in the hydroxylation of copper nitroporphyrins only the nitro group is replaced whilst the halo group is left untouched. This chemoselectivity was expected as the intermediate carbanion formed during the *ipso* substitution can be more easily stabilised on the porphyrin ring than the phenyl ring which is orthogonal to the plane of the porphyrin. We were therefore interested to see whether it would be possible to substitute the halo atom in the absence of the nitro substituent. For this study we used [5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]nickel(II) **20** as the



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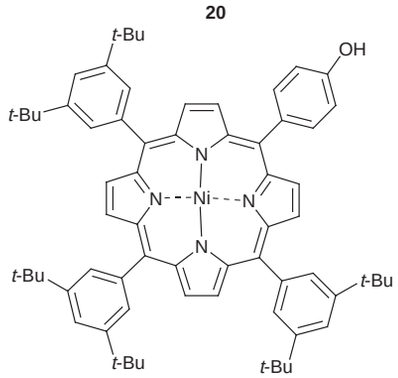

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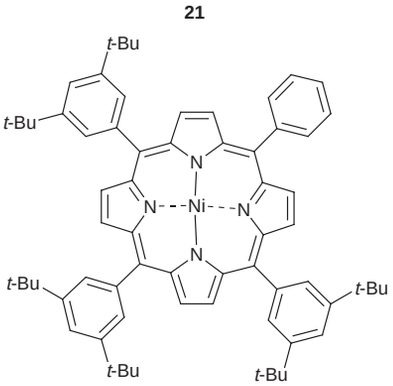

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substrate. The bromo derivative was used instead of the iodo as it is the more electronegative halo atom and nickel was chelated to the porphyrin inner periphery as it has a similar electronegativity to copper but is diamagnetic so analysis of the products could be easily carried out using ^{1}H NMR. Treatment of **20** under the conditions used for the substitution of the nitro group gave none of the corresponding nickel hydroxyphenylporphyrin **21**. Instead two compounds were isolated; the first was recovered nickel bromophenyl porphyrin **20**, returned in 69% yield, and the second was [5-phenyl-10,15,20-tris(3′,5′-di-*tert*-butylphenyl)porphinato]nickel(II) **22** which was formed in a 16% yield. We believe **22** is formed by metallation of **20**

followed by quenching of the phenyl anion. Under more vigorous conditions, using dimethyl sulfoxide as the only solvent, and heating the reaction mixture at 150 °C, we recovered **20** in a 12% yield and isolated the debrominated porphyrin **22** in 33% yield. We had initially thought that **22** might be formed by metallation of **20** followed by quenching of the new anion on work-up. However, quenching the reaction mixture with deuterium oxide incorporated no deuterium indicating that protonation of the phenyl anion intermediate occurs during the reaction.

The copper bromophenylhydroxyporphyrins, **13a**,**b**,**c**,**d**, were oxidised to the corresponding copper bromphenylporphyrin-α-diones **16a** and **16b** with the Dess–Martin periodinane using dichloromethane as the solvent.[21] Under these conditions **13a**,**b** was oxidised to **16a** in an 80% yield, and **13c** and **13d** were oxidised to **16b** in yields of 56 and 52% respectively. The chelated copper was then removed from **16a** and **16b** by treatment with concentrated sulfuric acid to give the two free base porphyrin-α-diones **17a** and **17b** in 67 and 60% yields respectively. We have also found that the oxidation and demetallation reactions can be carried out in the reverse order. For example, the copper was removed from the copper iodophenylhydroxyporphyrins **14a**,**b**, **14c**, and **14d** to give the free-base porphyrins **15a**,**b**, **15c**, and **15d** which were then immediately oxidised to the porphyrin-α-diones **18a** in 73%, from **14a**,**b**; and **18b** in 68 and 62%, from **14c** and **14d** respectively. Although the nitrohalophenylporphyrins can be partially separated and converted individually to the porphyrin-α-diones, for larger scale preparations we did not separate the isomers of the nitroporphyrins but carried them through and separated the free base porphyrin-α-diones at the end of the sequence. For example, hydroxylation of a mixture of the four copper bromophenylnitroporphyrin isomers **11a**,**b**,**c**,**d** followed by column chromatography to remove minor impurities, gave a mixture of the four copper bromophenylhydroxyporphyrin isomers **13a**,**b**,**c**,**d** in an 88% yield. Demetallation of this mixture with concentrated sulfuric acid, followed by oxidation of the crude product with the Dess–Martin periodinane gave a mixture of the two free-base porphyrin-α-diones which could be easily separated by column chromatography over silica to give **17a** and **17b** in yields of 48 and 20% respectively, which is a total porphyrin-α-dione yield of 68% for the last two steps. The overall yield of diketones **17a** and **17b** for the five steps from the free-base bromophenylporphyrin **4** was 58%. In comparison, separating the nitroporphyrins and carrying out the syntheses on the different isomers in the original sequence gave a combined porphyrin-α-dione yield of 41%.

Conclusion

We have successfully developed the synthetic methodology for the preparation of porphyrin-α-diones with *meso*-halophenyl substituents. The halophenylporphyrins can be made in reasonable yields by the condensation of the required *meso*-aryldipyrromethanes with 3,5-di-*tert*-butylbenzaldehyde and dipyrromethane **1**. The β-pyrrolic positions can then be functionalised to give the porphyrin-α-diones leaving the halophenyl moieties intact. The key hydroxylation step was found to go chemoselectively with only the nitro group being displaced. In the absence of the nitro group we found that the bromo atom could not be substituted with the benzaldoximate anion even under vigorous conditions. The synthetic route gives rise to two porphyrin-α-dione isomers which are useful 'building blocks' for the synthesis of *meso*-linked bis-porphyrin arrays.

Experimental

Measurements

^{1}H NMR spectra were recorded on a Bruker AM-500 (500 MHz) or a Varian Gemini 200 (200 MHz) spectrometer. Infrared spectra were recorded using KBr disks 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 either spectrophotometric grade chloroform or dichloromethane. For the free-base porphyrins the dichloromethane was filtered through a plug of potassium carbonate immediately before use. The absorption spectra of the porphyrin-α-diones all had a broad absorption, relative to the other absorption peaks, at long wavelengths. The absorption whilst broad often showed a number of features. Fast Atom Bombardment (FAB) mass spectra (*m*/*z*) were recorded on a VG Autospec spectrometer. Atmospheric Pressure Chemical Ionization (APCI) mass spectra were recorded on a VG Platform spectrometer. Major peaks are listed with intensities quoted as percentages of the base peak. Due to the combination of metal chelation, halogen substituents, and size of molecules the molecular weight observed by mass spectroscopy generally appeared as a complex isotopic cluster around the expected parent ion. In these cases we have quoted the most abundant peak for each compound. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. We found that although the compounds did not melt, some partially decomposed on heating. This was observable by analysis with thin-layer chromatography which showed the presence of more than one compound after heating. Therefore, these melting points are quoted as decomposition below the highest temperature measured. Microanalyses were performed in either the Dyson Perrins Laboratory or Inorganic Chemistry Laboratory, Oxford. All solvents for recrystallization were distilled before use. Dichloromethane and dimethyl sulfoxide were dried over calcium hydride and freshly distilled before use. Tetrahydrofuran was dried over sodium wire and freshly distilled before use. Light petroleum refers to the fraction of boiling point 60–80 °C and ether refers to diethyl ether. 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}. Preparative layer chromatography was performed using glass plates coated with silica gel GF_{254} with a concentration band. 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.

meso-(3,5-Di-*tert*-butylphenyl)dipyrromethane 1

A solution of 3,5-di-*tert*-butylbenzaldehyde[19] (6.00 g, 27.5 mmol) in dry pyrrole (115 cm^3, 1.92 mol) was degassed by bubbling with argon for 20 min. Trifluoroacetic acid (0.21 cm^3, 2.75 mmol) was added, and the reaction stirred for 20 min to give an orange solution. The solution was diluted with dichloromethane (100 cm^3), and washed with sodium hydroxide solution (0.1 M, 50 cm^3) and water (100 cm^3), dried over anhydrous sodium sulfate, filtered, and the dichloromethane completely removed. The excess pyrrole was removed by rotary evaporation under high vacuum to leave a brown oil. The crude product was purified by column chromatography over silica with ethyl acetate–light petroleum–triethylamine (20 : 80 : 1) as the eluent, to leave a brown oil which was recrystallised from light petroleum (bp 30–40 °C) to give **1** as a white crystalline solid (5.03 g, 55%), mp 106–107 °C (Found: C, 83.0; H, 9.2; N, 8.3. $C_{23}H_{30}N_2$ requires C, 82.6; H, 9.0; N, 8.4%); ν_{max}(KBr disc)/cm^{-1} 3418 (N–H), 3398 (N–H); ν_{max}(CH_2Cl_2)/cm^{-1} 3457 (N–H); λ_{max}($CHCl_3$)/nm (log (ε/dm^3mol^{-1} cm^{-1})) 242 (3.92); δ_H(200 MHz; $CDCl_3$) 1.35 (18 H, s, *t*-Bu H), 5.48 (1 H, s, benzyl H), 5.99 (2 H, br s, pyrrole H), 6.21 (2 H, dd, $J = 3$ Hz, $J = 6$ Hz, pyrrole H), 6.72 (2 H, br dd, pyrrole H), 7.12 (2 H, d, $J_{4',2'} = J_{4',6'} = 2.0$ Hz, C(2′)H and C(6′)H), 7.38 (1 H, dd, $J_{2',4'} = J_{6',4'} = 2.0$ Hz, C(4′)H), and 7.93 (2H, br s, NH); *m*/*z* (FAB) 333 ($M^+ - 1$, 100%).

5-(4′-Bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)-porphyrin 4

A solution of 3,5-di-*tert*-butylbenzaldehyde (3.92 g, 17.9 mmol), **2**[17] (2.70 g, 8.97 mmol), and **1** (3.00 g, 8.97 mmol) in dry dichloromethane (230 cm^3, 0.08 M with respect to the aldehyde) was deoxygenated by bubbling with argon for 13 min. Trifluoroacetic acid (1.4 cm^3, 18 mmol) was added and the reaction mixture stirred for 3.5 h to give a dark purple solution. 2,3-Dichloro-5,6-dicyanobenzoquinone (6.11 g, 26.9 mmol) was then added, and stirring continued for 10 min, to give a black mixture. The reaction mixture was washed with water (100 cm^3) and then the separated aqueous layer was extracted with dichloromethane (3 × 100 cm^3). The combined organic layers were washed with sodium bicarbonate solution (5%, 200 cm^3), and water (200 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed to leave a black solid. The residue was passed through a plug of silica using a dichloromethane–light petroleum mixture (1:4) as eluent, and the purple filtrate was collected and the solvent completely removed. The crude product was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (1:4) as eluent. Three main fractions were collected and the solvent completely removed. The residues were recrystallised from a dichloromethane–methanol mixture to give 5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrin **6** as a purple solid (0.45 g, 10%) which co-chromatographed with and had an identical ^1H NMR spectrum to an authentic sample; **4** as a purple solid (1.05 g, 11%), mp >300 °C (Found: C, 79.3; H, 7.7; N, 5.4; MH^+, 1029.537. $C_{68}H_{77}N_4Br$ requires C, 79.3; H, 7.5; N, 5.4%; MH^+, 1029.541); ν_{max}(KBr disc)/cm^{-1} 3317 (N–H); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 421 (5.69), 518 (4.25), 553 (3.95), 592 (3.72) and 648 (3.62); δ_H(500 MHz; $CDCl_3$) −2.71 (2 H, s, NH), 1.53 (18 H, s, *t*-Bu H), 1.54 (36 H, s, *t*-Bu H), 7.80–7.81 (3 H, m, C(4″)H), 7.90 and 8.12 (4 H, AA′BB′, C(2′)H, C(3′)H, C(5′)H, and C(6′)H), 8.08 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 8.09 (4 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 8.83 (2 H, ½ × ABq, J_{AB}= 4.5 Hz, β-pyrrolic H) and 8.91 (6 H, br m, β-pyrrolic-H); and an inseparable mixture of 5,10-bis(4′-bromophenyl)-15,20-bis(3″,5″-di-*tert*-butylphenyl)porphyrin **5a** and 5,15-bis(4′-bromophenyl)-10,20-bis(3″,5″-di-*tert*-butylphenyl)porphyrin **5b** as a purple solid (300 mg, 7%), mp >300 °C (Found: MH^+ 997.323. $C_{60}H_{60}N_4Br_2$ requires MH^+ 997.324); ν_{max}(KBr disc)/cm^{-1} 3321 (N–H); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 421 (5.69), 517 (4.25), 553 (3.95), 592 (3.72), and 648 (3.62); δ_H(500 MHz; $CDCl_3$) −2.76 (2 H, s, NH), 1.53–1.54 (36 H, *t*-Bu H), 7.81–7.83 (2 H, m, C(4″)H), 7.89–7.91 (4 H, m, C(3′)H and C(5′)H), 8.07–8.11 (8 H, m, C(2′)H, C(6′)H, C(2″)H, and C(6″)H), and 8.83 and 8.92 (8 H, m, β-pyrrolic H).

[5-(4′-Bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl) porphinato]copper(II) 9

A mixture of **4** (1.03 g, 1.00 mmol), copper(II) acetate monohydrate (340 mg, 1.70 mmol) in dichloromethane (100 cm^3) and methanol (30 cm^3) was heated at reflux for 0.5 h, and then allowed to cool. The solvent was completely removed and then the residue was dissolved in dichloromethane and passed through a plug of silica using dichloromethane as eluent. The filtrate was collected and the solvent completely removed to leave **9** as a red solid (1.08 g, 99%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture, mp >300 °C (Found: M^+, 1089.448. $C_{68}H_{75}N_4BrCu$ requires M^+ 1089.447); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 418 (5.74), and 541 (4.33).

[2-, 3-, 12- and 13-Nitro-5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]copper(II) 11c, 11d, 11b, and 11a

A solution of **9** (731 mg, 0.670 mmol) in dichloromethane (100 cm^3) was treated with aliquots of a solution of nitrogen dioxide in light petroleum (936 mg in 50 cm^3; 4.0 cm^3). The reaction was monitored by thin layer chromatography (dichloromethane–light petroleum 1:4), and addition of nitrogen dioxide solution was continued until no starting material remained. The reaction mixture was passed through a plug of silica using dichloromethane as eluent to remove excess nitrogen dioxide, and the solvent completely removed to leave a purple solid. The residue was purified using a mixture of column and chromatotron chromatography over silica using dichloromethane–light petroleum mixtures (1:4–3:7) as eluent. Three main fractions were collected and the solvent completely removed. Porphyrins **11a** and **11b** were isolated as an inseparable mixture of isomers as a purple solid (392 mg, 51%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture, mp >300 °C (Found: C, 71.9; H, 6.5; N, 6.0. $C_{68}H_{74}N_5BrO_2Cu$ requires C, 71.85; H, 6.6; N, 6.2%); ν_{max}(KBr disc)/cm^{-1} 1530 (NO_2); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 426 (5.36), 549 (4.20), and 590 (3.98); *m*/*z* (FAB) 1136.2 (M^+, 100%). Porphyrin **11c** was isolated as a purple solid (137 mg, 18%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture, mp >300 °C (Found: C, 71.9; H, 6.6; N, 6.2. $C_{68}H_{74}N_5BrO_2Cu$ requires C, 71.85; H, 6.6; N, 6.2%); ν_{max}(KBr disc)/cm^{-1} 1526 (NO_2); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 426 (5.35), 550 (4.19), and 591 (3.99); *m*/*z* (FAB) 1136.3 (M^+, 100%). Porphyrin **11d** was isolated as a purple solid (164 mg, 22%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture, mp >300 °C (Found: C, 71.8; H, 6.8; N, 5.8. $C_{68}H_{74}N_5BrO_2Cu$ requires C, 71.85; H, 6.6; N, 6.2%); ν_{max}(KBr disc)/cm^{-1} 1522 (NO_2); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 427 (5.22), 551 (4.09), and 595 (3.95); *m*/*z* (FAB) 1136.4 (M^+, 100%).

[12- and 13-Hydroxy-5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]copper(II) 13b and 13a

A mixture of dimethyl sulfoxide (70 cm^3) and sodium hydride (60% dispersion in mineral oil) (118 mg, 2.96 mmol) was stirred under argon at 70–80 °C for 40 min to give a clear, pale yellow solution. The solution was added to benzaldoxime (394 mg, 3.25 mmol) to give a bright yellow solution and this was immediately transferred to a solution of **11a** and **11b** (336 mg, 0.296 mmol) in dry tetrahydrofuran (70 cm^3) heated at reflux. The reaction mixture was heated at reflux for 50 min, by which time thin layer chromatography (dichloromethane–light petroleum 1:4) indicated that all the starting material was consumed. The reaction mixture was allowed to cool, diluted with ether (100 cm^3), washed with water (5 × 100 cm^3), 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 (1:4) as eluent to give an inseparable mixture of **13a** and **13b** as a red solid (258 mg, 79%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture to give a purple solid, mp >300 °C (Found: C, 74.1; H, 7.0; N, 5.5. $C_{68}H_{75}N_4BrOCu$ requires C, 73.7; H, 6.8; N, 5.1%); ν_{max}(KBr disc)/cm^{-1} 3487 (O–H); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 418 (5.48), 540 (4.16), and 580 (3.62); *m*/*z* (FAB) 1107.3 (M^+, 100%).

[2-Hydroxy-5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]copper(II) 13c

A mixture of dimethyl sulfoxide (10 cm^3) and sodium hydride (60% dispersion in mineral oil) (18 mg, 0.44 mmol) was stirred under argon at 70–80 °C for 35 min to give a clear, pale yellow solution. The solution was added to benzaldoxime (59 mg, 0.48 mmol) to give a bright yellow solution which was immediately transferred to a solution of **11c** (50 mg, 0.04 mmol) in dry tetrahydrofuran (10 cm^3) heated at reflux. The reaction mixture was heated at reflux for 10 min, by which time thin layer chromatography (dichloromethane–light petroleum 1:4) indi-

cated that all the starting material was consumed. The reaction mixture was allowed to cool, diluted with ether (50 cm^3), washed with water (6 × 25 cm^3), 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 (1:4) as eluent to give **13c** as a red solid (48 mg, 98%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture to give a purple solid, mp >300 °C (Found: C, 73.3; H, 6.9; N, 5.2. $C_{68}H_{75}N_4BrOCu$ requires C, 73.7; H, 6.8; N, 5.1%); ν_{max}(KBr disc)/cm^{-1} 3492 (O-H); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 418 (5.54), 540 (4.21), and 580 (3.70); *m*/*z* (FAB) 1107.5 (M^+, 100%).

[3-Hydroxy-5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]copper(II) 13d

A mixture of dimethyl sulfoxide (20 cm^3) and sodium hydride (60% dispersion in mineral oil) (36 mg, 0.88 mmol) was stirred under argon at 65–75 °C for 30 min to give a clear, pale yellow solution. The solution was added to benzaldoxime (120 mg, 0.97 mmol) to give a bright yellow solution and a portion of this (10 cm^3) was immediately transferred to a solution of **11d** (50 mg, 0.04 mmol) in dry tetrahydrofuran (10 cm^3) heated at reflux. The reaction mixture was heated at reflux for 10 min, by which time thin layer chromatography (dichloromethane–light petroleum 1:4) indicated that all the starting material was consumed. The reaction mixture was allowed to cool, diluted with ether (50 cm^3), washed with water (4 × 25 cm^3), 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 (1:4–2:3) as eluent to give **13d** as a red solid (25 mg, 51%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture to give a purple solid, mp >300 °C (Found *m*/*z* 1105.444 (M^+). $C_{68}H_{75}N_4BrOCu$ requires 1105.442); ν_{max}(KBr disc)/cm^{-1} 3537 (O–H); λ_{max}-(CH_2Cl_2)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 419 (5.55), 540 (4.22), and 580 (3.68).

[17,18-Dioxo-5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)chlorinato]copper(II) 16a

The Dess–Martin periodinane (42 mg) was added to a solution of **13a** and **13b** (31 mg, 0.03 mmol) in dichloromethane (10 cm^3) and the mixture was stirred in the dark for 1.7 h. The solvent was completely removed, and the residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:3) as eluent to give **16a** as a green solid (25 mg, 80%), decomp <300 °C (Found: C, 73.0; H, 6.8; N, 4.8. $C_{68}H_{73}N_4BrO_2Cu$ requires C, 72.8; H, 6.6; N, 5.0%); ν_{max}(KBr disc)/cm^{-1} 1728 (C=O); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 408 (5.10), 486 (4.37), 637sh (3.64), and 714 (3.78); *m*/*z* (FAB) 1123.5 (M^++2, 100%).

[7,8-Dioxo-5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)chlorinato]copper(II) 16b

Method 1. The Dess–Martin periodinane (200 mg) was added in aliquots over 1.3 h to a stirred solution of **13c** (67 mg, 0.06 mmol) in dichloromethane (10 cm^3) in the dark, and the reaction was monitored by thin layer chromatography (dichloromethane–light petroleum 2:3). The solvent was completely removed, and the residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:3–1:1) as eluent to give **16b** as a green solid (38 mg, 56%), decomp. <300 °C (Found: C, 72.95; H, 6.6; N, 4.8. $C_{68}H_{73}N_4BrO_2Cu$ requires C, 72.8; H, 6.6; N, 5.0%); ν_{max}(KBr disc)/cm^{-1} 1726 (C=O); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 408 (5.13), 487 (4.39), 636sh (3.63), and 716 (3.82); *m*/*z* (FAB) 1123.5 (M^+ + 2, 100%).

Method 2. The Dess–Martin periodinane (149 mg) was added in aliquots over 2 h to a solution of **13d** (25 mg, 0.02 mmol) in dichloromethane (10 cm^3) in the dark, and the reaction was monitored by thin layer chromatography (dichloromethane–light petroleum 2:3). The solvent was completely removed, and the residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:3–1:1) as eluent to give **16b** as a green solid (13 mg, 52%) which co-chromatographed with and had an identical IR spectrum to an authentic sample.

17,18-Dioxo-5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)chlorin 17a

A solution of **16a** (141 mg, 0.126 mmol) in dichloromethane (25 cm^3) was treated with concentrated sulfuric acid (98%, 0.5 cm^3) and stirred for 5 min. The solution was then poured onto an ice–water mixture, and the ice was allowed to melt. The aqueous layer was separated, and extracted with dichloromethane (3 × 30 cm^3). The combined organic layers were washed with sodium bicarbonate solution (5%, 50 cm^3), and water (100 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent removed. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:3) as eluent to give **17a** as an olive green solid (89 mg, 67%), decomp. <300 °C (Found: C, 76.5; H, 7.4; N, 5.1. $C_{68}H_{75}N_4BrO_2$ requires C, 77.0; H, 7.1; N, 5.3%); ν_{max}(KBr disc)/cm^{-1} 3354 (N–H), 1738 (C=O), 1726 (C=O); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 407 (5.36), 476 (4.36), 537sh (3.88), 605 (3.76), 651 (3.72), and 744sh (3.42); δ_H(500 MHz; $CDCl_3$) −2.03 and −2.01 (2 H, 2 × s, NH), 1.485, 1.49, and 1.52 (54 H, 3 × s, *t*-Bu H), 7.73 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 7.74 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 7.77 (1 H, dd, $J_{2'',4''} = J_{6'',4''} = 2.0$ Hz, C(4″)H), 7.78 (1 H, dd, $J_{2'',4''} = J_{6'',4''} = 2.0$ Hz, C(4″)H), 7.81 (1 H, dd, $J_{2'',4''} = J_{6'',4''} = 2.0$ Hz, C(4″)H), 7.89 and 8.03 (4 H, AA′BB′, C(2′)H, C(3′)H, C(5′), and C(6′)H), 8.00 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 8.56 and 8.65 (2 H, ABq, $J_{AB} = 4.5$ Hz, C(7)H and C(8)H), and 8.64, 8.65, 8.73, and 8.82 (4 H, 2 × br ABq, C(2)H, C(3)H, C(12)H, and C(13)H); *m*/*z* (FAB) 1061.8 (MH^+, 100%).

7,8-Dioxo-5-(4′-bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)chlorin 17b

A solution of **16b** (37 mg, 0.033 mmol) in dichloromethane (10 cm^3) was treated with concentrated sulfuric acid (98%, 0.5 cm^3) and stirred for 10 min. The solution was then poured onto an ice–water mixture, and the ice was allowed to melt. The aqueous layer was separated, and extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were washed with water (25 cm^3), sodium bicarbonate solution (5%, 25 cm^3), water (25 cm^3), 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 (2:3) as eluent to give **17b** as an olive–green solid (21 mg, 60%), decomp. <300 °C (Found: MH^+, 1059.516. $C_{68}H_{75}N_4BrO_2$ requires MH^+ 1059.515); ν_{max}(KBr disc)/cm^{-1} 3355 (N–H) and 1730 (C=O); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 408 (5.39), 478 (4.32), 536sh (3.87), 601 (3.74), 653 (3.72), and 746sh (3.42); δ_H(500 MHz; $CDCl_3$) −1.94 and −1.92 (2 H, 2 × s, NH), 1.48, 1.51, and 1.515 (54 H, 3 × s, *t*-Bu H), 7.73 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 7.77 (1 H, dd, $J_{2'',4''} = J_{6'',4''} = 2.0$ Hz, C(4″)H), 7.78–7.80 (4 H, m, C(4″)H, C(3′)H and C(5′)H), 7.83 (2 H, $\frac{1}{2}$ × AA′BB′, C(2′)H and C(6′)H), 7.98 and 7.99 (4 H, 2 × d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), and 8.57, 8.64, and 8.80 (4 H, 2 × br ABq, C(2)H, C(3)H, C(12)H, and C(13)H), and 8.63 (2 H, s, C(17)H and C(18)H).

[5-(4′-Bromophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)-porphinato]nickel(II) 20

A solution of **4** (100 mg, 0.097 mmol) and nickel(II) acetate tetrahydrate (87 mg, 0.35 mmol) in dimethylformamide (50 cm^3) was heated at reflux for 2.3 h and then allowed to cool. The solution was diluted with ether (50 cm^3) and washed with water (4 × 50 cm^3), brine (50 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was dissolved and passed through a plug of silica using a dichloromethane–light petroleum mixture (1:4) as eluent. The filtrate was collected and the solvent completely removed. The residue was recrystallised from a dichloromethane–methanol mixture to give **20** as a red solid (85 mg, 80%), mp >300 °C (Found: C, 75.0; H, 7.1; N, 5.1. $C_{68}H_{75}N_4BrNi$ requires C, 75.1; H, 6.95; N, 5.15%); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 417 (5.45) and 529 (4.28); δ_H(500 MHz; $CDCl_3$) 1.47 (18 H, s, *t*-Bu H), 1.48 (36 H, s, *t*-Bu H), 7.71–7.73 (3 H, m, C(4″)H), 7.82 and 7.91 (4 H, AA′BB′, C(2′)H, C(3′)H, C(5′)H, and C(6′)H), 7.87–7.88 (6 H, m, C(2″)H and C(6″)H), 8.71 and 8.81 (4 H, ABq, J_{AB} = 5.0 Hz, C(2)H, C(3)H, C(7)H, C(8)H) and 8.82 (4 H, s, C(12)H, C(13)H, C(17)H, and C(18)H); *m*/*z* (FAB) 1086.7 (M^+, 100%).

[5-Phenyl-10,15,20-tris(3′,5′-di-*tert*-butylphenyl)porphinato]-nickel(II) 22

A mixture of dry dimethyl sulfoxide (10 cm^3) and sodium hydride (60% dispersion in mineral oil, 15 mg, 0.37 mmol) was stirred under argon at 80 °C for 30 min to give a clear, pale yellow solution. The solution was added to benzaldoxime (49 mg, 0.40 mmol) to give a bright yellow solution which was then added to a mixture of **20** (39 mg, 0.04 mmol) in dry dimethyl sulfoxide (10 cm^3) heated at 120 °C. The temperature was increased over 1.8 h to 150 °C to dissolve the porphyrin, and the reaction mixture stirred for a further 16 h before being allowed to cool. The mixture was diluted with ether (25 cm^3), washed with water (3 × 50 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was purified by preparative layer chromatography over silica using a dichloromethane–light petroleum mixture (1:24) as eluent and two bands were isolated. Porphyrin **20** was returned as a red solid (5 mg, 12%) which co-chromatographed with and had an identical ^1H NMR spectrum to an authentic sample. Porphyrin **22** was isolated as a red solid (12 mg, 33%), mp >300 °C (Found: M^+ 1006.544. $C_{68}H_{76}N_4Ni$ requires M^+ 1006.542); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 417 (5.43) and 529 (4.26); δ_H(500 MHz; $CDCl_3$) 1.48 (18 H, s, *t*-Bu H), 1.483 (36 H, s, *t*-Bu H), 7.65–7.70 (3 H, m, Ar-H), 7.72–7.73 (3 H, m, C(4″)H), 7.88–7.89 (6 H, m, C(2″)H and C(6″)H), 8.03–8.05 (2 H, m, Ar-H), 8.75 and 8.79 (4 H, ABq, J_{AB} = 5.0 Hz, C(2)H, C(3)H, C(7)H, C(8)H), and 8.81 (4 H, s, C(12)H, C(13)H, C(17)H, and C(18)H); *m*/*z* (FAB) 1007.5 (MH^+, 100%).

5-(4′-Iodophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)-porphyrin 7

A solution of 3,5-di-*tert*-butylbenzaldehyde (2.44 g, 11.2 mmol), **3**[17] (1.95 g, 5.59 mmol), and **1** (1.87 g, 5.59 mmol) in dry dichloromethane (140 cm^3, 0.08 M with respect to the aldehyde) was deoxygenated by bubbling with argon for 20 min. Trifluoroacetic acid (0.85 cm^3, 11 mmol) was added and the reaction mixture stirred for 3.5 h at room temperature to give a dark purple solution. 2,3-Dichloro-5,6-dicyanobenzoquinone (3.80 g, 16.8 mmol) was added, and stirring was continued for 10 min. The reaction mixture was washed with water (100 cm^3) and the separated aqueous layer was extracted with dichloromethane (3 × 30 cm^3). The combined organic layers were washed with sodium bicarbonate solution (5%, 100 cm^3), water (100 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed to leave a black solid. The residue was dissolved and passed through a plug of silica using a dichloromethane–light petroleum mixture (1:4) as eluent. The filtrate was collected and the solvent completely removed. The crude product was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (1:4–2:3) as eluent. Three main fractions were isolated and the solvent completely removed. Samples for analysis were recrystallised from a dichloromethane–methanol mixture. Porphyrin **6** was isolated as a purple solid (0.18 g, 6%) which co-chromatographed with and had an identical ^1H NMR spectrum to an authentic sample. Porphyrin **7** was isolated as a purple solid (0.62 g, 10%) mp >300 °C (Found: C, 75.8; H, 7.2; N, 5.3. $C_{68}H_{77}N_4I$ requires C, 75.8; H, 7.2; N, 5.2%); ν_{max}(KBr disc)/cm^{-1} 3316 (N–H); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 421 (5.75), 518 (4.28), 554 (4.01), 593 (3.73), and 648 (3.73); δ_H(500 MHz; $CDCl_3$) −2.71 (2 H, s, NH), 1.53 (18 H, s, *t*-Bu H), 1.54 (36 H, *t*-Bu H), 7.80 (1 H, dd, $J_{2'',4''} = J_{6'',4''}$ = 2.0 Hz, C(4″)H), 7.81 (2 H, dd, $J_{2'',4''} = J_{6'',4''}$ = 2.0 Hz, C(4″)H), 7.99 and 8.11 (4 H, AA′BB′, C(2′)H, C(3′)H, C(5′)H, and C(6′)H), 8.09 (2 H, d, $J_{4'',2''} = J_{4'',6''}$ = 2.0 Hz, C(2″)H and C(6″)H), 8.10 (4 H, d, $J_{4'',2''} = J_{4'',6''}$ = 2.0 Hz, C(2″)H and C(6″)H), 8.84 and 8.92 (4 H, ABq, J_{AB}= 4.5 Hz, C(2)H, C(3)H, C(17)H, and C(18)H) and 8.92 (4 H, br ABq, C(7)H, C(8)H, C(12)H, C(13)H); *m*/*z* (FAB) 1077.4 (MH^+, 100%). Porphyrins **8a** and **8b** in which **8a** was the major component were isolated as a purple solid (0.22 g, 7%) mp >300 °C (Found: C, 66.4; H, 5.9; N, 5.25. $C_{60}H_{60}N_4I_2$ requires C, 66.1; H, 5.5; N, 5.1%); ν_{max}(KBr disc)/cm^{-1} 3315 (N–H); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 425 (5.71), 486 (3.58), 517 (4.30), 553 (4.02), 592 (3.78), and 648 (3.72); δ_H(500 MHz; $CDCl_3$) for **8a** (*cis* isomer) −2.73 (2 H, s, NH), 1.57 (36 H, *t*-Bu H), 7.85 (2 H, dd, $J_{2'',4''} = J_{6'',4''}$ = 2.0 Hz, C(4″)H), 7.98 and 8.10 (8 H, AA′BB′, C(2′)H, C(3′)H, C(5′)H, and C(6′)H), 8.11 (4 H, d, $J_{4'',2''} = J_{4'',6''}$ = 2.0 Hz, C(2″)H and C(6″)H), 8.85–8.97 (8 H, pyrrolic H); *m*/*z* (FAB) 1091.2 (MH^+, 100%).

[5-(4′-Iodophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]copper(II) 10

A mixture of **7** (1.00 g, 0.928 mmol), copper(II) acetate monohydrate (315 mg, 1.58 mmol), dichloromethane (100 cm^3), and methanol (30 cm^3) was heated at reflux for 0.5 h, and then allowed to cool. The solvent was completely removed and the residue dissolved and passed through a plug of silica using dichloromethane as eluent. The filtrate was collected and the solvent completely removed to leave **10** as a red solid (1.05 g, 99%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture, mp >300 °C (Found: C, 71.5; H, 6.8; N, 4.9. $C_{68}H_{75}N_4ICu$ requires C, 71.7; H, 6.6; N, 4.9%); $\lambda_{max}(CH_2Cl_2)$/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 419 (5.72), 541 (4.32), and 577 (3.53); *m*/*z* (FAB) 1138.4 (MH^+, 100%).

[2-, 3-, 12- and 13-Nitro-5-(4′-iodophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]copper(II) 12a-d

A solution of **10** (1.01 g, 0.885 mmol) in dichloromethane (100 cm^3) was treated with a solution of nitrogen dioxide in light petroleum (0.55 g in 50 cm^3; 5.4 cm^3). The reaction was monitored by thin layer chromatography (dichloromethane–light petroleum 1:4), and addition of nitrogen dioxide solution was continued until no starting material remained. The reaction mixture was passed through a plug of silica using dichloromethane as eluent to remove excess nitrogen dioxide. The filtrate was collected and the solvent completely removed to leave a purple solid. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (1:4) as eluent. Three main fractions were collected and the solvent completely removed. Samples for analysis were recrystallised from a dichloromethane–methanol mixture. Porphyrins **12a** and **12b** were isolated as an inseparable mixture of isomers as a purple solid (576 mg, 55%), mp >300 °C (Found: C, 68.6; H, 6.6; N, 5.9. $C_{68}H_{74}N_5IO_2Cu$ requires C,

69.0; H, 6.3; N, 5.9%); ν_{max}(KBr disc)/cm^{-1} 1528 (NO_2); λ_{max}($CHCl_3$)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 427 (5.31), 550 (4.15), and 592 (3.94); *m*/*z* (FAB) 1183.3 (MH^+, 100%). Porphyrin **12c** was isolated as a purple solid (220 mg, 21%), mp >300 °C (Found: C, 69.05; H, 6.6; N, 5.9. $C_{68}H_{74}N_5IO_2Cu$ requires C, 69.0; H, 6.3; N, 5.9%); ν_{max}(KBr disc)/cm^{-1} 1526 (NO_2); λ_{max}($CHCl_3$)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 428 (5.26), 552 (4.11), and 589 (3.90); *m*/*z* (FAB) 1183.2 (MH^+, 100%). Porphyrin **12d** was isolated as a purple solid (255 mg, 24%), mp >300 °C (Found: C, 68.75; H, 6.3; N, 5.9. $C_{68}H_{74}N_5IO_2Cu$ requires C, 69.0; H, 6.3; N, 5.9%); ν_{max}(KBr disc)/cm^{-1} 1522 (NO_2); λ_{max}($CHCl_3$)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 429 (5.26), 552 (4.13), and 596 (4.01); *m*/*z* (FAB) 1183.4 (MH^+, 100%).

[12- and 13-Hydroxy-5-(4′-iodophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]copper(II) 14b and 14a

A mixture of dry dimethyl sulfoxide (260 cm^3) and sodium hydride (60% dispersion in mineral oil, 279 mg, 6.98 mmol) was stirred under argon at 75–80 °C for 35 min to give a clear, pale yellow solution. Benzaldoxime (1.54 g, 12.7 mmol) was added to give a bright yellow solution of sodium benzaldoximate and a portion of the solution (100 cm^3) was transferred to a solution of **12a**,**b** (540 mg, 0.45 mmol) in dry tetrahydrofuran (100 cm^3) heated at reflux. The reaction mixture was heated at reflux for 25 min, by which time thin layer chromatography (dichloromethane–light petroleum 1:4) indicated that all the starting material was consumed. The reaction mixture was allowed to cool, diluted with ether (200 cm^3), washed with water (200 cm^3 and 4 × 100 cm^3) and brine (100 cm^3), 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 (1:4–2:3) as eluent and two fractions were collected and the solvent completely removed. Porphyrins **14a** and **14b** were isolated as an inseparable mixture as a red solid (388 mg, 74%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture, decomp. <300 °C (Found: C, 70.7; H, 6.6; N, 4.8. $C_{68}H_{75}N_4IOCu$ requires C, 70.7; H, 6.55; N, 4.85%); ν_{max}(KBr disc)/cm^{-1} 3486 (O–H); λ_{max}($CHCl_3$)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 419 (5.54), 541 (4.24), and 581 (3.70); *m*/*z* (FAB) 1154.2 (MH^+, 100%). [17,18-Dioxo-5-(4′-iodophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)chlorinato]copper(II) **19** was isolated as a green solid (88 mg, 17%), decomp. <300 °C (Found: 1168.412 (MH^+). $C_{68}H_{73}N_4IO_2Cu$ requires 1168.415); ν_{max}(KBr disc)/cm^{-1} 1728 (C=O); λ_{max}(CH_2Cl_2)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 408 (5.08), 486 (4.35), 636sh (3.67), and 712 (3.76).

[2-Hydroxy-5-(4′-iodophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]copper(II) 14c

Sodium benzaldoximate solution (40 cm^3) (as prepared for the reaction of **14a**,**b**) was added to a solution of **12c** (196 mg, 0.166 mmol) in dry tetrahydrofuran (40 cm^3) heated at reflux. The reaction mixture was heated at reflux for 10 min, by which time thin layer chromatography (dichloromethane–light petroleum 1:4) indicated that all the starting material was consumed. The reaction mixture was allowed to cool, diluted with ether (100 cm^3) and washed with water (100 cm^3). The aqueous layer was separated and then extracted with ether (30 cm^3). The combined organic layers were washed with water (4 × 50 cm^3), brine (50 cm^3), 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 (1:4) as eluent to give **14c** as a red solid (152 mg, 80%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture to give a purple crystalline solid, decomp. <300 °C (Found: C, 70.7; H, 6.6; N, 4.7. $C_{68}H_{75}N_4IOCu$ requires C, 70.7; H, 6.55; N, 4.85%); ν_{max}(KBr disc)/cm^{-1} 3489 (O–H); λ_{max}(CH_2Cl_2)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 419 (5.58), 540 (4.25), and 580 (3.75); *m*/*z* (FAB) 1154.5 (MH^+, 100%).

[3-Hydroxy-5-(4′-iodophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)porphinato]copper(II) 14d

Sodium benzaldoximate solution as prepared above (40 cm^3) was added to a solution of **12d** (226 mg, 0.191 mmol) in dry tetrahydrofuran (40 cm^3) heated at reflux. The reaction mixture was heated at reflux for 10 min, by which time thin layer chromatography (dichloromethane–light petroleum 1:4) indicated that all the starting material was consumed. The reaction mixture was allowed to cool, diluted with ether (150 cm^3), washed with water (200 cm^3 and 4 × 50 cm^3) and brine (50 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent removed. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (1:4) as eluent to give **14d** as a red solid (128 mg, 58%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture to give a purple crystalline solid, decomp. <300 °C (Found: C, 70.7; H, 6.4; N, 4.8. $C_{68}H_{75}N_4IOCu$ requires C, 70.7; H, 6.55; N, 4.85%); ν_{max}(KBr disc)/cm^{-1} 3519 (O-H); λ_{max}(CH_2Cl_2)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 419 (5.57), 540 (4.23), and 580 (3.69); *m*/*z* (FAB) 1154.5 (MH^+, 100%).

17,18-Dioxo-5-(4′-iodophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)chlorin 18a

A solution of **14a**,**b** (308 mg, 0.267 mmol) in dichloromethane (50 cm^3) was treated with concentrated sulfuric acid (98%, 2.0 cm^3) and stirred for 5 min. The solution was then poured onto an ice–water mixture, and the ice was allowed to melt. The organic layer was separated and washed with water (100 cm^3), sodium bicarbonate solution (5%, 100 cm^3), water (100 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was dissolved in dichloromethane (50 cm^3), Dess–Martin periodinane (300 mg) was added and the mixture was stirred for 30 min. The solution was filtered through a plug of silica using dichloromethane as the eluent. The filtrate was collected and the solvent completely removed. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:3) as eluent to give **18a** as a green solid (220 mg, 73%), mp >300 °C (Found: 1107.501 (MH^+). $C_{68}H_{75}N_4IO_2$ requires 1107.501); ν_{max}(KBr disc)/cm^{-1} 3352 (N–H), 1738 (C=O), and 1727 (C=O); λ_{max}(CH_2Cl_2)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 407 (5.37), 476 (4.35), 534sh (3.89), 603 (3.76), 653 (3.72), and 732sh (3.49); δ_H(500 MHz; $CDCl_3$) −2.05 and −2.02 (2 H, 2 × s, NH), 1.47, 1.48, and 1.51 (54 H, 3 × s, *t*-Bu H), 7.715 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 7.72 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 7.75–7.78 (2 H, 2 × dd, C(4″)H), 7.80 (1 H, dd, $J_{2'',4''} = J_{6'',4''} = 2.0$ Hz, C(4″)H), 7.89 and 8.09 (4 H, AA′BB′, C(2′)H, C(3′)H, C(5′)H, C(6′)H), 7.99 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 8.56 and 8.63 (2 H, ABq, $J_{AB} = 4.5$ Hz, C(7)H and C(8)H), and 8.63, 8.64, 8.73, and 8.81 (4 H, 2 × ABq, $J_{AB} = 5.0$ Hz, C(2)H, C(3)H, C(12)H, and C(13)H).

7,8-Dioxo-5-(4′-iodophenyl)-10,15,20-tris(3″,5″-di-*tert*-butylphenyl)chlorin 18b

Method 1. A solution of **14c** (102 mg, 0.088 mmol) in dichloromethane (25 cm^3) was treated with concentrated sulfuric acid (98%, 1.0 cm^3) and stirred for 5 min. The solution was then poured onto an ice–water mixture (100 cm^3), and the ice was allowed to melt. The organic layer was separated and washed with water (50 cm^3), sodium bicarbonate solution (5%, 50 cm^3), water (50 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was dissolved in dichloromethane (25 cm^3), Dess–Martin periodinane (100 mg) was added and the solution was stirred for 20 min at room

temperature in the dark. The solution was filtered through a plug of silica using dichloromethane as eluent. The filtrate was collected and the solvent completely removed. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:3) as eluent to give **18b** as a green solid (67 mg, 68%), decomp. <300 °C (Found: 1107.501 (MH^+). $C_{68}H_{75}N_4IO_2$ requires 1107.501); ν_{max}(KBr disc)/cm^{-1} 3353 (N–H) and 1730 (C=O); λ_{max}(CH_2Cl_2)/nm (log (ε/dm^3 mol^{-1} cm^{-1})) 408 (5.40), 478 (4.33), 541sh (3.86), 604 (3.74), 652 (3.72), and 745sh (3.44); δ_H(500 MHz; $CDCl_3$) −1.94 and −1.92 (2 H, 2 × s, NH), 1.48, 1.506, and 1.51 (54 H, 3 × s, *t*-Bu H), 7.67 and 8.03 (4 H, AA′BB′, C(2′)H, C(3′)H, C(5′)H, and C(6′)H), 7.73 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 7.76 (1 H, dd, $J_{2'',4''} = J_{6'',4''} = 2.0$ Hz, C(4″)H), 7.79, (1 H, dd, $J_{2'',4''} = J_{6'',4''} = 2.0$ Hz, C(4″)H), 7.80 (1 H, dd, $J_{2'',4''} = J_{6'',4''} = 2.0$ Hz, C(4″)H), 7.98 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 7.99 (2 H, d, $J_{4'',2''} = J_{4'',6''} = 2.0$ Hz, C(2″)H and C(6″)H), 8.58, 8.64, and 8.80 (4 H, 2 × ABq, C(2)H, C(3)H, C(12)H, and C(13)H), 8.63 (2 H, tight ABq, C(7)H and C(8)H).

Method 2. A solution of **14d** (137 mg, 0.119 mmol) in dichloromethane (25 cm^3) was treated with concentrated sulfuric acid (98%, 1.0 cm^3) and stirred for 5 min. The solution was then poured onto an ice–water mixture, and the ice was allowed to melt. The organic layer was separated and washed with water (25 cm^3), sodium bicarbonate solution (5%, 50 cm^3), water (25 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was dissolved in dichloromethane (25 cm^3), Dess–Martin periodinane (150 mg) was added and the solution was stirred for 30 min at room temperature in the dark. The solution was filtered through a plug of silica using dichloromethane as eluent. The filtrate was collected and the solvent completely removed. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:3) as eluent to give **18b** (81 mg, 62%) which co-chromatographed with and had an identical ^{1}H NMR spectrum to an authentic sample.

References

1 R. W. Wagner, T. E. Johnson and J. S. Lindsey, *J. Am. Chem. Soc.*, 1996, **118**, 11166.
2 V. S.-Y. Lin, S. G. Di Magno and M. J. Therien, *Science*, 1994, **264**, 1105.
3 A. Osuka, N. Tanabe, S. Nakajima and K. Maruyama, *J. Chem. Soc., Perkin Trans. 2*, 1996, 199.
4 K. Susumu, T. Shimidzu, K. Tanaka and H. Segawa, *Tetrahedon Lett.*, 1996, **37**, 8399.
5 A. K. Burrell, D. L. Officer and D. C. W. Reid, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 900.
6 J. A. Cowan, J. K. M. Sanders, G. S. Beddard and R. J. Harrison, *J. Chem. Soc., Chem. Commun.*, 1987, 55.
7 D. B. Amabilino, C. O. Deitrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1996, **118**, 3285.
8 S. Anderson, H. L. Anderson, A Bashall, M. McPartlin and J. K. M Sanders, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1096.
9 D. P. Arnold and D. A. James, *J. Org. Chem.*, 1997, **62**, 3460.
10 A. Osuka and H. Shimidzu, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 135.
11 H. L. Anderson, S. J. Martin and D. D. C. Bradley, *Angew. Chem., Int. Ed. Engl.* 1994, **33**, 655.
12 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1991, 1569.
13 D. L. Officer, A. K. Burrell and D. C. W. Reid, *Chem. Commun.*, 1996, 1657.
14 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1987, 39.
15 J. Seth, V. Palaniappan, T. E. Johnson, S. Prathapan, J. S. Lindsey and D. F. Bocian, *J. Am. Chem. Soc.*, 1994, **116**, 10579.
16 J.-S. Hsiao, B. P. Krueger, R. W. Wagner, T. E. Johnson, J. K. Delaney, D. C. Mauzerall, G. R. Fleming, J. S. Lindsey, D. F. Bocian and R. J. Donohoe, *J. Am. Chem. Soc.*, 1996, **118**, 11181.
17 C.-H. Lee and J. S. Lindsey, *Tetrahedron*, 1994, **50**, 11427.
18 J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney and A. M. Marguerettaz, *J. Org. Chem.*, 1987, **52**, 827.
19 M. S. Newman and L. F. Lee, *J. Org. Chem.*, 1972, **37**, 4468.
20 M. M. Catalano, M. J. Crossley, M. M. Harding and L. G. King, *J. Chem. Soc., Chem. Commun.*, 1984, 1535.
21 R. Beavington, P. A. Rees and P. L. Burn, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2847.

Paper 8/09515I