Investigation of a 'reverse' approach to extended porphyrin systems. Synthesis of a 2,3-diaminoporphyrin and its reactions with α-diones

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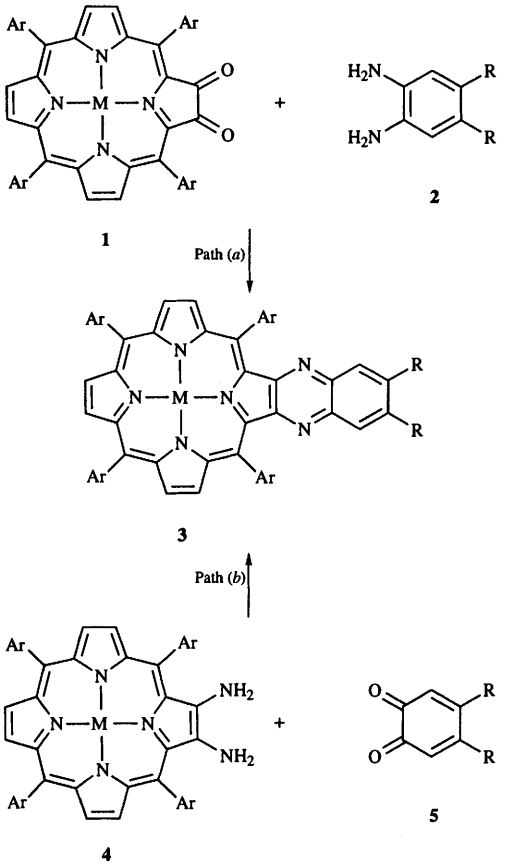
A 2,3-diaminoporphyrin has been synthesised for the first time and its reaction with α-diones has been examined. Two regioselective routes to the precursor 2-amino-3-nitroporphyrins have been established. 2-Aminoporphyrins are directly nitrated on the porphyrin ring in the 3-position while 2-nitroporphyrins react with acylamide ions regioselectively at the 3-position and can be converted to the required 2-amino-3-nitroporphyrins by hydrolysis of the amide bond. 2,3-Diamino-5,10,15,20-tetraarylporphyrins are prepared by transfer hydrogenation of the corresponding 2-amino-3-nitroporphyrins but are relatively unstable. Electrochemical measurements show that 2,3-diaminoporphyrins are easily oxidised and this probably accounts for their instability. Condensation of the 2,3-diaminoporphyrin 29 with the α-diones benzil and cyclohexane-1,2-dione occurs readily and in good yield to give the ring annulated systems 31 and 32, respectively. Reaction with *o*-benzoquinone, however, causes decomposition of the diaminoporphyrin 29 making 'reverse' synthesis of quinoxalinoporphyrins and related polyporphyrin systems much less attractive than the alternate approach involving condensation of a porphyrin-2,3-dione with *o*-phenylenediamine and related diamines.

A synthetic route to extended porphyrin systems (*e.g.*, the quinoxalinoporphyrin **3**) involves the condensation of a porphyrin-2,3-dione **1** with an *o*-diaminoarene **2** [Scheme 1, path (*a*)][1-3] and has been extended to the synthesis of doubly annulated porphyrins by condensation of porphyrin-2,3,12,13- and -2,3,7,8-tetraones with *o*-diaminoarenes and 1,2,4,5-benzenetetramine.[4] While this is an efficient entry into such extended systems, the versatility of the approach would be enhanced if the positions of the *o*-diamino and α-dione functionalities could also be interchanged in the starting materials. In this way, extended porphyrin systems such as the quinoxalinoporphyrin **3** could also be accessed by condensation of a 2,3-diaminoporphyrin **4** and an *o*-quinone **5** [Scheme 1, path (*b*)].



Scheme 1

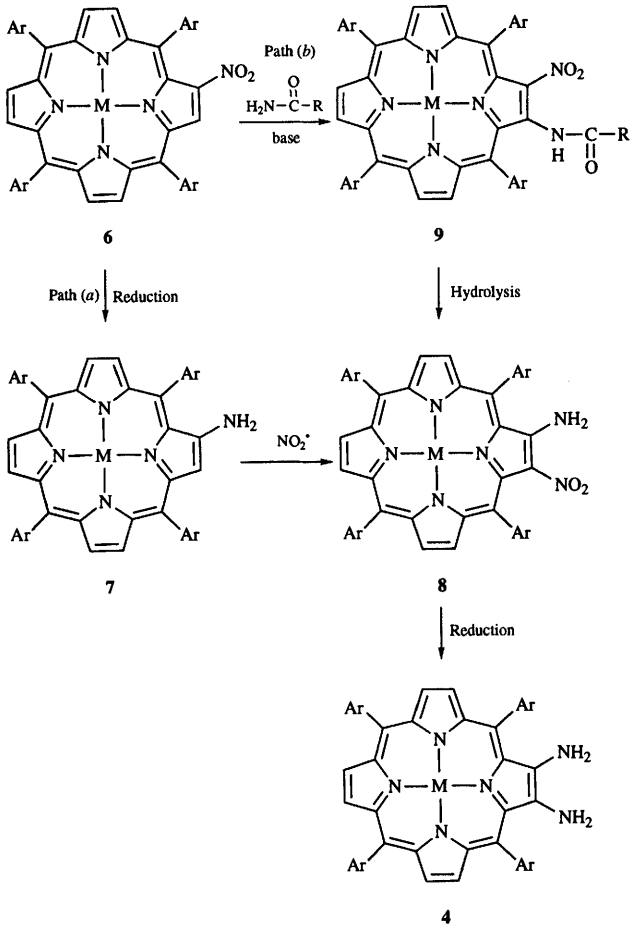
2,3-Diaminoporphyrins **4** have not been reported previously. We envisaged two approaches to such compounds (Scheme 2). Nitration of a metallo-2-aminoporphyrin **7**, which can be obtained from the corresponding nitro compound **6** by reduction,[5] might afford the 2-amino-3-nitroporphyrin **8**, and subsequent reduction would afford 2,3-diaminoporphyrin **4** [Scheme 2, path (*a*)]. This sequence requires the amino group to direct nitration to the adjacent β-pyrrolic position. We anticipated that this might be a highly regioselective process given the fact that 2-aminoporphyrins form Tröger's base analogues in very good yield in a process that clearly requires the reaction to be directed in such a way.[6] The second approach [Scheme 2, path (*b*)] involves nucleophilic substitution of hydrogen by an acyl amide ion at the β-pyrrolic position adjacent to a nitro group. There is a good analogy for this process in the reaction with oxy-anions with 2-nitroporphyrins.[7,8] In the present case the resultant 2-amido-3-nitroporphyrin **9** should then be able to be converted into 2-amino-3-nitroporphyrin **8** and thence to 2,3-diaminoporphyrin **4** by hydrolysis followed by reduction (Scheme 2).

We have found that both pathways of Scheme 2 afford 2-amino-3-nitroporphyrins in reasonable yield. We now report these investigations and we also report the conversion of a zinc(II) 2-amino-3-nitroporphyrin **16** into the corresponding 2,3-diaminoporphyrin **29** and its subsequent reaction with α-diones.

Results and discussion

Preparation of 2-amino-3-nitroporphyrins

Both routes to 2,3-diaminoporphyrins outlined in Scheme 2 require the initial synthesis of the corresponding 2-amino-3-nitroporphyrins. The first route to 2-amino-3-nitroporphyrins involves the nitration of 2-aminoporphyrins [Scheme 2, path (*a*)]. The required metallo-2-aminoporphyrins, **13–15**, were readily available by reduction of the corresponding zinc(II), copper(II) and palladium(II) 2-nitroporphyrins, **10–12** respect-



Scheme 2

ively, by a hydrogen transfer process using $NaBH_4$ in the presence of 10% palladium on carbon catalyst (Scheme 3), the metallonitroporphyrins being prepared by metallation of 2-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin. These metalloporphyrins were chosen to span a range of metal ion electronegativities (Pauling electronegativities Zn 1.65, Cu 1.90 and Pd 2.20) as the nature of the chelated metal has been shown to be a determining factor in the regiochemical outcome of nitrations of other metallotetraarylporphyrins.[9] 2-Aminoporphyrins are photolabile[10] and somewhat prone to oxidation and so compounds **13–15** were used immediately.

Each aminoporphyrin **13–15** was treated with a solution of nitrogen dioxide in CH_2Cl_2 until TLC analysis showed that no starting material remained (between 1.8 and 2.1 equiv. of nitrogen dioxide was required).[9] The reaction product was fractionated on silica gel. A single aminonitroporphyrin regioisomer, the 2-amino-3-nitroporphyrin, was obtained in each case along with products resulting from *N*-nitrosation of the amino group.

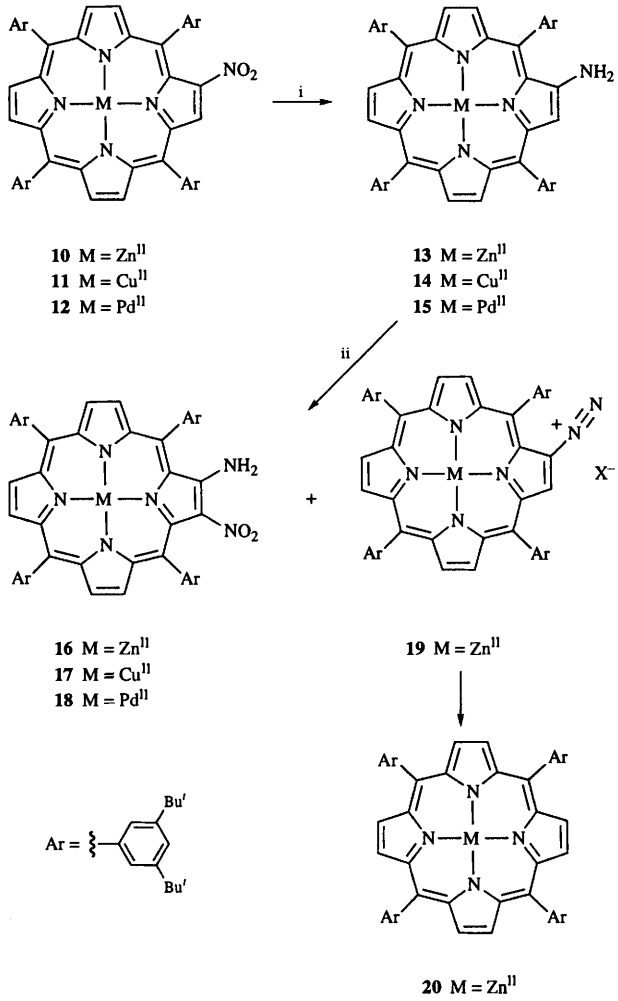
The reaction of the zinc(II) 2-aminoporphyrin **13** with nitrogen dioxide at −78 °C gave the zinc(II) 2-amino-3-nitroporphyrin **16** in 50% yield for the two steps from zinc(II) 2-nitroporphyrin **10**, while the reaction at 25 °C gave **16** in 42% overall yield. In the latter reaction zinc(II) porphyrin **20** (12% yield) and several highly coloured non-polar bands, each in very low yield, and a major, unstable and relatively polar by-product (about 30% yield) were also isolated by chromatography over silica.

The ^1H NMR spectrum of **16** showed resonances of six protons in the β-pyrrolic region. Two AX systems (δ 8.58 and 8.87, J 4.7 Hz, and δ 8.93 and 9.07, J 4.8 Hz) and an AB quartet (δ 8.83 and 8.86, J_{AB} 4.6 Hz) were observed. This pattern of signals is only consistent with vicinal substitution on a β,β′-pyrrolic position on the porphyrin periphery. The IR spectrum of **16** showed absorbances consistent with the presence of a primary amine (ν_{max} 3475 and 3341 cm^{-1}) and a nitro (ν_{max} 1534 cm^{-1}) group.

Examination of the crude reaction mixture by ^1H NMR spectroscopy in a separate experiment showed the presence of only two products before chromatography. The 2-amino-3-nitroporphyrin **16** (*ca.* 55%) and a compound we tentatively assigned as the porphyrin diazonium salt **19** (*ca.* 45%) because of a strong absorbance (ν_{max} 2130 cm^{-1}) in the IR spectrum consistent with the presence of a diazonium group[11,12] and the nature of decomposition products, including the deaminated porphyrin **20**, resulting from chromatography.

It is known that primary amines are diazotised by treatment with dinitrogen tetroxide,[13,14] by reaction with the equilibrium amounts of nitrosonium nitrate present. Although the use of a solution of nitrogen dioxide in light petroleum has been referred to throughout this work, the predominant species in these solutions is dinitrogen tetroxide.[15] Porphyrin diazonium salts have been prepared previously by treatment of an aminoporphyrin with sodium nitrite in tetrafluoroboric acid at −5 °C,[16] or with sodium nitrite and sulfuric acid in a tetrahydrofuran–methanol mixture.[17] Interestingly, neither zinc(II) 2-nitroporphyrin **10** nor the corresponding nitroporphyrin diazonium salt was formed, indicating both that the porphyrin diazonium salt **19** is deactivated toward nitration compared to the aminoporphyrin **13**, and that the 2-amino-3-nitroporphyrin **16** is less reactive at the amino group toward nitrosation than is the 2-aminoporphyrin **13**.

Under the same nitration conditions as above at 25 °C, both the copper(II) and palladium(II) 2-amino-3-nitroporphyrins **17** and **18** were obtained in 22% yield from their



Scheme 3 *Reagents and conditions:* i, $NaBH_4$, 10% Pd–C in CH_2Cl_2–MeOH (4:1); ii, NO_2–light petroleum, CH_2Cl_2

corresponding metallo-2-aminoporphyrins, **14** and **15** respectively. The IR spectra of products **17** and **18** indicated the presence of both amine and nitro groups and the ^{1}H NMR spectrum of the diamagnetic palladium(II) compound **18** was only consistent with vicinal substitution of one pyrrolic ring. The major by-product in the latter reaction is putatively assigned as the corresponding palladium(II) porphyrin diazonium salt (ν_{max} 2130 cm^{-1}).

The absence of 2-amino-*x*-nitroporphyrin regioisomers of the corresponding 2-amino-3-nitroporphyrin in each case—these would result from nitration elsewhere on the 2-aminoporphyrin ring—shows that the amino group exerts a powerful directing effect. This effect of the amino group may be contrasted with that of the methyl group, which has only a small influence on the nitration reaction. Indeed, all seven possible copper(II) 2-methyl-*x*-nitro-5,10,15,20-tetraphenylporphyrin regioisomers are obtained from the nitration of copper(II) 2-methyl-5,10,15,20-tetraphenylporphyrin.[9] The nitro group directs nitration away from the adjacent site, so that the other five possible copper(II) 2,*x*-dinitro-5,10,15,20-tetraarylporphyrins are obtained but not the 2,3-dinitro isomer from nitration of either copper(II) 2-nitro-5,10,15,20-tetraphenylporphyrin **22** or the corresponding octa-*tert*-butylated derivative **11**.[4,9]

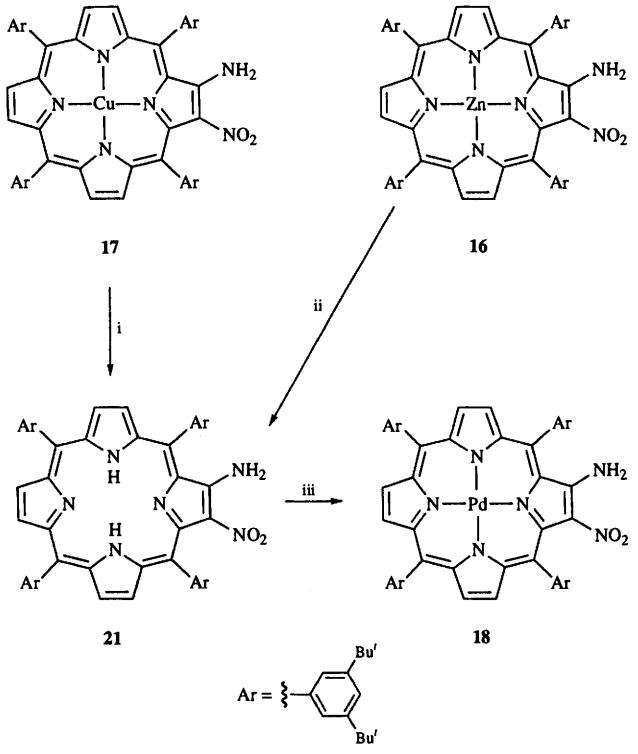
Interestingly, the nitration of zinc(II) aminoporphyrin **13** gave a higher yield (at least 42–50%) of the nitrated analogue **16** than did the corresponding nitration of zinc(II) porphyrin **20**, which gave zinc(II) nitroporphyrin **10** in 13% yield along with ring-opened compounds. In both cases, the mechanism of nitration involves the initial oxidation of the metalloporphyrin by nitrogen dioxide to a porphyrin π-cation radical, followed by a radical combination with further nitrogen dioxide and proton loss.[9] The π-cation radical of zinc(II) porphyrin is likely to have a highest occupied orbital of a_{2u} symmetry which results in predominant *meso*-reactions and subsequent ring opening.[9] Introduction of the amine group destabilises the orbital of a_{1u} symmetry, which becomes the highest occupied orbital and causes predominant β-pyrrolic reactions under the cation-radical conditions.[18]

2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin **21** was prepared by the demetallation of either zinc(II) 2-amino-3-nitroporphyrin **16** or copper(II) 2-amino-3-nitroporphyrin **17** (Scheme 4). Demetallation of zinc(II) 2-amino-3-nitroporphyrin **16** by shaking with hydrochloric acid gave **21** in 87% yield. Similarly, demetallation of **17** with a mixture of sulfuric acid and trifluoroacetic acid gave **21** in 78% yield. The demetallation of copper(II) 2-amino-3-nitroporphyrin **17** provided additional evidence for the proposed structure of this compound.

Free-base 2-amino-3-nitroporphyrin **21** could be easily metallated by normal procedures. For example, treatment of free-base 2-amino-3-nitroporphyrin **21** with excess palladium(II) chloride in an acetic acid–chloroform mixture heated at reflux gave palladium(II) 2-amino-3-nitroporphyrin **18** in 90% yield.

The other route [Scheme 2, path (*b*)] to 2-amino-3-nitroporphyrins requires regiospecific amination of a metallo-2-nitroporphyrin. Sodamide was the first nitrogen nucleophile investigated. Treatment of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **22** in *N*,*N*-dimethylformamide with 2–12 equiv. of sodamide over 18 h did not yield any (2-amino-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II). The major product was (2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **23** in yields of 63–68% (Scheme 5).

The formamide product presumably arose from the initial reaction of sodamide with the solvent. In this event, transamidation by attack of amide ion on *N*,*N*-dimethylformamide would afford formamide. Deprotonation of the formamide by the liberated dimethylamide ion, or by the amide ion, would then form the nucleophile to attack the nitroporphyrin **22**.



Scheme 4 *Reagents and conditions:* i, H_2SO_4 (18 mol dm^{-3}), CF_3CO_2H; ii, HCl (7 mol dm^{-3}), Et_2O; iii, $PdCl_2$, NaOAc, AcOH–$CHCl_3$ (2:1), reflux, 16 h

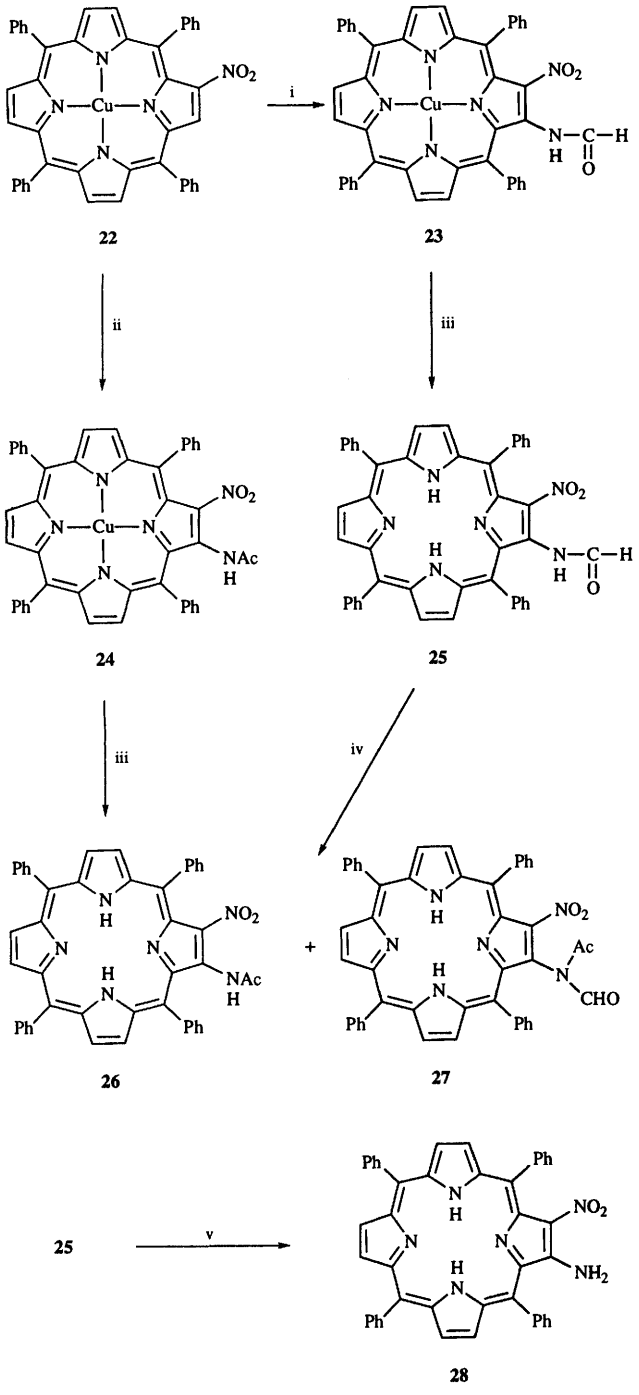
Independent evidence for the role of formamide ion as the nucleophile in this reaction was sought. (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **22** was therefore treated with formamide ion (5 equiv.), which had been generated in Me_2SO. This reaction again afforded (2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **23**, in 57% yield, supporting the assumed formation of the formamide ion in the *N*,*N*-dimethylformamide reaction.

The reactivity of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **22** toward acylamide ions was further evident by its reaction with the sodium salt of acetamide. Thus, stirring a Me_2SO solution of the sodium salt of acetamide (5 equiv.) with (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **22** overnight afforded (2-acetamido-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **24** in 43% yield.

The reaction of amide nucleophiles with (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **22** clearly parallels that of the hydroxide ion.[8] The site of nucleophilic attack for these nitrogen nucleophiles is at the vicinal β-pyrrolic carbon to that bearing the nitro group. Furthermore, there is no indication of a chlorin product from a second attack of an amide nucleophile at the β-pyrrolic carbon.

Demetallation of the copper(II) 2-amido-3-nitroporphyrins **23** and **24**, in the standard procedure using concentrated sulfuric acid, afforded high yields of the free-base porphyrins, 2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrin **25** (91%) and 2-acetamido-3-nitro-5,10,15,20-tetraphenylporphyrin **26** (87%).

The structures of the 2-amido-3-nitroporphyrins **23**–**26** were evident from the spectra of these compounds. The IR spectra indicated the presence of nitro and amide carbonyl groups in each case. The visible spectra confirmed the porphyrin rather than chlorin structures.[8,19] The 400 MHz ^{1}H NMR spectrum of the free-base 2-acetamido-3-nitro-5,10,15,20-tetraphenylporphyrin **26** also supported the assigned structure, showing six β-pyrrolic protons as three AB quartets, a broad one-proton



Scheme 5 *Reagents and conditions:* i, DMF, N_2, sodamide, 18 h; ii, NaH, Me_2SO, N_2, 65°C, 45 min, then stirred overnight; iii, CH_2Cl_2, H_2SO_4 (18 mol dm^{-3}), 4 min; iv, pyridine, acetic anhydride, reflux, 1 h; v, THF, KOH (10%), reflux, 18 h

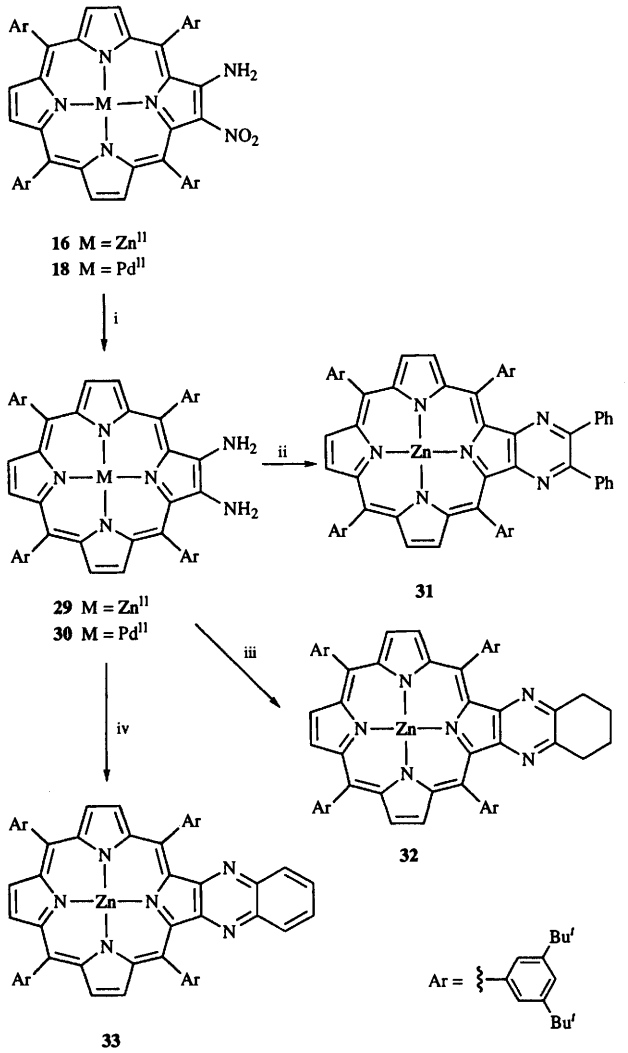
singlet corresponding to an amide proton (δ 7.42) and a three-proton singlet for the acetamide methyl group (δ 1.72). The ^{1}H NMR spectrum of the free-base 2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrin **25** was not consistent with a single structure. Investigation by variable temperature ^{1}H NMR experiments revealed this compound to be a 1 : 1 mixture of *cis*- and *trans*-amide isomers. The mass spectra of porphyrins **23**–**26** showed a clear molecular ion only in the case of (2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **23** but were consistent with the assigned structures. As was observed for (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) and the alkoxy-3-nitroporphyrins, the mass spectra of these 2-amido-3-nitroporphyrins each showed a major fragment 45 mass units less than the expected parent ion, due to hydrogenation of the 2,3-β-pyrrolic bond of the parent porphyrin in the inlet system of the mass spectrometer and subsequent elimination of nitrous acid.[8]

The structure of 2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrin **25** was further established by acylation. Treatment of **25** with a 1 : 1 mixture of acetic anhydride and pyridine at reflux for 1 h afforded 2-acetamido-3-nitro-tetraphenylporphyrin **26** (40%), together with the mixed diacylimide 2-(*N*-formylacetamido)-3-nitro-5,10,15,20-tetraphenylporphyrin **27** (59%) (Scheme 5). The structure of this imide **27** was supported by the IR spectrum, which showed two carbonyl stretches [ν_{max} 1725 and 1700 cm^{-1}], the porphyrin-like visible spectrum and the ^{1}H NMR spectrum, which showed six β-pyrrolic protons and resonances corresponding to the acetamide methyl group (δ 2.33) and the formyl proton (δ 9.08).

Base-catalysed hydrolysis of 2-formamido-3-nitroporphyrin **25** afforded 2-amino-3-nitroporphyrin **28** in 72% yield.

Reduction of 2-amino-3-nitroporphyrins to 2,3-diaminoporphyrins

Reduction of zinc(II) 2-amino-3-nitroporphyrin **16** and of palladium(II) 2-amino-3-nitroporphyrin **18** by hydrogen transfer from sodium borohydride in the presence of a 10% palladium on carbon catalyst gave the corresponding metallo-2,3-diaminoporphyrins (Scheme 6). The metallo-2,3-diamino-



Scheme 6 *Reagents and conditions:* i, $NaBH_4$, 10% Pd–C in CH_2Cl_2–MeOH (4:1); ii, PhCOCOPh, CH_2Cl_2; iii, cyclohexane-1,2-dione, CH_2Cl_2; iv, *o*-benzoquinone, CH_2Cl_2

Table 1 Electrochemical half-wave potentials *vs.* Fc/Fc^+ for metallated complexes in CH_2Cl_2–0.1 mol dm^{-3} Bu_4NBF_4[a]

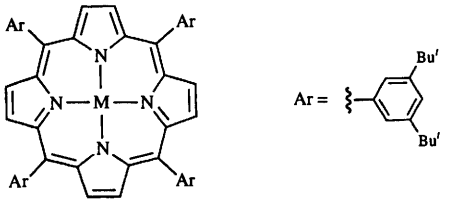
	$E^{\frac{1}{2}}$/mV	
Porphyrin	Oxidation 1	Oxidation 2
20	294	584
34	445	785
35	566	1030
13	190	476
14	250	580
15	302	696
29	−227[b]	362[c,d]
30	−201[b]	460[c,d]

[a] All measurements made at room temperature. Solutions were purged by bubbling with argon. [b] Quasi-reversible. [c] Irreversible. [d] $E^{\frac{1}{2}}$ Estimated from differential pulse voltammogram (DPV) potential by adding 25 mV to the DPV experimental value.

porphyrins were bright red and were slightly more polar than the corresponding 2-amino-3-nitroporphyrins when chromatographed on silica gel. Zinc(II) 2,3-diaminoporphyrin **29** and palladium(II) 2,3-diaminoporphyrin **30** proved to be unstable both as a solid and in solution, and a ^1H NMR spectrum of these materials free from impurities could not be obtained. An attempt to similarly reduce 2-amino-3-nitro-5,10,15,20-tetraphenylporphyrin **28** led to an extremely air-sensitive product, presumably the diaminoporphyrin, which could not be isolated.

Electrochemistry of metalloaminoporphyrins and metallodiaminoporphyrins

In other work which investigated how valence orbital levels of metalloporphyrins were modulated by substituents at the β-pyrrolic positions, electrochemical measurements showed that copper(II) 2-amino-5,10,15,20-tetraphenylporphyrin was oxidised at a potential 207 mV lower than copper(II) 5,10,15,20-tetraphenylporphyrin.[18] We expect that 2,3-diaminoporphyrins would be even easier to oxidise. In order to quantify the effect of successive amino substitution, we examined the electrochemistry of zinc(II) 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin **20**, copper(II) 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin **34**, palladium(II) 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin **35**, the correspondingly metallated 2-aminoporphyrins **13–15** and the freshly prepared zinc(II) and palladium(II) 2,3-diaminoporphyrins **29** and **30**.



34 M = Cu^{II}
35 M = Pd^{II}

Electrochemical half-wave potentials of these compounds are collected in Table 1. The cyclic voltammogram of each metalloaminoporphyrin **13–15** showed two reversible one-electron oxidation processes with peak separations (ΔE_p) in the range of 57–78 mV, which were substantially independent of the sweep rate (v = 50–500 mV s^{-1}), while the peak currents i_{pa} and i_{pc} increased linearly with $\sqrt{v}$. At sweep rates $v \geq 1$ V s^{-1}, the two oxidations of zinc(II) aminoporphyrin **13** were quasi-reversible. No reductions were observed within the solvent window.

The cyclic voltammogram showed that the first oxidation of each metallodiaminoporphyrin **29** and **30** was quasi-reversible with peak separations in the range of 94–105 mV at low scan rates (v = 50–100 mV s^{-1}). The first oxidation became more irreversible (*i.e.* larger peak separation) as the scan rate was increased. Peak currents i_{pa} and i_{pc} increased linearly with $\sqrt{v}$. The second oxidation of each metallodiaminoporphyrin was found to be irreversible.

It can be seen that zinc(II) porphyrins are easier to oxidise than the corresponding copper(II) compounds, which are in turn easier to oxidise than the corresponding palladium(II) compounds. This trend is a common feature of metalloporphyrin electrochemistry and reflects the fact that the more electronegative the chelated metal ion, the harder it is to oxidise the metalloporphyrin.[20,21]

Addition of an electron-donating amino group to the porphyrin periphery lowers the oxidation potential by 100–260 mV. One-electron oxidation of unsubstituted zinc(II), copper(II) and palladium(II) porphyrins yields the metalloporphyrin π-cation radical, and a second oxidation is known to afford a porphyrin π-dication.[20,21] The first and second oxidation potentials of the 2-aminoporphyrins **13–15** parallel those of the unsubstituted porphyrins **20**, **34** and **35**, strongly suggesting that the oxidations are occurring at the porphyrin π-system rather than at the metal centre or the amino group. This is the same behaviour as was seen with the corresponding copper(II) tetraphenylporphyrins,[18] the half-cell potentials being nearly the same as those in the present case when corrected for reference electrode potential. Copper(II) 2-amino-5,10,15,20-tetraphenylporphyrin was shown to be oxidised at the a_{1u} porphyrin π-level orbital.[18]

Oxidation of the 2,3-diaminoporphyrins **29** and **30** occur at even lower potential, as expected. The palladium(II) 2,3-diaminoporphyrin **30** is easier to oxidise by 760 mV than the palladium(II) porphyrin **35** and the corresponding zinc(II) 2,3-diaminoporphyrin **29** has a lower first oxidation potential than zinc(II) porphyrin **20** by 621 mV. In these 2,3-diaminoporphyrin cases, we have not established the site of oxidation but we note that oxidants as weak as atmospheric oxygen can oxidise both the metallo-2,3-diaminoporphyrins **29** and **30**. We expect the same to be true of the corresponding metallo-2,3-diamino-5,10,15,20-tetraphenylporphyrins. The ease of oxidation thus accounts for the instability in air of the 2,3-diaminoporphyrins.

Investigation of the reaction of 2,3-diaminoporphyrin 29 with α-diones

Despite the instability of zinc(II) 2,3-diaminoporphyrin **29**, it could be used for the preparation of extended systems by treating it with an appropriate dione. Treatment of freshly prepared zinc(II) 2,3-diaminoporphyrin **29** with benzil or cyclohexane-1,2-dione gave the corresponding adducts, zinc(II) diphenylpyrazinoporphyrin **31** and zinc(II) $2^2,2^3,2^4,2^5$-tetrahydroquinoxalinoporphyrin **32**, in 64 and 70% yield for the two steps from zinc(II) 2-amino-3-nitroporphyrin **16**. By contrast, treatment of freshly prepared zinc(II) 2,3-diaminoporphyrin **29** with *o*-benzoquinone gave only a 4% yield of the expected condensation product, zinc(II) quinoxalinoporphyrin **33**. The low yield of zinc(II) quinoxalinoporphyrin **33** may be due to oxidation of zinc(II) 2,3-diaminoporphyrin **29** catalysed by *o*-benzoquinone.

Conclusions

Two routes to 2-amino-3-nitroporphyrins have been developed, both of which are highly regioselective. Nitration of zinc(II), copper(II) and palladium(II) 2-amino-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrins **13–15**, respectively, afford the corresponding 2-amino-3-nitroporphyrins **16–18** regioselectively. The second approach involves regioselective nucleophilic substitution. Thus, 2-amido-3-nitroporphyrins are formed by treatment of the copper(II) 2-nitro-5,10,15,20-tetra-

phenylporphyrin **22** with acylamide ion. Demetallation and subsequent base hydrolysis converts copper(II) 2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrin **23** into the corresponding 2-amino-3-nitroporphyrin **28** in good overall yield.

2,3-Diaminoporphyrins can be prepared by reduction of 2-amino-3-nitroporphyrins as expected, but are prone to oxidation. This behaviour is similar to that of *o*-diaminobenzene derivatives and related hydroquinones and as such the 2,3-diaminoporphyrins can be considered as ring-expanded aromatic analogues of the *o*-disubstituted benzenes.

Reaction with *o*-benzoquinone causes decomposition of the diaminoporphyrin **29** making this 'reverse' synthesis [Scheme 1, path (*b*)] of quinoxalinoporphyrins and related polyporphyrin systems much less attractive than the alternate approach involving reaction of a porphyrin-2,3-dione with *o*-phenylenediamine and related diamines [Scheme 1, path (*a*)]. Less redox active α-diones, however, react smoothly with the diaminoporphyrin **29** to give ring annulated porphyrins.

The new porphyrin transformations reported above further illustrate the versatility of 2-nitroporphyrins as starting materials for the introduction of new functionality to β-pyrrolic positions of the porphyrin ring.[4,6 8,10,22-26]

Experimental

General procedures

Melting points were recorded on a Reichert melting point stage and are uncorrected. Microanalyses were performed by the Microanalytical Unit, The University of New South Wales, or by the Australian Mineral Development Laboratory, Melbourne. Infrared spectra of chloroform solutions were collected with a Perkin-Elmer Series 1600 FTIR spectrometer. Electronic spectra were collected in chloroform solutions on a Hitachi 150-20 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AMX400 (400 MHz) spectrometer. Deuteriochloroform was used as the solvent with tetramethylsilane as an internal standard unless otherwise stated. Electron impact (EI) mass spectra were recorded on an AEI MS902 spectrometer. Chemical ionisation (CI) mass spectra were recorded on a Triple Stage Quadrapole FINNIGAN MAT spectrometer. Matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectra were recorded on a VG TofSpec spectrometer. Mass spectra recorded using this instrument are obtained as an envelope of the isotope peaks of the molecular ion. The mass corresponding to the envelope's maxima is reported and was compared with the maxima of a simulated spectrum. The MALDI-TOF mass spectra were accurate to ±1 a.m.u. (*ca.* 0.10%).

Column chromatography was performed using Merck silica gel 60 Type 9385 (40–60 μm). Analytical thin layer chromatography (TLC) was run on Merck silica gel 60 F_{254} precoated sheets (0.2 mm). Where solvent mixtures are used, proportions are given by volume.

Light petroleum refers to the fraction of bp 60–80 °C. Ether refers to diethyl ether. Dichloromethane and light petroleum were routinely redistilled prior to use. Ether was distilled over crushed calcium chloride and stored over sodium wire. Merck AR grade methanol was used.

Electrochemistry was performed using a BAS 100B Electrochemical Analyser. All measurements were made at room temperature on 1.0 mmol dm^{-3} solutions in dichloromethane–0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate by using a Teflon-shrouded gold disk working electrode, platinum wire auxiliary electrode, and a Ag/AgCl/KCl (sat.) reference electrode. The working electrode was polished with diamond paste prior to use and polished with alumina prior to each measurement. The internal standard was the ferrocenium/ferrocene couple which had an oxidation at $E^{\frac{1}{2}}$ 541 mV under these conditions. Tetrabutylammonium tetrafluoroborate was purified by recrystallisation from cold ethyl acetate–ether three times and dried under high vacuum over P_2O_5 for 2 days. Solutions were prepared under argon and a positive pressure of argon maintained in the sample cell. All glassware was oven dried overnight prior to use. Dichloromethane for electrochemistry was purified by heating at reflux over P_2O_5 under nitrogen for 2 days followed by distillation from P_2O_5 under nitrogen.

Samples of metalloaminoporphyrins and metallodiaminoporphyrins for electrochemistry were prepared by the following procedure: a mixture of the appropriate metallonitroporphyrin or metalloaminonitroporphyrin and a 10% palladium on carbon catalyst (850 mg mmol^{-1}) was suspended in a dichloromethane–methanol (4:1) mixture (120 cm^3 mmol^{-1}) and purged with nitrogen. Sodium borohydride (25 equiv.) was added in portions over 10 min and the mixture stirred in the dark under nitrogen for 30 min. The mixture was evaporated to dryness under reduced pressure. The remainder of the workup was performed in a glove bag under nitrogen. The residue was dissolved in dichloromethane and filtered through a plug of silica (Type 7736, dichloromethane) and the filtrate evaporated to dryness to give the reduced product which was stored under nitrogen and used without further purification.

[2-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) 10

Method 1. A mixture of 2-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (702 mg, 0.633 mmol), zinc(II) acetate dihydrate (474 mg, 2.16 mmol), dichloromethane (40 cm^3) and methanol (4 cm^3) was heated at reflux for 30 min, allowed to cool, and evaporated to dryness. The residue was dissolved in dichloromethane and filtered through a plug of silica (Type 9385, dichloromethane). The filtrate was evaporated to dryness and the residue was purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:2). The major green band was collected and evaporated to give [2-*nitro*-5,10,15,20-*tetrakis*(3,5-*di*-tert-*butylphenyl*)*porphyrinato*]-*zinc*(II) **10** (695 mg, 94%) as a purple amorphous powder. A sample for analysis, recrystallised from a dichloromethane–methanol mixture, had mp > 300 °C (Found: C, 77.6; H, 7.95; N, 5.9. $C_{76}H_{91}N_5O_2Zn$ requires C, 77.9; H, 7.8; N, 6.0%); ν_{max}(CHCl$_3$)/cm^{-1} 1516 (NO_2) and 1336 (NO_2); λ_{max}(CHCl$_3$)/nm 309 (log ε 4.29), 431 (5.37), 526sh (3.61), 563 (4.16) and 608 (4.06); δ_H(400 MHz, $CDCl_3$) 1.51–1.53 (72 H, m, *tert*-butyl H), 7.76 (1 H, t, *J* 1.8, aryl H_p), 7.79 (2 H, t, *J* 1.8, aryl H_p), 7.81 (1 H, t, *J* 1.8, aryl H_p), 8.02 (2 H, d, *J* 1.8, aryl H_o), 8.04 (2 H, d, *J* 1.8, aryl H_o), 8.05–8.06 (4 H, m, aryl H_o), 8.93–8.97 (5 H, m, β-pyrrolic H), 9.02 (1 H, d, *J* 4.8, β-pyrrolic H) and 9.22 (1 H, s, H-3); *m/z* (CI) 1170 (M + H, 100%).

Method 2. A solution of [5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) **20** (101 mg, 0.089 mmol) in dichloromethane (6 cm^3) was treated with aliquots of a solution of nitrogen dioxide in light petroleum (0.1 mol dm^{-3}, 0.035 cm^3) every 5 min until TLC analysis showed that no zinc(II) porphyrin **20** remained. The mixture was evaporated to dryness and the residue purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:2). The major green band was collected and evaporated to dryness to give [2-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]-zinc(II) **10** (14 mg, 13%) as a purple amorphous powder which co-eluted with, and had an identical ^{1}H NMR spectrum to, a sample prepared by Method 1.

[2-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]palladium(II) 12

A mixture of 2-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (406 mg, 0.37 mmol) and sodium acetate (121 mg, 1.47 mmol) was dissolved in an acetic acid–chloroform mixture (2:1, 120 cm^3) and heated. Just before reflux, palladium(II) chloride (132 mg, 0.75 mmol) was added and the mixture heated at reflux for 16 h. The mixture was allowed to

cool and ether (80 cm^3) was added. The organic phase was washed with water (4 × 80 cm^3), aqueous sodium carbonate (5%, 80 cm^3) and brine (80 cm^3), dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated to dryness and the residue purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:3). The major red band was collected and evaporated to dryness to give [2-*nitro*-5,10,15,20-*tetrakis*(3,5-*di*-tert-*butylphenyl*)*porphyrinato*]-*palladium*(II) **12** (428 mg, 96%) as a red amorphous powder, mp > 300 °C (Found: C, 75.1; H, 7.8; N, 5.5. $C_{76}H_{91}N_5O_2Pd$ requires C, 75.25; H, 7.6; N, 5.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1522 (NO_2) and 1347 (NO_2); $\lambda_{max}(CHCl_3)/nm$ 295 (log ε 4.19), 386sh (4.47), 429 (5.26), 532 (4.27) and 572 (4.03); δ_H(400 MHz, $CDCl_3$) 1.50–1.51 (72 H, m, *tert*-butyl H), 7.74 (1 H, t, *J* 1.8, aryl H_p), 7.78–7.79 (2 H, m, aryl H_p), 7.80 (1 H, t, *J* 1.8, aryl H_p), 7.97–8.00 (8 H, m, aryl H_o), 8.77 (1 H, d, *J* 5.0, β-pyrrolic H), 8.79–8.83 (4 H, m, β-pyrrolic H), 8.80 (1 H, d, *J* 5.0, β-pyrrolic H) and 9.12 (1 H, s, H-3); *m/z* (MALDI-TOF) 1212 (M + H requires 1213).

[2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) 16

Method 1. [2-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) **10** (200 mg, 0.171 mmol) and 10% palladium on carbon catalyst (148 mg) were suspended in a dichloromethane–methanol mixture (4:1, 40 cm^3) and purged with nitrogen. Sodium borohydride (162 mg, 4.29 mmol) was added in small portions over a 10 min period and the mixture stirred in the dark under nitrogen for 45 min. The mixture was evaporated to dryness, taken up in dichloromethane, filtered through a plug of silica (Type 9385), and evaporated to dryness. The residue was dissolved in dichloromethane (40 cm^3) and treated with aliquots of nitrogen dioxide in light petroleum solution (0.1 mol dm^{-3}, 0.10 cm^3) every 5 min until TLC analysis showed that none of the starting material remained. Methanol (10 cm^3) was added and the mixture evaporated to dryness. The residue was purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:1) and the major green band collected and evaporated to dryness to give [2-*amino*-3-*nitro*-5,10,15,20-*tetrakis*(3,5-*di*-tert-*butylphenyl*)-*porphyrinato*]*zinc*(II) **16** (81 mg, 40%) as a purple amorphous powder. A sample for analysis, recrystallised from a dichloromethane–methanol mixture, had mp > 300 °C (Found: C, 77.2; H, 8.1; N, 6.7. $C_{76}H_{92}N_6O_2Zn$ requires C, 76.8; H, 7.9; N, 7.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3481 (NH_2), 3353 (NH_2), 1604 and 1534 (NO_2); $\lambda_{max}(CHCl_3)/nm$ 318 (log ε 4.33), 349sh (4.33), 445 (5.24), 518 (3.81), 567 (4.20) and 607 (4.01); δ_H(400 MHz, $CDCl_3$) 1.50–1.53 (72 H, m, *tert*-butyl H), 6.45 (2 H, br s, NH_2), 7.65 (1 H, t, *J* 1.8, aryl H_p), 7.76–7.79 (2 H, m, aryl H_p), 7.90 (1 H, t, *J* 1.8, aryl H_p), 7.97 (2 H, d, *J* 1.9, aryl H_o), 8.02–8.05 (4 H, m, aryl H_o), 8.09 (2 H, d, *J* 1.7, aryl H_o), 8.58 and 8.87 (2 H, AX, *J* 4.7, β-pyrrolic H), 8.83 and 8.86 (2 H, AB, *J* 4.6, β-pyrrolic H), 8.93 and 9.07 (2 H, AX, *J* 4.8, β-pyrrolic H); *m/z* (CI) 1185 (M + H, 100%).

Method 2. [2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) **16** (94 mg, 50%) was prepared from [2-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) **10** (187 mg, 0.160 mmol) following the previous method except that the nitration with a solution of nitrogen dioxide in light petroleum was performed at −78 °C under an atmosphere of nitrogen. The product, a purple amorphous powder, co-eluted with, and had an identical ^1H NMR spectrum to, an authentic sample.

Method 3. [2-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) **10** (1.08 g, 0.86 mmol) was reduced with sodium borohydride (799 mg, 21.1 mmol) in the presence of 10% palladium on carbon catalyst (757 mg) and thence treated with nitrogen dioxide following similar procedure to Method 1 above. The crude product, [$\nu_{max}(CHCl_3)/cm^{-1}$ 3481m, 3353m, 2130s] was purified by chromatography over silica (Type 9385, dichloromethane–light petroleum; 1:1 changing to ether when the major green band had been collected). The bands less polar than the major green band were collected and evaporated to dryness to give a dark purple amorphous powder (114 mg) which was further purified as described later. The major green band was collected and evaporated to dryness to give [2-amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) **16** (433 mg, 42%) as a purple amorphous powder which co-eluted with, and had an identical ^1H NMR spectrum to, an authentic sample.

The materials which were less polar than **16** were purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:4). The major purple band was collected and evaporated to dryness to give zinc(II) porphyrin **20** (42 mg, 4%) as a purple amorphous powder. The remaining bands were collected and evaporated to dryness to give a dark purple amorphous powder (55.3 mg) (85% mass recovery of the non-polar fraction).

The bands more polar than the major green band were collected and evaporated to dryness to give an impure dark purple amorphous powder (413 mg), $\nu_{max}(CHCl_3)/cm^{-1}$ 2130. This material was rechromatographed over silica (Type 9385, dichloromethane–light petroleum, 1:4, changing to ether after the less polar bands had eluted). The major non-polar purple band was collected and evaporated to dryness to give further [5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]-zinc(II) **20** (76 mg, 8%, combined 12% overall from **10**) which co-eluted with, and had an identical ^1H NMR spectrum to, an authentic sample. The bands which were more polar than zinc(II) porphyrin **20** were collected and evaporated to dryness to give a dark purple amorphous powder (296 mg) (90% mass recovery of the polar fraction).

[2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]copper(II) 17

[2-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]copper(II) **11** (404 mg, 0.346 mmol) was reduced with sodium borohydride (325 mg, 8.59 mmol) in the presence of 10% palladium on carbon catalyst (285 mg) and thence treated with nitrogen dioxide following similar procedures to the preparation of [2-amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) **16**. The residue was purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 2:5, increasing to 1:1 when the major non-polar bands had eluted) and the major green band collected and evaporated to dryness to give [2-*amino*-3-*nitro*-5,10,15,20-*tetrakis*(3,5-*di*-tert-*butylphenyl*)*porphyrinato*]-*copper*(II) **17** (88 mg, 22%) as a purple amorphous powder. A sample for analysis, recrystallised from a dichloromethane–methanol mixture, had mp > 300 °C (Found: C, 76.8; H, 7.95; N, 7.0. $C_{76}H_{92}CuN_6O_2$ requires C, 77.0; H, 7.8; N, 7.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3482 (NH_2), 3355 (NH_2), 1611 and 1541 (NO_2); $\lambda_{max}(CHCl_3)/nm$ 309 (log ε 4.29), 404sh (4.76), 419sh (4.91), 442 (5.16), 560 (4.10), 604 (3.94) and 660 (3.23); *m/z* (MALDI-TOF) 1184 (M + H requires 1185).

[2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]palladium(II) 18

Method 1. 2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin **21** (89.4 mg, 0.080 mmol) and sodium acetate (23.8 mg, 0.290 mmol) were dissolved in an acetic acid–chloroform mixture (2:1, 30 cm^3) and heated. Just before reflux, palladium(II) chloride (36.3 mg, 0.205 mmol) was added and the mixture heated at reflux until the reaction had gone to completion as determined by TLC analysis. After allowing the mixture to cool, ether (20 cm^3) was added and the organic phase washed successively with water (4 × 20 cm^3), aqueous sodium carbonate (5%, 20 cm^3) and brine (20 cm^3), and then dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated to dryness and the residue was

purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 2:3) and the major red band collected and evaporated to dryness to give [2-*amino*-3-*nitro*-5,10,15,20-*tetrakis*(3,5-*di*-tert-*butylphenyl*)*porphyrinato*]-*palladium*(II) **18** (88 mg, 90%) as a red amorphous powder. A sample for analysis, recrystallised from a dichloromethane–methanol mixture, had mp > 300 °C (Found: C, 74.1; H, 7.8; N, 6.7. $C_{76}N_{92}N_6O_2Pd$ requires C, 74.3; H, 7.55; N, 6.85%); ν_{max}($CHCl_3$)/cm^{-1} 3481 (NH_2), 3352 (NH_2), 1612 and 1541 (NO_2); λ_{max}($CHCl_3$)/nm 323sh (log ε 4.26), 353sh (4.32), 374sh (4.62), 444 (5.15), 509 (3.72), 546 (4.27) and 587 (4.12); δ_H(400 MHz, $CDCl_3$) 1.49 (18 H, s, *tert*-butyl H), 1.50–1.52 (54 H, m, *tert*-butyl H), 6.51 (2 H, br s, NH_2), 7.64 (1 H, t, *J* 1.8, aryl H_p), 7.75–7.78 (2 H, m, aryl H_p), 7.89 (1 H, t, *J* 1.8, aryl H_p), 7.94 (2 H, d, *J* 1.8, aryl H_o), 7.97–7.99 (4 H, m, aryl H_o), 8.05 (2 H, d, *J* 1.8, aryl H_o), 8.45 (1 H, d, *J* 4.9, β-pyrrolic H), 8.70 (1 H, d, *J* 4.9, β-pyrrolic H), 8.74–8.78 (3 H, m, β-pyrrolic H) and 8.90 (1 H, d, *J* 5.0, β-pyrrolic H); *m/z* (MALDI-TOF) 1228 (M + H requires 1227).

Method 2. [2-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]palladium(II) **12** (200 mg, 0.165 mmol) was reduced using sodium borohydride in the presence of 10% palladium on carbon catalyst and thence treated with nitrogen dioxide following similar procedures to that used for the preparation of [2-amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) **16**. The crude product was purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:2) and the major red band collected and evaporated to dryness to give [2-amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]-palladium(II) **18** (45 mg, 22%) as a red amorphous powder which co-eluted with, and had an identical ^{1}H NMR spectrum to, a sample prepared by Method 1.

2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrin 21

Method 1. [2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]copper(II) **17** (47 mg, 0.039 mmol) was moistened with trifluoroacetic acid, concentrated sulfuric acid (0.25 cm^3) was added, and the mixture stirred for 15 min and poured onto ice (20 g). Ether (20 cm^3) was added and the organic phase washed successively with water (2 × 15 cm^3), aqueous sodium carbonate (5%, 15 cm^3) and brine (15 cm^3), and then dried over anhydrous sodium sulfate, filtered and the filtrate evaporated to dryness. The residue was purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:2) and the major brown band collected and evaporated to dryness to give 2-*amino*-3-*nitro*-5,10,15,20-*tetrakis*(3,5-*di*-tert-*butylphenyl*)*porphyrin* **21** (35 mg, 78%) as a purple amorphous powder. A sample for analysis, recrystallised from a dichloromethane–methanol mixture, had mp > 300 °C (Found: C, 81.1; H, 8.3; N, 7.3. $C_{76}H_{94}N_6O_2$ requires C, 81.2; H, 8.4; N, 7.5%); ν_{max}($CHCl_3$)/cm^{-1} 3475 (NH_2), 3341 (NH_2), 1608 and 1534 (NO_2); λ_{max}($CHCl_3$)/nm 317 (log ε 4.30), 392sh (4.65), 439 (5.14), 535 (4.15), 575 (3.92), 607 (3.80) and 668 (3.51); δ_H(400 MHz, $CDCl_3$) −2.52 (1 H, br s, inner NH), −2.28 (1 H, br s, inner NH), 1.51 (18 H, s, *tert*-butyl H), 1.53 (36 H, s, *tert*-butyl H), 1.54 (18 H, s, *tert*-butyl H), 6.72 (2 H, br s, NH_2), 7.67 (1 H, t, *J* 1.8, aryl H_p), 7.77–7.80 (2 H, m, aryl H_p), 7.92 (1 H, t, *J* 1.8, aryl H_p), 8.02–8.06 (6 H, m, aryl H_o), 8.21 (2 H, d, *J* 1.8, aryl H_o), 8.63 (1 H, d, *J* 5.0, β-pyrrolic H), 8.66 and 8.69 (2 H, AB, *J* 4.6, β-pyrrolic H), 8.82–8.87 (2 H, m, β-pyrrolic H) and 9.06 (1 H, d, *J* 5.0, β-pyrrolic H); *m/z* (MALDI-TOF) 1125 (M + H requires 1124).

Method 2. [2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) **16** (120 mg, 0.101 mmol) was dissolved in ether (25 cm^3) and shaken with hydrochloric acid (7 mol dm^{-3}, 25 cm^3) for 5 min. The organic phase was separated and washed with aqueous sodium carbonate (5%, 25 cm^3) and brine (25 cm^3), dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated to dryness and the residue purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:2). The major brown band was collected and evaporated to dryness to give 2-amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin **21** (98 mg, 87%) as a purple amorphous powder which co-eluted with, and had identical ^{1}H NMR spectrum to a sample prepared by Method 1.

(2-Formamido-3-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) 23

Method 1. A solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **22** (267 mg, 0.371 mmol) in dry, distilled *N*,*N*-dimethylformamide (60 cm^3) was stirred under nitrogen with sodamide ($NaNH_2$) (50% suspension in benzene, 70 mg, 0.90 mmol) for 18 h. The mixture was then diluted with dichloromethane (150 cm^3), washed with water (6 × 200 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed over silica (Type 9385) eluting with dichloromethane. The major, polar, brown–green band was collected to yield (2-*formamido*-3-*nitro*-5,10,15,20-*tetraphenylporphyrinato*)*copper*(II) **23** (177 mg, 63%) which was recrystallised from dichloromethane–hexane to yield a fine dark purple powder, mp 331–333 °C (Found: C, 70.8; H, 3.8; N, 10.6. $C_{45}H_{28}CuN_6O_3$ requires C, 70.7; H, 3.7; N, 11.0%); ν_{max}(Nujol)/cm^{-1} 3350br (NH), 1700 (C=O), 1570 (NO_2), 1510 and 1330 (NO_2); λ_{max}($CHCl_3$)nm 390sh (log ε 4.57), 425 (5.28), 551 (4.11) and 594 (3.95); *m/z* 763 (M^+, 12%), 733 (12), 732 (11), 731 (16), 721 (19), 720 (36), 719 (39), 718 (M + 2H − HNO_2, 70), 717 (18), 716 (16), 706 (10), 705 (21), 704 (31), 703 (61), 702 (70), 701 (M + 2H − HNO_2 − OH, 100), 700 (51), 699 (44), 698 (13), 694 (14), 693 (18), 692 (29), 691 (31), 690 (43), 689 (21) and 688 (30).

Method 2. A solution of sodium methylsulfinylmethanide was prepared by stirring sodium hydride (50% suspension in oil, 90 mg, 1.9 mmol) with dry, distilled Me_2SO (60 cm^3) under nitrogen at 65 °C for 45 min. On cooling to room temperature, formamide (0.10 cm^3, 2.5 mmol) was added and the mixture was stirred for 15 min. (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **22** (297 mg, 0.413 mmol) was added and the mixture was stirred overnight. The mixture was then diluted with dichloromethane (100 cm^3), washed with water (6 × 100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed over silica (Type 9385) eluting with dichloromethane and the major, polar band was collected to yield (2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **23** (179 mg, 57%), identical in all respects to the sample prepared by Method 1.

(2-Acetamido-3-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) 24

A solution of sodium methylsulfinylmethanide was prepared by stirring sodium hydride (50% suspension in oil, 85 mg, 1.8 mmol) with dry, distilled Me_2SO (60 cm^3) under nitrogen at 65 °C for 45 min. On cooling, acetamide (113 mg, 1.92 mmol) was added and the mixture was stirred for 20 min. (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **22** (272 mg, 0.378 mmol) was added and the mixture was stirred overnight. The residue was chromatographed over silica (Type 9385) eluting with dichloromethane to yield (2-*acetamido*-3-*nitro*-5,10,15,20-*tetraphenylporphyrinato*)*copper*(II) **24** (127 mg, 43%). An analytical sample was recrystallised from dichloromethane–hexane to give a purple solid, mp 301–303 °C (Found: C, 70.7; H, 3.8; N, 10.7. $C_{46}H_{30}CuN_6O_3$ requires C, 71.0; H, 3.9; N, 10.8%); ν_{max}(Nujol)/cm^{-1} 1700br (C=O), 1570w (NO_2) and 1520; λ_{max}($CHCl_3$)/nm 427 (log ε 5.28), 551 (4.12) and 593 (3.93); *m/z* 735 (25%), 734 (56), 733 (44), 732 (M + 2H − HNO_2, 100), 690 (13), 689 (11), 688 (14), 677 (12), 676 (10) and 675 (18).

2-Formamido-3-nitro-5,10,15,20-tetraphenylporphyrin 25

A solution of (2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **23** (138 mg, 0.181 mmol) in dichloromethane (20 cm^3) was poured into rapidly-stirred concentrated sulfuric acid (15 cm^3) and the mixture was stirred for 4 min. The mixture was then poured onto ice (150 g) and extracted with dichloromethane (100 cm^3, 50 cm^3). The combined organic extracts were washed with water (3 × 150 cm^3), dried over anhydrous sodium sulfate and evaporated to dryness. The residue was chromatographed over silica (Type 9385) eluting with dichloromethane to yield a major, polar band of 2-*formamido*-3-*nitro*-5,10,15,20-*tetraphenylporphyrin* **25** (116 mg, 91%) as purple crystals. A sample for analysis, recrystallised from a dichloromethane–methanol mixture, had mp 302–304 °C (Found: C, 76.4; H, 4.3; N, 12.0. $C_{45}H_{30}N_6O_3$ requires C, 76.9; H, 4.3; N, 12.0%); ν_{max}(Nujol)/cm^{-1} 1690, 1575 (NO_2) and 1510; λ_{max}($CHCl_3$)/nm 434 (log ε 5.24), 532 (4.11), 602 (3.56) and 677 (3.85); δ_H(400 MHz, CD_2Cl_2) −2.56 (2 H, br s, inner NH), 7.12 (0.5 H, br s, *cis*-CHONH), 7.29 (0.5 H, br s, *trans*-CHONH), 7.66–7.92 (12 H, m, Ph H_m and H_p), 8.16–8.23 (6 H, m, Ph H_o), 8.25–8.30 (2 H, m, Ph H_o), 8.38 (0.5 H, br s, *trans*-CHOHN), 8.67 (2 H, s, β-pyrrolic H), 8.84–8.92 (3 H, m, β-pyrrolic H) and 8.98 (1 H, br s, β-pyrrolic H); *m/z* 720 (13%), 719 (15), 718 (M + ^{63}Cu + 2H − HNO_2, 25),† 705 (11), 704 (13), 703 (27), 702 (37), 701 (M + ^{63}Cu + 2H − HNO_2 − OH, 40), 700 (25), 699 (25), 693 (11), 692 (16), 691 (24), 690 (41), 689 (27), 688 (45), 659 (16), 658 (19), 657 (M + 2H − HNO_2, 100), 656 (37), 655 (19), 644 (16), 643 (15), 642 (24), 641 (50), 640 (91), 639 (43), 638 (11), 631 (13), 630 (23), 629 (32), 628 (35), 627 (21) and 612 (12).

2-Acetamido-3-nitro-5,10,15,20-tetraphenylporphyrin 26

A solution of (2-acetamido-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **24** (125 mg, 0.161 mmol) in dichloromethane (30 cm^3) was poured into rapidly-stirred concentrated sulfuric acid (20 cm^3) and the mixture was stirred for 4 min then poured onto ice (150 g). The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 50 cm^3). The combined organic layers were washed with water (2 × 200 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed over silica (Type 9385) eluting with dichloromethane to yield a major polar brown band which afforded on evaporation 2-*acetamido*-3-*nitro*-5,10,15,20-*tetraphenylporphyrin* **26** (100 mg, 87%). A sample for analysis, recrystallised from a dichloromethane–hexane mixture, had mp 308–309 °C (Found: C, 76.5; H, 4.2; N, 11.3. $C_{46}H_{32}N_6O_3$ requires C, 77.1; H, 4.5; N, 11.7%); ν_{max}(Nujol)/cm^{-1} 3350br (NH), 1690br (C=O) and 1520 (NO_2); λ_{max}($CHCl_3$)/nm 436 (log ε 5.22), 532 (4.10), 607 (3.53) and 675 (3.81); δ_H(400 MHz, $CDCl_3$) −2.49 (2 H, s, inner NH), 1.72 (3 H, s, CH_3), 7.42 (1 H, br s, NHCOCH$_3$), 7.68–7.89 (12 H, m, Ph H_m and H_p), 8.17–8.32 (8 H, m, Ph H_o), 8.61 (2 H, s, 12- and 13-H), 8.76 (2 H, br s, β-pyrrolic H), 8.78 and 8.91 (2 H, ABq, J_{AB} 5.0, β-pyrrolic H); *m/z* 735 (10%), 734 (23), 733 (18), 732 (M + ^{63}Cu + 2H − HNO_2, 41), 730 (16), 688 (15), 687 (27), 673 (16), 672 (56), 671 (M + 2H − HNO_2, 100), 670 (18), 669 (28), 659 (14), 656 (14), 644 (18), 633 (16), 632 (30), 631 (11), 630 (16), 629 (15), 628 (19), 614 (14), 613 (19) and 612 (27).

2-(*N*-Formylacetamido)-3-nitro-5,10,15,20-tetraphenylporphyrin 27

A solution of 2-formamido-3-nitro-5,10,15,20-tetraphenylporphyrin **25** (61 mg, 0.087 mmol) in a mixture of pyridine (18 cm^3) and acetic anhydride (18 cm^3) was heated under reflux for 1 h. On cooling, water (5 cm^3) was carefully added dropwise over 30 min. The mixture was allowed to stand for 20 min then dichloromethane (80 cm^3) was added and the mixture was washed with hydrochloric acid (3 mol dm^{-3}, 3 × 100 cm^3), water (100 cm^3), aqueous sodium hydrogen carbonate (5%, 50 cm^3) and water (100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed over silica (Type 9385) eluting with dichloromethane to yield a front running, brown band of 2-(N-*formylacetamido*)-3-*nitro*-5,10,15,20-*tetraphenylporphyrin* **27** (38 mg, 59%). A sample for analysis, recrystallised from a dichloromethane–hexane mixture, had mp 277–278 °C (Found: C, 75.8; H, 4.0; N, 11.2. $C_{47}H_{32}N_6O_4$ requires C, 75.8; H, 4.3; N, 11.3%; ν_{max}(Nujol)/cm^{-1} 3330w, 1725 (C=O), 1700 (C=O), 1510wbr, 1360 and 1340; λ_{max}($CHCl_3$)/nm 430 (log ε 5.15), 531 (3.95), 608 (3.39) and 671 (3.76); δ_H(400 MHz, $CDCl_3$) −2.64 (2 H, br s, inner NH), 2.33 (3 H, br s, COMe), 7.66–7.83 (12 H, m, Ph H_m and H_p), 7.95–8.06 (2 H, m, Ph H_o), 8.10–8.33 (6 H, br m, Ph H_o), 8.68 (2 H, s, 12- and 13-H), 8.68 and 8.81 (2 H, ABq, J_{AB} 5.0, β-pyrrolic H), 8.87 and 8.96 (2 H, ABq, J_{AB} 5.0, β-pyrrolic H) and 9.08 (1 H, br s, CHO); *m/z* 734 (13%), 733 (16), 732 (M + ^{63}Cu + 2H − CO − HNO_2, 27), 730 (12), 688 (12), 687 (22), 673 (15), 672 (55), 671 (M + 2H − CO − HNO_2, 100), 670 (45), 669 (72), 659 (11), 657 (12), 656 (22), 645 (12), 644 (19), 641 (10), 640 (17), 633 (15), 632 (31), 631 (15), 630 (27), 629 (20), 628 (27), 615 (12), 614 (21), 613 (16) and 612 (27).

Further elution with ethyl acetate–dichloromethane (1:9) yielded a more polar, brown band of 2-acetamido-3-nitro-5,10,15,20-tetraphenylporphyrin **26** (25 mg, 40%). This product was identical with authentic material by TLC and NMR comparison.

2-Amino-3-nitro-5,10,15,20-tetraphenylporphyrin 28

2-Formamido-3-nitro-5,10,15,20-tetraphenylporphyrin **25** (237 mg, 0.337 mmol) was dissolved in tetrahydrofuran (250 cm^3), aqueous potassium hydroxide (10%, 100 cm^3) was added and the two-phase system was stirred while heated at reflux for 18 h. The reaction mixture was separated and the organic phase washed with brine (100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent removed to yield a purple solid (384 mg). The crude product was purified by column chromatography over silica (Type 9385) with dichloromethane as the eluent to yield a purple solid (163 mg, 72%). The product was recrystallised from dichloromethane–methanol to give 2-*amino*-3-*nitro*-5,10,15,20-*tetraphenylporphyrin* **28** as purple crystals, mp 305–308 °C (dec.) (Found: C, 78.1; H, 4.3; N, 12.35. $C_{44}H_{30}N_6O_2$ requires C, 78.3; H, 4.5; N, 12.5%); ν_{max}($CHCl_3$)/cm^{-1} 3485w, 3346w, 3007w, 1611s, 1598m, 1550m, 1536m, 1507m, 1475m, 1443m, 1420s, 1369m, 1348m, 1300m, 1282m, 1138m, 1111m, 1074m, 1032m, 1002m and 965m; λ_{max}($CHCl_3$)/nm 264sh (log ε 4.20), 311 (4.26), 329sh (4.24), 439 (5.19), 493sh (3.63), 535 (4.18), 559 (3.80), 574sh (3.89), 594sh (3.63), 610 (3.78), 649sh (3.03) and 671 (3.39); *m/z* 629 (M − NO_2, 100%).

Attempted reduction of [2-amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]palladium(II) 18

[2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]palladium(II) **18** (73.1 mg, 0.060 mmol) and 10% palladium on carbon (52.4 mg) were suspended in a dichloromethane–methanol mixture (4:1, 8 cm^3) and purged with nitrogen. Sodium borohydride (56.3 mg, 1.49 mmol) was added in small portions over a 10 min period and the mixture stirred in the dark under nitrogen for 30 min. The mixture was evaporated to dryness, taken up in dichloromethane and filtered through a plug of silica (Type 7734). TLC analysis of the filtrate showed a red band slightly more polar than the starting material. Allowing the solution to stand over air for several min caused the solution to change from a red to a green colour. The formation of a red band, which was more polar than the starting material, was observed by TLC analysis. The mixture was evaporated to dryness. TLC analysis of the solid after it had

† Mass spectra of these free base porphyrins contain peaks due to sequestering of copper(II) ions from the copper tubes of the spectrometer.

been allowed to stand overnight showed a large number of bands, all more polar than the starting material.

[5,10,15,20-Tetrakis(3,5-di-*tert*-butylphenyl)-2^2,2^3-diphenylpyrazino[2,3-*b*]porphyrinato]zinc(II) 31

[2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **16** (72.8 mg, 0.061 mmol) and 10% palladium on carbon (65.6 mg) were suspended in a dichloromethane–methanol mixture (4:1, 8 cm^3) and purged with nitrogen. Sodium borohydride (67.7 mg, 1.79 mmol) was added in small portions over a 10 min period and the mixture stirred in the dark under nitrogen for 45 min. The mixture was evaporated to dryness, taken up in dichloromethane, filtered through silica (Type 9385) and evaporated to dryness. A mixture of the residue and benzil (18.9 mg, 0.090 mmol) was dissolved in dichloromethane (4 cm^3) and stirred at room temperature in the dark for 20 h. The mixture was evaporated to dryness and the residue purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:4). The major red band was collected and evaporated to dryness to give [5,10,15,20-*tetrakis*(3,5-*di*-tert-*butylphenyl*)-2^2,2^3-*diphenylpyrazino*[2,3-b]*porphyrinato*]*zinc*(II) **31** (52 mg, 64%) as a red amorphous powder, mp > 300 °C (Found: C, 79.1; H, 7.75; N, 5.9. $C_{90}H_{100}N_6Zn + 0.5CH_2Cl_2$ requires C, 79.15; H, 7.4; N, 6.1%); ν_{max}(Nujol)/cm^{-1} 1592, 1344, 1297, 1247, 1224, 1174, 1067, 1002, 937, 926 and 899; λ_{max}($CHCl_3$)/nm 334 (log ε 4.38), 388 (4.51), 439 (5.29), 487 (3.88), 512 (3.85), 559 (4.39) and 595 (3.76); δ_H(400 MHz, $CDCl_3$) 1.39 (36 H, s, *tert*-butyl H), 1.53 (36 H, s, *tert*-butyl H), 7.21–7.33 (6 H, m, Ph H), 7.36–7.40 (4 H, m, Ph H), 7.79 (2 H, t, *J* 1.8, aryl H_p), 7.85 (2 H, t, *J* 1.8, aryl H_p), 8.00 (4 H, d, *J* 1.8, aryl H_o), 8.10 (4 H, d, *J* 1.8, aryl H_o), 8.95 (2 H, s, 12- and 13-H), 8.97 and 9.01 (4 H, AA′XX′, *J* 4.7, 7-, 8-, 17- and 18-H); *m/z* (MALDI-TOF) 1331 (M + H requires 1330).

[5,10,15,20-Tetrakis(3,5-di-*tert*-butylphenyl)-2^2,2^3,2^4,2^5-tetrahydroquinoxalino[2,3-*b*]porphyrinato]zinc(II) 32

[2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **16** (81 mg, 0.068 mmol) was reduced with sodium borohydride in the presence of a 10% palladium on carbon catalyst following a similar procedure to that described above. A solution of the crude product and cyclohexane-1,2-dione (26 mg, 0.238 mmol) in dichloromethane (6 cm^3) was stirred in the dark for 3.5 h and evaporated to dryness. The residue was purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 1:2). The major purple–red band collected and evaporated to dryness to give [5,10,15,20-*tetrakis*(3,5-*di*-tert-*butylphenyl*)-2^2,2^3,2^4,2^5-*tetrahydroquinoxalino*[2,3-b]*porphyrinato*]*zinc*(II) **32** (59 mg, 70%) as a purple–red amorphous powder. A sample for analysis, recrystallised from a dichloromethane–methanol mixture, had mp > 300 °C (Found: C, 80.1; H, 8.2; N, 6.5. $C_{82}H_{98}N_6Zn$ requires C, 79.9; H, 8.0; N, 6.8%); ν_{max}($CHCl_3$)/cm^{-1} 2964, 2863, 1680, 1593, 1477, 1462, 1427, 1393, 1363, 1340, 1323, 1296, 1248, 1147, 1075, 1041, 1002, 938, 908, 882, and 820; λ_{max}($CHCl_3$)/nm 296 (log ε 4.23), 310sh (4.23), 378 (4.20), 411 (4.65), 430 (5.56), 489 (3.50), 516 (3.65), 554 (4.28) and 591 (3.82); δ_H(400 MHz, $CDCl_3$) 1.40 (36 H, s, *tert*-butyl H), 1.45 (36 H, s, *tert*-butyl H), 1.87–1.93 (4 H, m, CH_2), 2.78–2.83 (4 H, m, CH_2), 7.71 (2 H, t, *J* 1.8, aryl H_p), 7.73 (2 H, t, *J* 1.8, aryl H_p), 7.83 (4 H, d, *J* 1.8, aryl H_o), 8.02 (4 H, d, *J* 1.8, aryl H_o), 8.87 (2 H, s, 12- and 13-H), 8.93 and 8.95 (4 H, ABq, *J* 4.7, 7-, 8-, 17- and 18-H); *m/z* (MALDI-TOF) 1232 (M + H requires 1233).

[5,10,15,20-Tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-porphyrinato]zinc(II) 33

[2-Amino-3-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]zinc(II) **16** (81 mg, 0.068 mmol) was reduced with sodium borohydride in the presence of a 10% palladium on carbon catalyst following a similar procedure to that described above. A suspension of the crude product and *o*-benzoquinone (15 mg, 0.139 mmol) in dichloromethane (5 cm^3) was stirred for 3 days. The crude product was evaporated to dryness and the residue purified by chromatography over silica (Type 9385, dichloromethane–light petroleum, 2:1). The first green band was collected and evaporated to dryness to give {5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato}zinc(II) **33** (3.6 mg, 4%) as a purple amorphous powder which co-eluted with, and had an identical ^{1}H NMR spectrum to, an authentic sample.[27]

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