Construction of building blocks for extended porphyrin arrays by nitration of porphyrin-2,3-diones and quinoxalino[2,3-*b*]porphyrins†

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Nitration of metal(II) porphyrin-2,3-diones **3–5** and quinoxalino[2,3-*b*]porphyrins **13–15** with nitrogen dioxide gave a mixture of β-pyrrolic functionalised nitro-porphyrin isomers in relative abundance of 7-nitro- > 12-nitro- > 8-nitro. The large selectivity for reaction at the 7-position over the adjacent 8-position (>5 to 1 in the diones **3–5** and about 3 to 1 in the quinoxalinoporphyrins **13–15**) is especially striking. This selectivity results mainly from electronic effects and is consistent with a mechanism involving a porphyrin π-cation radical intermediate. A key step incorporated into the isomer separation sequence was to make use of the different chromatographic polarity of metalated compounds compared to unmetalated compounds coupled with the observation that introduction of a nitro group to the 7-position of free-base porphyrin-dione greatly increases its rate of metalation while introduction of the nitro group at the 12-position greatly decreases its rate of metalation, relative to the unsubstituted parent. Thus demetalation of zinc(II) nitro-porphyrin-dione isomers, which are difficult to separate, allows for highly selective remetalation of the 7-isomer and its very easy separation from the unmetalated 12-nitro-porphyrin-dione. These nitrated compounds are useful building blocks for more elaborate systems.

Introduction

Nitro groups are a very useful functionality to incorporate into porphyrin systems,[1–7] especially when positioned at the β-pyrrolic periphery.[8–16] A range of transformations have been developed, some of which are summarised in Scheme 1, that allow for the introduction of functional groups that are otherwise very difficult to access.[10,15–21] The porphyrin-2,3-dione **1** (M = 2H) is of particular use in condensation reactions[17] while the quinoxalinoporphyrin **2** (M = 2H) serves as a model for the development of chemistry on laterally extended oligoporphyrin systems.[22]

Porphyrin-2,3-diones **1** have been used as building blocks for the synthesis of laterally-bridged bis-porphyrins.[23] For more elaborate systems such as laterally-bridged oligoporphyrins, porphyrin-2,3,12,13- and -2,3,7,8-tetraones porphyrins have been prepared and used in analogous reactions; these tetraones being accessed from isomeric mixtures of dinitro-porphyrins.[24] Linear 'pseudo one-dimensional molecular wires' are accessible from the porphyrin-2,3,12,13-tetraones while bends can be introduced where the porphyrin-2,3,7,8-tetraones are incorporated into the framework.[25–27]

Selective incorporation of a nitro group into porphyrin-2,3-dione building blocks would provide a functionality that can be converted into a considerable range of other functionalised extended systems, as well as allowing substituents to act as handles for attachment to external redox centres and which might be used modulate properties.[28–30] A porphyrin macrocycle that contains both nitro and α-dione functionality would also be useful building blocks for controlled stepwise-synthesis of unsymmetrical oligoporphyrins.[31]

Nitro-quinoxalinoporphyrins are envisaged as building blocks for exploration of synthetic routes to porphyrin systems with two, three, and even all four pyrrolic rings annulated.[26] Nitrations of quinoxalino[2,3-*b*]porphyrins **2** would also be a good model for the determination and control of the likely outcome of nitration of more elaborated laterally-bridged oligoporphyrin systems. Control of the site of nitration of extended systems will be crucial for development of architectures based on a square-grid motif leading to two-dimensional arrays.

For such nitrated porphyrin-dione and quinoxalino-porphyrin building blocks to be especially useful, methodology needed to be developed which would allow them to be obtained as pure compounds rather than isomeric mixtures. To date, only the nitration of copper(II) 2-methyl-5,10,15,20-tetraphenylporphyrin and two copper(II) 2-nitro-5,10,15,20-tetraarylporphyrins has been reported and in each case the selectivity was low and only with considerable effort were small amounts of pure compounds, sufficient for individual

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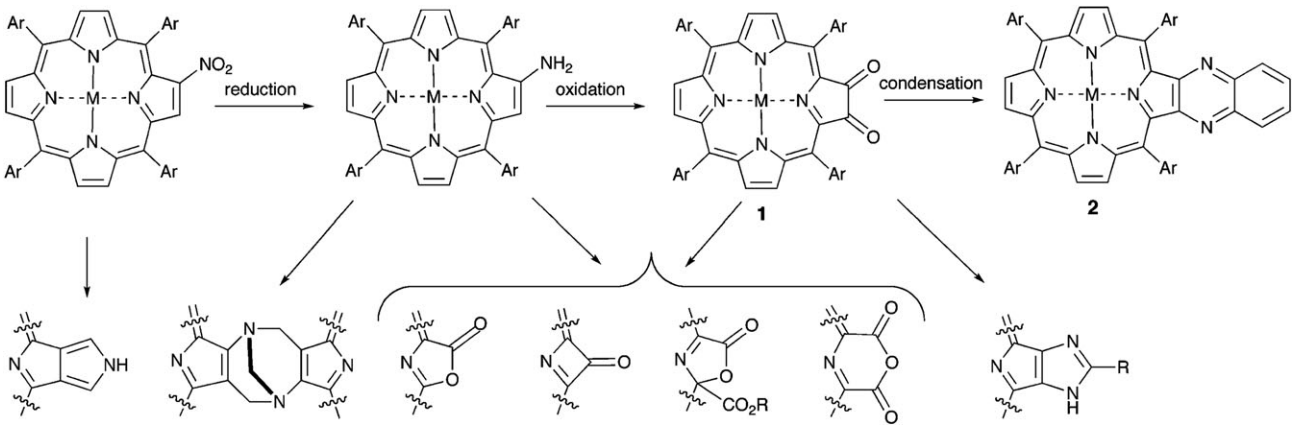
† Electronic supplementary information (ESI) available: List of NOE enhancements for 7- and 12-nitro-porphyrin-diones **6a** and **6c** and 7- and 12-nitro-quinoxalinoporphyrins **10a** and **10c**. The partial ^{1}H NMR spectrum (400 MHz) of zinc(II) 7-nitro-quinoxalinoporphyrin **10a** in $CDCl_3$ with additional signals of lower intensity belonging to the zinc(II) 8-nitro-quinoxalinoporphyrin **10b** is also given. See DOI: 10.1039/b712643c



Scheme 1 Some transformations involving ring annulations and ring modifications deriving from 2-nitroporphyrins (Ar = 3,5-di-*tert*-butylphenyl).

characterisation, obtained from the isomeric mixture of products.[9]

In this paper we explore the directive effects of the dione and fused quinoxaline groups on nitration of the porphyrin nucleus, we examine the influence of the co-ordinated metal ion on the reactions, and we develop a demetalation-selective remetalation strategy for relatively easy separation of some of the nitro-porphyrin-α-diones. A rationalisation on the relative abundance of the regioisomers that arise from nitration is also presented.

Results and discussion

Scheme 2 summarises nitration and ring annulation of zinc(II), copper(II) and palladium(II) 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin-2,3-diones **3–5**, prepared by direct metalation of free-base porphyrin-dione **1**, and nitration of the corresponding quinoxalino[2,3-*b*]porphyrins **13–15**, prepared by similar metalation of the free-base quinoxalinoporphyrin **2**.

Nitration of metal(II) porphyrin-2,3-diones

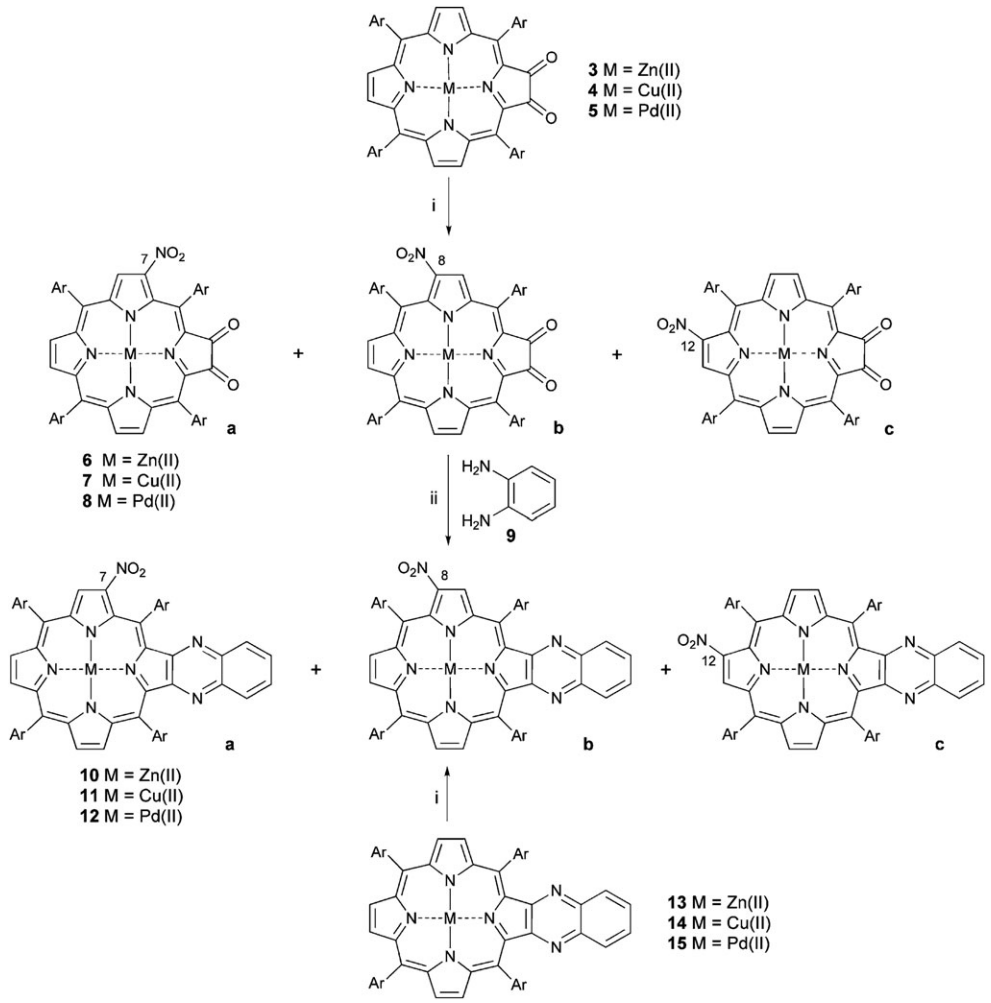
Zinc(II) porphyrin-dione **3**[32] was treated with aliquots of a solution of nitrogen dioxide in light petroleum until TLC analysis showed that none of the starting material remained. A mixture of zinc(II) nitro-porphyrin-diones **6a–c** was obtained in 80% yield. The remainder of the product was much more polar and consistent with porphyrin ring-cleaved compounds; such ring-cleaved compounds are the major product of nitration of simpler zinc(II) 5,10,15,20-tetraarylporphyrins and are the result of initial nitration at a meso-position rather than at a β-pyrrolic position.

The mixture of zinc(II) nitro-porphyrin-diones **6a–c** was observed as a single band by TLC analysis and could not be separated by column chromatography. It was found, however, that upon demetalation with hydrochloric acid and subsequent selective remetalation, achieved by stirring the mixture of free-base regioisomers with zinc(II) acetate at room temperature, zinc(II) chelation of free-base 7- and 8-nitro-porphyrin-diones **16a** and **16b** proceeded at a faster rate than free-base 12-nitro-porphyrin-dione **16c**. Reaction conditions were optimised to 0.75 equiv. of zinc(II) acetate and a reaction time of 30 min when zinc(II) chelation was found to have occurred exclusively to the 7- and 8-nitro-porphyrin-2,3-diones isomers. The resultant mixture was readily separated by chromatography to give zinc(II) 7-nitro-porphyrin-dione **6a** in 70% yield and free-base 12-nitro-porphyrin-dione **16c** (Scheme 3). The regiochemistry of the isomers was assigned by means of ^{1}H NMR decoupling and NOE experiments (see ESI†). Trace quantities of the 8-nitro-porphyrin-dione isomer **6b** were identified by ^{1}H NMR and TLC in latter dilute fractions during the fractionated collection of the band containing **6a** and could not be separated.

The large difference in metalation rates for free-base nitro-porphyrin-dione regioisomers **16a** and **16c** was readily observed by metalation of the separated isomers. The reaction of free-base 7-nitro-porphyrin-dione **16a** with 1.1 equiv. of zinc(II) acetate at 25 °C was complete after 20 min (Scheme 3). By contrast, the reaction of free-base 12-nitro isomer **16c** with zinc(II) acetate under similar conditions had gone to completion after stirring for 68 h. Metalation of **16c** with excess zinc(II) acetate in the dichloromethane–methanol mixture heated at reflux reduced the reaction time to 8 h. The reaction of the non-nitrated analogue, free-base porphyrin-dione **1**, with 1.1 equiv. of zinc(II) acetate at 25 °C was complete after 26 h to give zinc(II) porphyrin-dione **3**. Thus, introduction of a nitro group to the 7-position of free-base porphyrin-dione increases the rate of metalation while introduction of the nitro group at the 12-position decreases the rate of metalation relative to the unsubstituted parent.

The titration endpoint of the nitration of copper(II) and palladium(II) porphyrin-2,3-dione complexes **4** and **5**,[32] was determined by treating an aliquot from the reaction mixture with 1,2-benzenediamine **9** and examining this mixture by TLC analysis for the presence of the corresponding metallated quinoxalinoporphyrin[22] since the metalloporphyrin-diones co-eluted with nitration products. In each macrocycle nitration will be directed towards the β-pyrrolic periphery[9,33] to give three possible nitro-porphyrin-dione regioisomers: the 7-nitro-porphyrin-dione **6–8a**, the 8-nitro-porphyrin-dione **6–8b**, and the 12-nitro-porphyrin-dione **6–8c** (Scheme 2).

Selective remetalation could not be applied to the copper(II) or palladium(II) nitro-porphyrin-diones as they co-elute with



Scheme 2 *Reagents and conditions:* i, NO_2–light petroleum, CH_2Cl_2; ii, 1,2-benzenediamine, CH_2Cl_2, 1 h (Ar = 3,5-$Bu^t_2C_6H_3$).

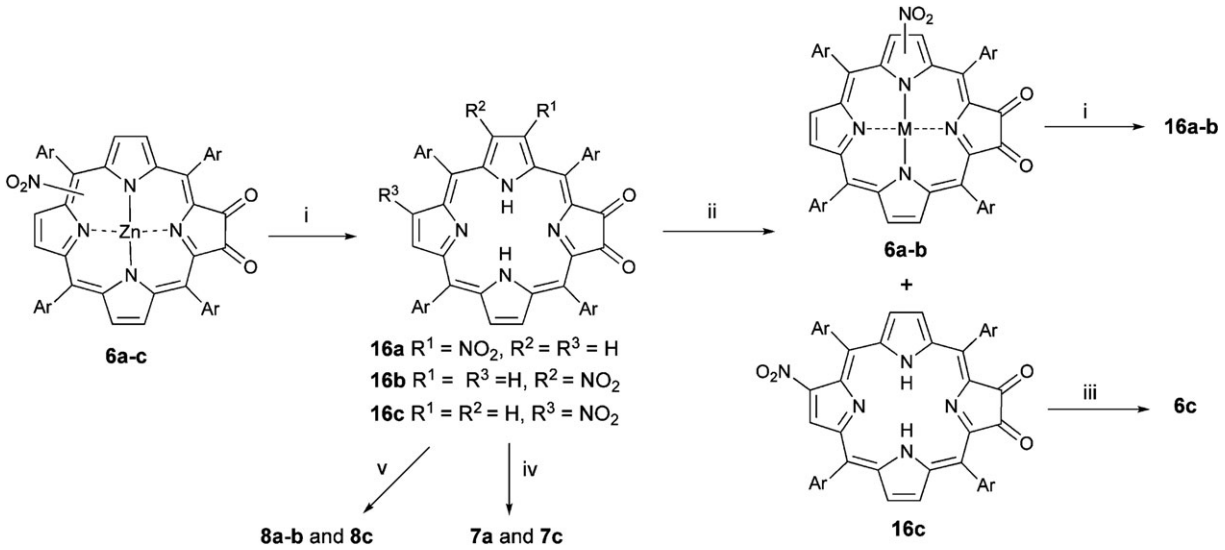
the free-base isomers **16a** and **16c**. In contrast to the mixture of zinc(II) isomers, copper(II) and palladium(II) nitro-porphyrin-dione regioisomers could be separated by chromatography. The copper(II) 7-nitro-porphyrin-dione **7a** and copper(II) 12-nitro-porphyrin-dione **7c** were isolated in yields of 42 and 28%, respectively, with the 8-nitro isomer **7b** not being isolated or detected. In a similar fashion palladium(II) 12-nitro and 8-nitro isomers **8c** and **8b** were isolated in combined yield of 43% (in a ratio of 3 : 1, respectively, determined by ^{1}H NMR), and the 7-nitro isomer **8a** was isolated in 49% yield (Scheme 2). The differing ratios of isomeric abundance for these two complexes, best demonstrated by the greater proportion in which the 8-nitro isomer is formed with the palladium(II) chelate, clearly indicate that the complexed metal ion influences nitration patterns. It should also be noted that the regiochemistry of the copper(II) and palladium(II) chelates was determined by condensation of the nitro-porphyrin-dione adduct with 1,2-benzenediamine **9** followed by comparison of the resultant nitro-quinoxalinoporphyrin with authentic samples of known regiochemistry (as described in the following section). This further condensation reaction was required as the copper(II) nitro-porphyrin-dione isomers are paramagnetic and could not be demetallated, while the ^{1}H NMR spectrum of the palladium(II) isomers was complex.

The copper(II) and palladium(II) regioisomers were also prepared by demetalation of zinc(II) nitro-porphyrin-dione isomers **6a–c** followed by remetalation with the appropriate metal(II) ion (Scheme 3). This approach allowed for the large scale purification of the copper(II) chelates. In the case of the palladium(II) isomers the metalation proceeded only after the reaction solvent was changed from acetic acid–chloroform to acetic acid–toluene, which allowed the solution to reflux at a higher temperature and improve solubility of the porphyrin (Scheme 3). Additionally, trace quantities of the metallated 8-nitro isomer were obtained as an inseparable mixture with the palladium(II) 12-nitro isomer **8c**.

Preparation of separated nitro-quinoxalinoporphyrin isomers

Preparation of pure nitro-quinoxalinoporphyrin regioisomers was important for the assignment of the regiochemistry of the products obtained by nitration of quinoxalinoporphyrins **15–17** and metal(II) porphyrin-diones **3–5**.

Zinc(II) nitro-porphyrin-dione isomers **6a–c** were reacted with 1,2-benzenediamine **9** and the resultant mixture of isomers separated by chromatography to give zinc(II) 7-nitro-quinoxalinoporphyrin **10a** in 65% yield and zinc(II) 12-nitro-quinoxalinoporphyrin **10c** in 23% yield (Scheme 2).



Scheme 3 *Reagents and conditions*: i, HCl (7 mol dm^{-3}), Et_2O; ii, $Zn(OAc)_2 \cdot 2H_2O$ (0.8 equiv.), CH_2Cl_2–CH_3OH, stir, r.t., 30 min; iii, $Zn(OAc)_2 \cdot 2H_2O$, CH_2Cl_2–MeOH, heat, 8 h; iv, $Cu(OAc)_2 \cdot H_2O$, CH_2Cl_2–MeOH, heat, 90 min; v, $PdCl_2$, NaOAc, AcOH–C_7H_8, heat, 5 min (Ar = 3,5-$Bu^t_2C_6H_3$).

The regiochemistry of the isomers was assigned by means of ^{1}H NMR decoupling and NOE experiments (see ESI†). The ^{1}H NMR spectrum of zinc(II) 7-nitro-quinoxalinoporphyrin **10a** also contained extra peaks which are due to the presence of the zinc(II) 8-nitro-quinoxalinoporphyrin **10b**; a singlet and an AB-quartet were observed along with additional peaks of undetermined multiplicity amongst the tight AB-quartet of **10a**. The ratio of **10a** to **10b** was 7 : 1 as determined by ^{1}H NMR analysis, in particular, by integration of the signals (δ 9.13 for **10a** and δ 9.27 for **10b**) of the protons next to the nitro group (see ESI,† Fig. S1). This ratio was used to determine the proportion of 8-nitro-porphyrin-dione **6b** produced during the nitration of **3**.

By contrast, the regioisomers of copper(II) nitro-quinoxalinoporphyrins **11a–c** and palladium(II) nitro-quinoxalinoporphyrins **12a–c** co-eluted and could not be prepared from a mixture of the corresponding nitro-porphyrin-dione isomers. Therefore demetalation of zinc(II) nitro-porphyrin-diones **6a–c** followed by separation of resultant free-base derivates (through zinc(II) remetalation) and condensation with 1,2-benzenediamine **9** was used to prepare these adducts (Scheme 4). As the zinc(II) 7-nitro-quinoxalinoporphyrin **10a** used in this experiment contained trace quantities of the 8-nitro isomer **10b**, small amounts of the 8-nitro isomer were also observed in the ^{1}H NMR spectra of free-base 7-nitro-quinoxalinoporphyrin **17a** and the corresponding palladium(II) complex **12a**. The ^{1}H NMR of these trace quantities of zinc(II) and palladium(II) 8-nitro isomers were of use when assigning the regiochemical outcomes from the nitration of quinoxalinoporphyrins **13–15** as it enabled the yield of each isomer to be quantified.

It should also be noted that ^{1}H NMR analysis of the resultant mixture of free-base nitro-quinoxalinoporphyrins produced from the condensation and subsequent demetalation of the copper(II) nitro-porphyrin-diones **7a–c** failed to detect the presence of the 8-nitro isomer.

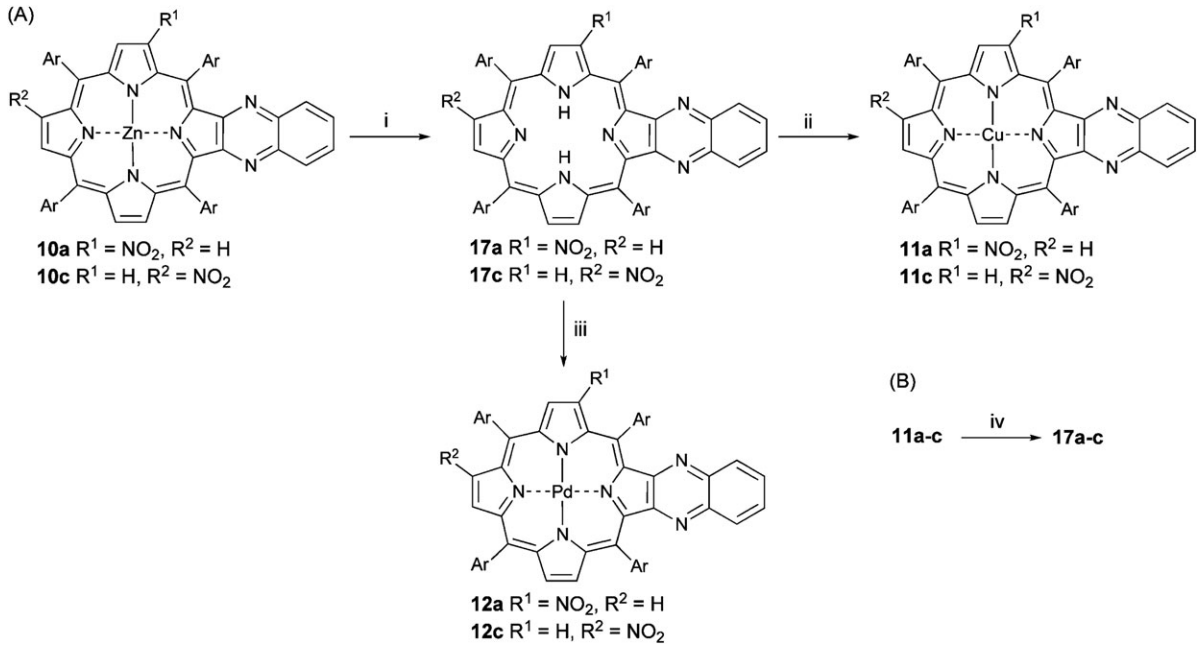
Nitration of metal(II) quinoxalinoporphyrins

The zinc(II), copper(II) and palladium(II) quinoxalinoporphyrins **13–15** used in this study were prepared using published procedures.[22] Each of the metal(II) quinoxalinoporphyrins was nitrated by treatment with aliquots of a solution of nitrogen dioxide in light petroleum until TLC analysis showed that none of the starting quinoxalinoporphyrin remained to give the corresponding metal(II) nitro-quinoxalinoporphyrins **10–12** (Scheme 2).

Nitration of zinc(II) quinoxalinoporphyrin **13** gave a mixture of zinc(II) 7-nitro-quinoxalinoporphyrin **10a** and zinc(II) 8-nitro-quinoxalinoporphyrin **10b** in 40% yield, and zinc(II) 12-nitro-quinoxalinoporphyrin **10c** in 13% yield. The ratio of **10a** to **10b**, determined by ^{1}H NMR analysis, was 3.4 : 1.

Nitration of copper(II) quinoxalinoporphyrin **14** gave an inseparable mixture of copper(II) nitro-quinoxalinoporphyrin regioisomers **11a–c** in 92% yield. In order to determine the ratio of nitro-quinoxalinoporphyrin isomers produced by this nitration, the mixture of **11a–c** was demetallated with sulfuric acid–trifluoroacetic acid followed by zinc(II) chelation to give separable isomers of which ^{1}H NMR spectra can be obtained (Scheme 4). Zinc(II) 7-nitro-quinoxalinoporphyrin **10a** and zinc(II) 8-nitro-quinoxalinoporphyrin **10b** were afforded in 61% yield, and zinc(II) 12-nitro-quinoxalinoporphyrin **10c** in 26%. The ratio of **10a** to **10b** was found to be 3.5 : 1.0 by ^{1}H NMR analysis.

Nitration of palladium(II) quinoxalinoporphyrin **15** also showed the formation of a single more polar band by TLC analysis. A mixture of palladium(II) nitro-quinoxalinoporphyrin isomers **12a–c** was obtained in 82% yield (Scheme 2). The ^{1}H NMR spectrum of the mixture of isomers had three singlets at δ 9.01, 9.05 and 9.18 which, by comparison with the ^{1}H NMR spectra of authentic samples of the individual isomers, are due to the β-pyrrolic proton adjacent to the nitro group of palladium(II) 7-nitro isomer **12a**, palladium(II)



Scheme 4 *Reagents and conditions*: (A), i, HCl (7 mol dm^{-3}), Et_2O; ii, $Cu(OAc)_2 \cdot H_2O$, CH_2Cl_2–CH_3OH, heat, 75 min; iii, $PdCl_2$, NaOAc, AcOH–$CHCl_3$, heat, 18 h; (B), iv, H_2SO_4–CF_3CO_2H, CH_2Cl_2 (Ar = 3,5-$Bu^t_2C_6H_3$).

12-nitro isomer **12c**, and palladium(II) 8-nitro-quinoxalinoporphyrin **12b**, respectively. By measuring the area under these resonances, the ratio of **12a** to **12b** to **12c** was 1.9 : 1.0 : 1.5.

Rationalisation of the isomeric abundance of nitro-porphyrin-α-diones and nitro-quinoxalinoporphyrins

The relative abundance of the nitro-porphyrin-dione regioisomers produced by the nitration of the porphyrin-diones **3–5** was 7 nitro- > 12 nitro- > 8 nitro-porphyrin-dione. The same trend was observed for the nitration of quinoxalinoporphyrins **13–15**. A summary of the percentage abundance of each isolated isomer is displayed in Table 1.

If the regiochemistry of the nitration was statistical, the isomers would be formed in equal amounts. This is clearly not the case. To investigate whether the relative abundance of the isomers was caused by steric hindrance of the β-pyrrolic carbons by the *meso*-aryl groups NOE experiments on zinc(II) porphyrin-dione **3**, palladium(II) porphyrin-dione **5**, zinc(II) quinoxalinoporphyrin **13**, and palladium(II) quinoxalinoporphyrin **15** were undertaken (Fig. 1). In these experiments enhancements of protons at the 8- and 12-positions were investigated as they are likely to have the same relaxation mechanism as these protons are both adjacent to the same *meso*-aryl group. The 8- and 12-β-pyrrolic positions of zinc(II) porphyrin-dione **3** showed a similar enhancement of 2.3 and 2.2%, respectively. For palladium(II) porphyrin-dione **7**, a similar enhancement was observed for the 8- and 12-positions (2.0 and 2.0%). This indicated that the 8-position was not sterically hindered relative to the 12-position. Similar NOE experiments on the quinoxalinoporphyrins **13** and **15** showed that the 8-position was less hindered than the 12-position (1.6 and 1.9% for **13** and 1.7 and 2.1% for **15**).

The trends observed in the enhancements of the β-pyrrolic protons when the *ortho*-protons of the *meso*-aryl groups are saturated do not explain the preference for nitration at the

Table 1 The regioisomer abundance[a] obtained from the nitration of respective metalloporphyrins is compared to calculated spin-density ratios for the cation radicals evaluated for the three reaction sites

	Observed product (%)[a]			Calculated cation-radical relative spin densities (%)		
Porphyrin starting material	7-Nitro (**a**)	8-Nitro (**b**)	12-Nitro (**c**)	7-Nitro (**a**)	8-Nitro (**b**)	12-Nitro (**c**)
3 Zn	64	10	26	52	14	34
4 Cu	60	—	40			
5 Pd	54	12	34	45	21	34
13 Zn	59	17	24	47	19	34
14 Cu	51	16	29			
15 Pd	42	23	35	39	29	32

[a] Percentage abundance of nitro regioisomers was calculated from isolated yields of the direct nitration product (for **4**), demetalation and subsequent remetalation with zinc(II) (for **14**) or its condensation derivative (for **3**). In all cases integration of ^{1}H NMR signals was used to determine distribution of the 7- and 8-isomers. For **4**, condensation with **9** followed by demetalation and then ^{1}H NMR analysis, failed to reveal the presence of the 8-isomer.

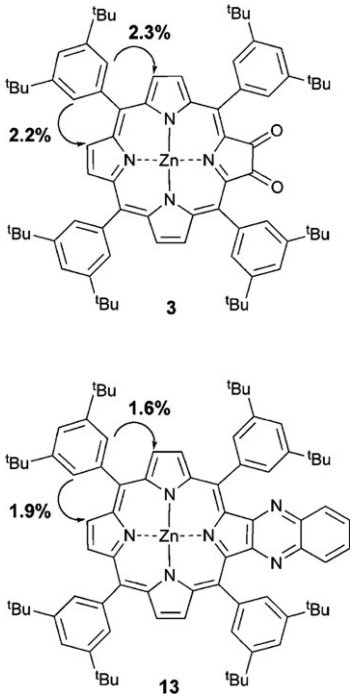


Fig. 1 Enhancement of each β-pyrrolic proton in **3** and **13** due to saturation of the *ortho*-protons on the *meso*-aryl groups.

12-position over the 8-position that was observed for the nitration of porphyrin-2,3-diones **3–5** and quinoxalinoporphyrins **13–15**. Thus the relative abundance of these isomers is not due to steric factors. The relatively higher yield of the 7-nitro isomer can be rationalised by either the quinoxaline group or α-diketone functionality restricting the rotation of the neighbouring aryl group, which would decrease the steric effect at the 7-position and thereby allow easier access for nitration. However, this explanation cannot solely account for the observed isomer distribution as the relative amounts of regioisomers is clearly dependent on metal(II) chelation.

Electronic factors appear to play an important role in regioisomer distribution. A relevant indicator is the extent to which the three sites of attachment participate in the highest-occupied molecular orbital (HOMO) of the reactant porphyrins. While typically the porphyrin HOMO is only slightly delocalised onto the reactive β carbons,[22] such delocalisation may indeed play a critical role in the reaction mechanism, say by facilitating attack on the starting material or a reaction intermediary. To access this effect, calculations of the spin densities of the cation radicals of the zinc(II) and palladium(II) starting materials were performed, and the relative participations at the 7-, 8- and 12- positions of the reactant porphyrins are compared to the experimental product distribution shown in Table 1. The palladium(II) quinoxalinoporphyrin **15** is observed to differentiate least between products (with ratios of 42 : 23 : 35 for the 7-, 8- and 12-products, respectively, a result which is directly paralleled by the spin densities (45 : 23 : 34, respectively). Similarly, the zinc(II) porphyrin-dione reactant **3** produces the greatest differentiation for the compared compounds (with observed ratios of 70 : 10 : 20), as is also predicted based upon the calculated spin densities (ratios of 52 : 14 : 34). These results imply the participation of the porphyrin HOMO orbital in the highest-energy transition state involved in the nitration mechanism. These results are consistent with a mechanism involving porphyrin π-cation radical intermediate.[9,14]

Conclusions

Metallated nitro-porphyrin-diones **6–8** were prepared by the treatment of the corresponding metalloporphyrin-diones **3–5** with nitrogen dioxide and in each case a mixture of regioisomers was produced with the relative abundance being 7-nitro- > 12-nitro- > 8-nitro-porphyrin-dione. Separation of these isomers exploited various demetalation-remetalation strategies. Most effective was that of zinc(II) chelation where it was shown that the rate of zinc(II) metalation was much slower for the 12-nitro isomer, thereby affording the facile separation of valuable difunctionalised building blocks.

In a similar fashion nitro-quinoxalinoporphyrins **10–12** were prepared by nitration with the same trend in relative abundance observed. Authentic samples of nitro-quinoxalinoporphyrin regioisomers were also prepared by condensation of respective nitro-porphyrin-diones with 1,2-benzenediamine **9**. These products assisted in determining regioisomer abundance whilst demonstrating the ability of these compounds to be further functionalised.

The relative abundance of nitro-porphyrin-2,3-diones and nitro-quinoxalinoporphyrins isomers was investigated by means of NOE experiments. It was found that the regioselectivity of the nitration was determined by steric factors at the 7 β-pyrrolic position but that electronic factors are also playing a role at other β-pyrrolic positions. These abundances were found to correlate with the small amount of the porphyrin HOMO orbital that is delocalized onto the reactive site of the porphyrin, implying the participation of this orbital in the highest-energy transition state accessed by the nitration process.

As well as the transformations arising from initial reduction of the nitro group shown in Scheme 1, methodologies have been developed previously for a range of nucleophilic *ipso*- and *cine*-substitution reactions on metallo-2-nitroporphyrins leading to introduction of many other functional groups in addition to or by displacement the nitro group.[1,33–39] The compounds prepared in this work thus offer access to a considerable range of compounds with modulated properties. In addition, nitro-porphyrin-2,3-diones are of interest in their own right for determining the degree of synergy between the groups as a function of the position of substitution. The dione unit of porphyrin-2,3-diones has been found to exhibit independent redox character to the macrocycle,[32] and strongly influences the position of inner periphery tautomerisation in free-base porphyrins.[32,40] The nitro group should work in concert with the dione when the groups are on opposite rings but compete against it when they are on adjacent rings on the porphyrin periphery. Studies of these properties are underway.

The nitro-porphyrin-2,3-diones prepared in this work have proved to be very valuable building blocks for the synthesis of asymmetric extended arrays of porphyrins and of compounds with in-built electronic bias for use as molecular rectifiers. The

nitro-quinoxalinoporphyrins have been very useful in exploration of synthetic routes to extended porphyrin systems in which two, three and four pyrrolic rings have been annulated. These studies will be reported soon.

Experimental

General procedures

Melting points were recorded on a Reichert melting point stage and are uncorrected. Microanalyses were performed at the Micro-analytical Unit, The University of New South Wales. Infra-red spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer in the stated solvents. Ultraviolet-visible spectra were routinely recorded on a Hitachi 150-20 spectrophotometer in chloroform that was deacidified by filtration through an alumina column. ^{1}H NMR spectra were recorded on either a Bruker AC-200 (200 MHz), a Bruker DPX-400 (400 MHz), or a Bruker AMX600 (600 MHz) spectrometer as stated. Deuteriochloroform was used as the solvent with tetramethylsilane (TMS) as an internal standard. Signals are recorded in terms of chemical shift (in ppm), multiplicity, coupling constants (in Hz) and assignment, in that order. The following abbreviations for multiplicity are used: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; tt, triplet of triplets; m, multiplet; br, broad; ABq, AB quartet. Matrix assisted laser desorption ionisation time of flight (MALDI-TOF) mass spectra were recorded on a VG TofSpec spectrometer. Mass spectra were 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. Column chromatography was routinely carried out using the gravity feed column technique on Merck silica gel Type 9385 (230–400 mesh). Analytical thin layer chromatography (TLC) analyses were performed on Merck silica gel 60 F_{254} precoated sheets (0.2 mm). All solvents used were routinely distilled prior to use, unless otherwise stated. Light petroleum refers to the fraction of bp 60–80 °C. Ether refers to diethyl ether and was distilled over crushed calcium chloride and stored over sodium wire. Ethanol-free chloroform was obtained by distillation from calcium chloride and passage through alumina. Merck AR grade methanol was used. Where solvent mixtures were used, the proportions are given by volume.

Syntheses

Nitration of [2,3-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) 3. A solution of [2,3-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **3** (2.73 g, 2.36 mmol) in dichloromethane (160 cm^3) was treated with an aliquot of nitrogen dioxide in light petroleum (0.1 mol dm^{-3}; 0.04 equiv.) every 5 min until TLC analysis showed that none of the starting material remained. The crude product was purified by chromatography over silica (dichloromethane–light petroleum; 3 : 2) and the major brown–green band collected and evaporated to dryness to give a mixture of zinc(II) nitro-porphyrin-2,3-diones **6a–c** (2.27 g, 80%) as an inseparable mixture which co-eluted and had a ^{1}H NMR spectrum which was a composite of authentic samples.

[2,3-Dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) 6a and 2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorin 16c. A mixture of [7-, 8- and 12-nitro-2,3-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6a–c** (1.07 g, 0.891 mmol) was dissolved in ether (60 cm^3) and shaken with aqueous hydrochloric acid (7 mol dm^{-3}; 60 cm^3) for 5 min. The organic phase was washed with water (60 cm^3), aqueous sodium carbonate (5%; 60 cm^3) and brine (60 cm^3), dried over anhydrous sodium sulfate, and filtered. The filtrate was evaporated to dryness and the residue dissolved in dichloromethane (60 cm^3). Zinc(II) acetate dihydrate (155 mg, 0.707 mmol) and methanol (6 cm^3) were added and the mixture stirred in the dark for 30 min and evaporated to dryness without heating. The residue was purified by dry-column flash chromatography over silica (dichloromethane–light petroleum, 1 : 2 changing to dichloromethane–light petroleum, 2 : 1 after the major brown band had been collected).

The major brown band was collected and evaporated to dryness to give 2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorin **16c** (277 mg, 27%) as a purple amorphous powder, mp >300 °C (Found: C, 80.0; H, 8.3; N, 5.9. $C_{76}H_{91}N_5O_4$ requires C, 80.2; H, 8.1; N, 6.15%); ν_{max}(CHCl$_3$)/cm^{-1} 3372 (NH), 2965, 2904, 2868, 1736, 1728 (CO), 1592, 1523 (NO$_2$), 1509, 1477, 1462, 1426, 1394, 1364, 1348 (NO$_2$), 1293, 1265, 1248, 1085, 1071, 1029, 1009, 923, 908, 884 and 854; λ_{max}(CHCl$_3$)/nm 265 (log ε 4.15), 374 (4.61), 421 (5.10), 483 (4.46), 529 sh (4.14) and 625 (3.83); δ_H(400 MHz; CDCl$_3$) −1.80 (1 H, br s, inner NH), −1.77 (1 H, br s, inner NH), 1.46–1.48 (36 H, m, *tert*-butyl H), 1.50 (18 H, s, *tert*-butyl H), 1.51 (18 H, s, *tert*-butyl H), 7.69–7.72 (4 H, m, aryl H$_o$), 7.75–7.77 (3 H, m, aryl H$_p$), 7.82 (1 H, t, *J* 1.8, aryl H$_p$), 7.96 (2 H, d, *J* 1.8, aryl H$_o$), 7.99 (2 H, d, *J* 1.8, aryl H$_o$), 8.58 (2 H, dd, ^3J 4.9 and ^4J 1.7, β-pyrrolic H), 8.77 (1 H, dd, ^3J 5.0 and ^4J 1.8, β-pyrrolic H) and 8.85–8.87 (2 H, m, 13-H and β-pyrrolic H); *m*/*z* (MALDI-TOF) 1139 (M + H requires 1139).

The major green band was collected and evaporated to dryness to give [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6a** (751 mg, 70%) as a green amorphous powder, mp >300 °C (Found: C, 74.5; H, 7.2; N, 5.3. $C_{76}H_{89}N_5O_4Zn$ + 0.25 CH_2Cl_2 requires C, 74.9; H, 7.4; N, 5.7%); ν_{max}(CHCl$_3$)/cm^{-1} 2965, 2905, 2868, 1727 (CO), 1592, 1523 (NO$_2$), 1498, 1477, 1465, 1427, 1394, 1364, 1332 (NO$_2$), 1291, 1248, 1176, 1115, 1069, 1014, 999, 936, 916, 900, 882, 854, 828 and 802; λ_{max}(CHCl$_3$)/nm 314 sh (log ε 4.24), 418 (5.05), 484 (4.32) and 652br (3.98); δ_H(400 MHz; CDCl$_3$) 1.44 (18 H, s, *tert*-butyl H), 1.45 (18 H, s, *tert*-butyl H), 1.48 (36 H, s, *tert*-butyl H), 7.59–7.61 (4 H, m, aryl H$_o$), 7.66 (1 H, t, *J* 1.8, aryl H$_p$), 7.70 (1 H, t, *J* 1.8, aryl H$_p$), 7.75 (1 H, t, *J* 1.8, aryl H$_p$), 7.76 (1 H, t, *J* 1.8, aryl H$_p$), 7.86 (2 H, d, *J* 1.8, aryl H$_o$), 7.87 (2 H, d, *J* 1.8, aryl H$_o$), 8.31 (1 H, d, *J* 4.8, β-pyrrolic H), 8.47 and 8.48 (2 H, ABq, *J* 4.7, β-pyrrolic H), 8.56 (1 H, d, *J* 4.8, β-pyrrolic H) and 8.76 (1 H, s, 8-H); *m*/*z* (CI) 1202 (M + H + 2, 100%) and 1200 (M + H, 31).

Trace quantities of [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6b** were obtained in mixture with **6a** in latter fractions obtained from the second band. This mixture was inseparable by column

chromatography and ^{1}H NMR analysis indicated that it accounted for less than 5% of nitrated products.

[2,3-Dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) 6c. 2,3-Dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorin **16c** (219 mg, 0.192 mmol) and excess zinc(II) acetate dihydrate (135 mg, 0.613 mmol) was dissolved in dichloromethane–methanol (10 : 1; 20 cm^3) and the mixture heated at reflux for 8 h (or stirred at 25 °C for 68 h). The crude product was purified by flash chromatography over silica (dichloromethane–light petroleum, 1 : 1) and the major brown band collected and evaporated to dryness to give [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6c** (230 mg, 99%) as a purple amorphous powder, mp > 300 °C (Found: C, 73.95; H, 7.5; N, 5.3. $C_{76}H_{89}N_5O_4Zn$ + 0.5 CH_2Cl_2 requires C, 73.8; H, 7.3; N, 5.6%); $\nu_{max}(CHCl_3)$/cm^{-1} 2965, 2904, 2868, 1729 (CO), 1593, 1524 (NO_2), 1506, 1477, 1427, 1394, 1364, 1341 (NO_2), 1293, 1248, 1166, 1139, 1093, 1028, 1008, 936, 900, 880, 863 and 832; $\lambda_{max}(CHCl_3)$/nm 321 sh (log ε 4.31), 371 (4.50), 423 (4.96), 486 (4.43), 518 sh (4.25), 573 sh (3.74), 621 (3.75) and 645–860 br (3.70); δ_H(400 MHz; $CDCl_3$) 1.44 (36 H, s, *tert*-butyl H), 1.47 (18 H, s, *tert*-butyl H), 1.48 (18 H, s, *tert*-butyl H), 7.59 (4 H, d, *J* 1.6, aryl H_o), 7.69–7.71 (3 H, m, aryl H_p), 7.75 (1 H, t, *J* 1.6, aryl H_p), 7.84 (2 H, d, *J* 1.6, aryl H_o), 7.85 (2 H, d, *J* 1.6, aryl H_o), 8.25–8.28 (2 H, m, 7- and 18-H), 8.50 (1 H, d, *J* 4.7, 17-H), 8.59 (1 H, d, *J* 4.8, 8-H) and 8.70 (1 H, s, 13-H); *m*/*z* (CI) 1200 (M + H, 100%).

2,3-Dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorin 16a. [2,3-Dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6a** (303 mg, 0.252 mmol) was dissolved in ether (25 cm^3) and shaken with aqueous hydrochloric acid (7 mol dm^{-3}; 25 cm^3) for 5 min. The organic phase was separated and washed with water (25 cm^3), 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 green band was collected and evaporated to dryness to give 2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorin **16a** (286 mg, 99%) as a purple amorphous powder, mp > 300 °C (Found: C, 79.8; H, 8.25; N, 5.8. $C_{76}H_{91}N_5O_4$ requires C, 80.2; H, 8.1; N, 6.15%); $\nu_{max}(CHCl_3)$/cm^{-1} 3346 (NH), 2965, 2904, 2868, 1732 (CO), 1592, 1534 (NO_2), 1476, 1426, 1394, 1364, 1344 (NO_2), 1279, 1248, 1214, 1206, 1151, 1121, 1106, 1068, 999, 992, 983, 920, 900, 882 and 846; $\lambda_{max}(CHCl_3)$/nm 265 (log ε 4.15), 414 (5.09), 475sh (4.35), 615 (3.92) and 683 sh (3.78); δ_H(400 MHz; $CDCl_3$) −1.66 to −1.26 (2 H, br m, inner NH), 1.46 (18 H, s, *tert*-butyl H), 1.47 (18 H, s, *tert*-butyl H), 1.50 (18 H, s, *tert*-butyl H), 1.51 (18 H, s, *tert*-butyl H), 7.69–7.72 (5 H, m, aryl $H_{o,p}$), 7.76 (1 H, t, *J* 1.8, aryl H_p), 7.78 (1 H, t, *J* 1.8, aryl H_p), 7.81 (1 H, t, *J* 1.8, aryl H_p), 7.94 (2 H, d, *J* 1.8, aryl H_o), 7.95 (2 H, d, *J* 1.8, aryl H_o), 8.52 and 8.53 (2 H, ABq, *J* 4.7, β-pyrrolic H), 8.58 (1 H, d, *J* 5.0, β-pyrrolic H), 8.74 (1 H, d, *J* 5.0, β-pyrrolic H) and 8.88 (1 H, s, 8-H); *m*/*z* (CI) 1138 (M + H, 100%).

[2,3-Dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]copper(II) 7a and [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]copper(II) 7c

Method 1. A solution of [2,3-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]copper(II) **4** (202 mg, 0.175 mmol) in dichloromethane (12 cm^3) was treated with an aliquot of nitrogen dioxide in light petroleum (0.1 mol dm^{-3}; 0.04 equiv.) every 5 min until TLC analysis showed that none of the starting material remained. The endpoint of the nitration was determined by shaking an aliquot of the reaction mixture with 1,2-benzenediamine **9** and examining the derivatives for the presence of copper(II) quinoxalinoporphyrin **14** by TLC analysis. The crude product was purified by chromatography over silica (dichloromethane–light petroleum, 1 : 3). The major brown band was collected and evaporated to dryness to give [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]copper(II) **7c** (58 mg, 28%) as a brown amorphous powder, mp > 300 °C (from dichloromethane–acetonitrile) (Found: C, 75.8; H, 7.3; N, 5.6. $C_{76}H_{89}CuN_5O_4$ requires C, 76.1; H, 7.5; N, 5.8%); $\nu_{max}(CHCl_3)$/cm^{-1} 2965, 2905, 2869, 1726 (CO), 1593, 1528 (NO_2), 1509, 1477, 1427, 1394, 1364, 1344, 1295, 1265, 1248, 1168, 1099, 1072, 1052, 1032, 1010, 936, 900, 880, 865 and 832; $\lambda_{max}(CHCl_3)$/nm 370sh (log ε 4.50), 419 (4.95), 486 (4.37), 510 (4.26), 659sh (3.71) and 710 (3.76); *m*/*z* (MALDI-TOF) 1200 (M + H requires 1200).

The major green band was collected and evaporated to dryness to give [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]copper(II) **7a** (89 mg, 42%) as a green amorphous powder, mp > 300 °C (from dichloromethane–acetonitrile) (Found: C, 75.7; H, 7.4; N, 5.5. $C_{76}H_{89}CuN_5O_4$ requires C, 76.1; H, 7.5; N, 5.8%); $\nu_{max}(CHCl_3)$/cm^{-1} 2965, 2905, 2868, 1727 (CO), 1593, 1527 (NO_2), 1477, 1427, 1394, 1364, 1334, 1294, 1248, 1178, 1119, 1074, 1015, 1002, 936, 916, 900, 856 and 828; $\lambda_{max}(CHCl_3)$/nm 418 (log ε 4.98), 477sh (4.29), 653 (3.91) and 707 (3.92); *m*/*z* (MALDI-TOF) 1201 (M + H requires 1200).

Method 2. A mixture of [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6a**, [2,3-dioxo-8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6b** and [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6c** (2.2 : 1) (1.03 g, 0.86 mmol) was dissolved in ether (60 cm^3) and shaken with hydrochloric acid (7 mol dm^{-3}, 60 cm^3) for 5 min. The organic phase was separated and washed with water (60 cm^3), aqueous sodium carbonate (5%; 60 cm^3) and brine (60 cm^3), dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated to dryness and the residue dissolved in a dichloromethane–methanol mixture (10 : 1; 60 cm^3). Copper(II) acetate monohydrate (526 mg, 2.64 mmol) was added and the mixture heated at reflux for 90 min. The crude product was purified by chromatography over silica (column diameter: 40 mm, packing height: 350 mm, maximum loading: 500 mg, dichloromethane–light petroleum, 1 : 3).

The major brown band was collected and evaporated to dryness to give [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]copper(II) **7c** (281 mg, 27%) as a brown amorphous powder. The major green band was

collected and evaporated to dryness to give [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]copper(II) **7a** (600 mg, 58%) as a green amorphous powder. The 8-nitro isomer **7b** was not detected.

[2,3-Dioxo-7-, 8- and 12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) 8a–c

Method 1. A solution of [2,3-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) **5** (1.01 g, 0.846 mmol) in dichloromethane (55 cm^3) was treated with an aliquot of nitrogen dioxide in light petroleum (0.1 mol dm^{-3}; 0.04 equiv.) every 5 min until TLC analysis showed that none of the starting material remained. The endpoint of the nitration was determined by shaking an aliquot of the reaction mixture with 1,2-benzenediamine **9** and examining the derivatives for the presence of palladium(II) quinoxalinoporphyrin by TLC analysis. The crude product was purified by chromatography over silica (dichloromethane–light petroleum, 1 : 3).

The first major green band was collected and evaporated to dryness to give a mixture of [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) **8c** and [2,3-dioxo-8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) **8b** (3 : 1) (453 mg, 43%) as a green amorphous powder, mp >300 °C (from dichloromethane–methanol) (Found: C, 73.2; H, 7.35; N, 5.4. $C_{76}H_{89}N_5O_4Pd$ requires C, 73.4; H, 7.2; N, 5.6%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2965, 2905, 2869, 1727 (CO), 1593, 1529 (NO_2), 1514, 1477, 1427, 1394, 1364, 1347, 1299, 1276, 1248, 1168, 1104, 1077, 1060, 1038, 1018, 972, 952, 940, 900, 880, 868 and 834; $\lambda_{max}(CHCl_3)$/nm 271 ($\log\varepsilon$ 4.38), 363 (4.43), 413 (5.00), 478 (4.39), 507 (4.24), 639sh (3.78) and 674 (3.80); δ_H(600 MHz; $CDCl_3$) Palladium(II) 12-nitro-porphyrin-2,3-dione **8c**: 1.436 (18 H, s, *tert*-butyl H), 1.440 (18 H, s, *tert*-butyl H), 1.46 (18 H, s, *tert*-butyl H), 1.48 (18 H, s, *tert*-butyl H), 7.55–7.57 (4 H, m, aryl H_o), 7.69–7.71 (3 H, m, aryl H_p), 7.77 (1 H, t, *J* 1.8, aryl H_p), 7.80 (2 H, d, *J* 1.8, aryl H_o), 7.82 (2 H, d, *J* 1.7, aryl H_o), 8.17 (1 H, d, *J* 5.0, β-pyrrolic H), 8.20 (1 H, d, *J* 5.0, β-pyrrolic H), 8.39 (1 H, d, *J* 5.0, β-pyrrolic H), 8.51 (1 H, d, *J* 5.0, β-pyrrolic H) and 8.73 (1 H, s, β-pyrrolic H). Palladium(II) 8-nitroporphyrin-2,3-dione **8b**: 1.44 (18 H, s, *tert*-butyl H), 1.45 (18 H, s, *tert*-butyl H), 1.47 (18 H, s, *tert*-butyl H), 1.48 (18 H, s, *tert*-butyl H), 7.56 (2 H, d, *J* 1.8, aryl H_o), 7.57 (2 H, d, *J* 1.7, aryl H_o), 7.71-7.73 (3 H, m, aryl H_p), 7.76 (1 H, t, *J* 1.8, aryl H_p), 7.82 (2 H, d, *J* 1.8, aryl H_o), 7.84 (2 H, d, *J* 1.8, aryl H_o), 8.26 (1 H, d, *J* 5.0, β-pyrrolic H), 8.47–8.50 (2 H, m, β-pyrrolic H), 8.51 (1 H, s, β-pyrrolic H) and 8.56 (1 H, d, *J* 5.0, β-pyrrolic H); *m*/*z* (MALDI-TOF) 1241 (M + H requires 1243).

The second major green band was collected and evaporated to dryness to give [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) **8a** (512 mg, 49%) as a green amorphous powder, mp >300 °C (from dichloromethane–methanol) (Found: C, 73.3; H, 7.45; N, 5.4. $C_{76}H_{89}N_5O_4Pd$ requires C, 73.4; H, 7.2; N, 5.6%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2965, 2904, 2869, 1729 (CO), 1593, 1530 (NO_2), 1477, 1447, 1427, 1394, 1364, 1350, 1337, 1320, 1299, 1274, 1248, 1182, 1140, 1124, 1078, 1012, 940, 918, 900, 882, 860 and 828; $\lambda_{max}(CHCl_3)$/nm 269 ($\log\varepsilon$ 4.39), 410 (5.02), 475 (4.28), 512sh (3.77), 625 (3.94) and 669 (3.92); δ_H(400 MHz; $CDCl_3$) 1.43 (18 H, s, *tert*-butyl H), 1.44 (18 H, s, *tert*-butyl H), 1.47 (18 H, s, *tert*-butyl H), 1.48 (18 H, s, *tert*-butyl H), 7.56-7.58 (4 H, m, aryl H_o), 7.66 (1 H, t, *J* 1.7, aryl H_p), 7.70 (1 H, t, *J* 1.8, aryl H_p), 7.75 (1 H, t, *J* 1.7, aryl H_p), 7.77 (1 H, t, *J* 1.7, aryl H_p), 7.82–7.84 (4 H, m, aryl H_o), 8.25 (1 H, d, *J* 5.0, β-pyrrolic H), 8.45–8.48 (3 H, m, β-pyrrolic H) and 8.68 (1 H, s, β-pyrrolic H); *m*/*z* (MALDI-TOF) 1242 (M + H requires 1243).

Method 2. A mixture of [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6a**, [2,3-dioxo-8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]-zinc(II) **6b** and [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6c** (36.0 mg, 0.030 mmol) was dissolved in dichloromethane (30 cm^3) and shaken with hydrochloric acid (7 mol dm^{-3}, 30 cm^3) for 2 min. The organic layer was washed with water (100 cm^3), sodium carbonate solution (10%, 2 × 100 cm^3), water (2 × 100 cm^3), dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated to dryness and the residue dissolved in a toluene–glacial acetic acid mixture (1 : 1; 24 cm^3). Palladium(II) chloride (43.0 mg, 0.243 mmol) and sodium acetate (62.0 mg, 0.756 mmol) were added and the mixture was heated at reflux for 5 min. Dichloromethane (40 cm^3) was added and the organic phase separated, washed with water (100 cm^3), sodium carbonate solution (10%, 2 × 100 cm^3), water (2 × 100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The crude mixture was purified by chromatography over silica (dichloromethane–light petroleum, 1 : 3). The first running green band was collected and the solvent was removed to give [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) **8c** (major) and [2,3-dioxo-8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) **8b** (20 : 1) (12.2 mg, 33%) as a green microcrystalline solid. The second major green band was collected and the solvent removed to afford [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) **8a** (19.5 mg, 52%) as a green microcrystalline solid.

[7-, 8- and 12-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]zinc(II) 10a–c

Method 1. A solution of [5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]zinc(II) **13** (201 mg, 0.163 mmol) in dichloromethane (10 cm^3) was treated with an aliquot of nitrogen dioxide in light petroleum (0.1 mol dm^{-3}; 0.04 equiv.) every 5 min until TLC analysis showed that none of the starting material remained. The crude product was purified by chromatography over silica (dichloromethane–light petroleum, 2 : 5). The first major band was collected and evaporated to dryness to give a mixture of [7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-porphyrinato]zinc(II) **10a** and [8-nitro-5,10,15,20-tetrakis-(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]zinc(II) **10b** (17 : 5) (83 mg, 40%) as a purple amorphous powder. The second major band was collected and evaporated to dryness to give [12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-quinoxalino[2,3-*b*]porphyrinato]zinc(II) **10c** (27 mg, 13%) as a purple amorphous powder.

Method 2. A mixture of [7-, 8- and 12-nitro-2,3-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]zinc(II) **6a–c** (628 mg, 0.523 mmol) and 1,2-benzenediamine **9** (243 mg, 2.24 mmol) was dissolved in dichloromethane (9 cm^3) and stirred in the dark for 2 h. The mixture was evaporated to dryness and the residue purified by chromatography over silica (dichloromethane–light petroleum, 1 : 2). The first major band gave 7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino-[2,3-*b*]porphyrinato]zinc(II) **10a** (436 mg, 65%) as a purple amorphous powder, mp >300 °C (from dichloromethane–methanol) (Found: C, 77.1; H, 7.5; N, 7.5. $C_{82}H_{93}N_7O_2Zn$ requires C, 77.3; H, 7.4; N, 7.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2965, 2904, 2868, 1593, 1522 (NO_2), 1476, 1425, 1393, 1363, 1334, 1297, 1282, 1248, 1185, 1165, 1120, 1106, 1072, 1002, 943, 908 and 856; $\lambda_{max}(CHCl_3)$/nm 339 (log ε 4.40), 449 (5.12), 541 (3.81), 576 (4.02), 623 (4.26) and 780 (3.07); δ_H(400 MHz; $CDCl_3$) 1.47 (18 H, s, *tert*-butyl H), 1.48 (18 H, s, *tert*-butyl H), 1.52 (18 H, s, *tert*-butyl H), 1.53 (18 H, s, *tert*-butyl H), 7.77–7.87 (6 H, m, quinoxalino H and aryl H_p), 7.90 (1 H, t, *J* 1.4, aryl H_p), 7.92–7.95 (5 H, m, aryl $H_{o,p}$), 8.02 (2 H, d, *J* 1.6, aryl H_o), 8.05 (2 H, d, *J* 1.9, aryl H_o), 8.83 and 8.85 (2 H, ABq, *J* 4.7, β-pyrrolic H), 8.95 and 9.00 (2 H, AX, *J* 4.7, β-pyrrolic H) and 9.13 (1 H, s, β-pyrrolic H); *m*/*z* (CI) 1272 (M + H, 100%). The sample also contained approximately 13% of [8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]zinc(II) **10b**. δ_H(400 MHz; $CDCl_3$, β-pyrrolic region) 8.82–8.87 (multiplicity unknown), 8.92 and 9.01 (AX, *J* 4.7) and 9.27 (s).

The second major band gave [12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]zinc(II) **10c** (156 mg, 23%) as a purple amorphous powder, mp >300 °C (from dichloromethane–methanol) (Found: C, 76.95; H, 7.4; N, 7.3. $C_{82}H_{93}N_7O_2Zn$ requires C, 77.3; H, 7.4; N, 7.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2965, 2904, 2888, 1728, 1649, 1593, 1525, 1502, 1477, 1424, 1364, 1314, 1248, 1176, 1110, 1068, 1015, 944, 900, 863 and 830; $\lambda_{max}(CHCl_3)$/nm 338 (log ε 4.46), 455 (5.01), 540 (3.84), 581 (4.26), 614 (4.01) and 650 (2.99); δ_H(400 MHz; $CDCl_3$) 1.48 (36 H, s, *tert*-butyl H), 1.51 (18 H, s, *tert*-butyl H), 1.52 (18 H, s, *tert*-butyl H), 7.76 (1 H, t, *J* 1.6, aryl H_p), 7.78–7.82 (3 H, m, quinoxalino H and aryl H_p), 7.85–7.90 (2 H, m, quinoxalino H), 7.91-7.93 (6 H, m, aryl $H_{o,p}$), 8.01 (2 H, d, *J* 1.6, aryl H_o), 8.02 (2 H, d, *J* 2.1, aryl H_o), 8.89 and 8.96 (2 H, AX, *J* 4.7, β-pyrrolic H), 8.96 and 8.98 (2 H, ABq, *J* 4.7, β-pyrrolic H) and 9.08 (1 H, s, β-pyrrolic H); *m*/*z* (CI) 1272 (M + H, 100%).

[7-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]copper(II) 11a

Method 1. 7-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin **17a** (61.6 mg, 0.051 mmol) and copper(II) acetate monohydrate (32.1 mg, 0.161 mmol) were dissolved in a dichloromethane–methanol solution (10 : 1; 4 cm^3) and the mixture heated at reflux for 60 min. The solvent was evaporated to dryness and the residue purified by chromatography over silica (dichloromethane–light petroleum, 1 : 2). The major green band collected and evaporated to dryness to give [7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]copper(II) **11a** (59 mg, 91%) as a purple amorphous powder, mp >300 °C (from dichloromethane–methanol) (Found: C, 77.1; H, 7.6; N, 7.4. $C_{82}H_{93}CuN_7O_2$ requires C, 77.4; H, 7.4; N, 7.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2965, 2904, 2868, 1593, 1526 (NO_2), 1495, 1476, 1426, 1393, 1363, 1338 (NO_2), 1294, 1288, 1248, 1168, 1124, 1110, 1076, 1006, 943, 922, 900, 883, 858, 823, 806 and 795; $\lambda_{max}(CHCl_3)$/nm 287 (log ε 4.40), 336 (4.50), 444 (5.24), 529 (3.90), 565 (4.07) and 612 (4.35); *m*/*z* (MALDI-TOF) 1273 (M + H requires 1273).

Method 2. A solution of [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]copper(II) **7a** (102 mg, 0.085 mmol) and 1,2-benzenediamine **9** (18.5 mg, 0.171 mmol) in dichloromethane (6 cm^3) was stirred at room temperature for 30 min. The mixture was evaporated to dryness and the residue purified by chromatography over silica (dichloromethane–light petroleum, 1 : 3). The major green band was collected and evaporated to dryness to give [7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-b]porphyrinato]copper(II) **11a** (102 mg, 95%) as a purple amorphous powder.

[12-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]copper(II) 11c

Method 1. 12-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin **17c** (61.0 mg, 0.050 mmol) and copper(II) acetate monohydrate (32.2 mg, 0.161 mmol) were dissolved in a dichloromethane–methanol solution (10 : 1, 4 cm^3) and the mixture heated at reflux for 60 min. The solvent was evaporated to dryness and the residue purified by chromatography over silica (dichloromethane–light petroleum, 1 : 2). The major brown band collected and evaporated to dryness to give [12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]copper(II) **11c** (60 mg, 94%) as a purple amorphous powder, mp >300 °C (from dichloromethane–methanol) (Found: C, 77.2; H, 7.6; N, 7.4. $C_{82}H_{93}CuN_7O_2$ requires C, 77.4; H, 7.4; N, 7.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2964, 2904, 2869, 1593, 1514 (NO_2), 1477, 1427, 1393, 1364, 1345, 1298, 1248, 1230, 1182, 1166, 1113, 1072, 1043, 1012, 945, 899, 881 and 866; $\lambda_{max}(CHCl_3)$/nm 306 (log ε 4.36), 340 (4.46), 420sh (4.77), 462 (5.06), 526 (3.86), 565 (4.26) and 598sh (3.91); *m*/*z* (MALDI-TOF) 1273 (M + H requires 1273).

Method 2. A solution of [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]copper(II) **7c** (103 mg, 0.085 mmol) and 1,2-benzenediamine **9** (20.4 mg, 0.189 mmol) in dichloromethane (6 cm^3) was stirred at room temperature for 30 min. The mixture was evaporated to dryness and the residue purified by chromatography over silica (dichloromethane–light petroleum, 1 : 2). The major brown band was collected and evaporated to dryness to give [12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-b]porphyrinato]copper(II) **11c** (107 mg, 98%) as a purple amorphous powder.

Nitration of [5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]copper(II) 14. A solution of [5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-b]porphyrinato]copper(II) **14** (352 mg, 0.287 mmol) in dichloromethane (20 cm^3) was treated with an aliquot of nitrogen

dioxide in light petroleum (0.1 mol dm^{-3}; 0.04 equiv.) every 5 min until TLC analysis showed that none of the starting material remained. The crude product was purified by chromatography over silica (dichloromethane–light petroleum, 1 : 4). The major band was collected and evaporated to dryness to give a mixture of copper(II) nitro-quinoxalino[2,3-*b*]porphyrin regioisomers **11a–c** (334 mg, 92%). $\nu_{max}(CHCl_3)/cm^{-1}$ 1526 (NO_2) and 1344 (NO_2); *m*/*z* (MALDI-TOF) 1272 (M + H requires 1273).

7-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin 17a

Method 1. [7-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]zinc(II) **10a** (496 mg, 0.390 mmol) was dissolved in ether (25 cm^3) and shaken with aqueous hydrochloric acid (7 mol dm^{-3}; 25 cm^3) for 10 min. The organic phase was separated and shaken with aqueous 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 dry-flash chromatography over silica (dichloromethane–light petroleum, 1 : 2). The major brown band was collected and evaporated to dryness to give 7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin **17a** (454 mg, 96%) as a purple amorphous powder, mp >300 °C (from dichloromethane-methanol) (Found: C, 81.7; H, 7.8; N, 7.85. $C_{82}H_{95}N_7O_2$ requires C, 81.35; H, 7.9; N, 8.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3336 (NH), 2965, 2868, 1593, 1532 (NO_2), 1476, 1427, 1394, 1363, 1346 (NO_2), 1281, 1248, 1166, 1120, 1105, 999, 909, 883 and 851; $\lambda_{max}(CHCl_3)/nm$ 296 (log ε 4.33), 359 (4.49), 441 (5.24), 533 (4.12), 571 (4.06), 605 (4.02), 662 (3.37) and 752 (3.12); δ_H(400 MHz; $CDCl_3$) −2.00 (2 H, br s, inner NH), 1.47 (18 H, s, *tert*-butyl H), 1.48 (18 H, s, *tert*-butyl H), 1.53 (36 H, s, *tert*-butyl H), 7.70–7.79 (4 H, m, quinoxalino H), 7.80 (1 H, t, *J* 1.8, aryl H_p), 7.83 (1 H, t, *J* 1.8, aryl H_p), 7.89 (1 H, t, *J* 1.8, aryl H_p), 7.93 (1 H, t, *J* 1.8, aryl H_p), 7.95–7.98 (4 H, m, aryl H_o), 8.03–8.06 (4 H, m, aryl H_o), 8.67 and 8.69 (2 H, ABq, β-pyrrolic H), 8.92 (1 H, d, *J* 5.0, β-pyrrolic H), 9.01 (1 H, d, *J* 5.0, β-pyrrolic H) and 9.07 (1 H, s, 8-H); *m*/*z* (MALDI-TOF) 1210 (M + H requires 1211). The sample also contained approximately 11% of 8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin **17b**. δ_H(400 MHz; $CDCl_3$, β-pyrrolic H region) 8.75 (d, *J* 4.7) and 9.24 (s).

Method 2. [7-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]copper(II) **11a** (60.6 mg, 0.048 mmol) was moistened with trifluoroacetic acid (1.5 cm^3). Concentrated sulfuric acid (18 mol dm^{-3}; 0.20 cm^3) was added and the mixture stirred for 15 min, then poured onto ice (10 g). Ether (10 cm^3) was added and the organic phase washed with water (3 × 10 cm^3). Water (10 cm^3) was added to the organic phase and sodium carbonate added to the two phase system with vigorous stirring until no more gas was produced. The organic phase was washed with water (10 cm^3), brine (10 cm^3), dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated to dryness and purified by chromatography over silica (dichloromethane–light petroleum, 1 : 2). The major brown band collected and evaporated to dryness to give 7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin **17a** (52 mg, 89%) as a purple amorphous powder.

12-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin 17c

Method 1. [12-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]zinc(II) **10a** (221 mg, 0.174 mmol) was dissolved in ether (30 cm^3) and shaken with aqueous hydrochloric acid (7 mol dm^{-3}; 30 cm^3) for 5 min. The organic phase was separated and shaken with aqueous 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 (dichloromethane–light petroleum, 1 : 2). The major brown band was collected and evaporated to dryness to give 12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-b]porphyrin **17c** (186 mg, 88%) as a purple amorphous powder, mp >300 °C (from dichloromethane-methanol) (Found: C, 81.0; H, 8.1; N, 7.9. $C_{82}H_{95}N_7O_2$ requires C, 81.35; H, 7.9; N, 8.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3520, 3412, 3363 (NH), 2964, 2905, 2866, 1681, 1593, 1556, 1507, 1477, 1427, 1394, 1363, 1348 (NO_2), 1294, 1247, 1168, 1135, 1097, 1032, 1097, 1032, 1011, 1000, 908, 883 and 855; $\lambda_{max}(CHCl_3)/nm$ 302 (log ε 4.35), 341 (4.48), 393sh (4.59), 453 (5.22), 542 (4.21), 604 (3.89) and 666 (3.64); δ_H(400 MHz; $CDCl_3$) −2.30 (2 H, br s, inner NH), 1.48–1.49 (36 H, m, *tert*-butyl H), 1.53–1.55 (36 H, m, *tert*-butyl H), 7.72–7.77 (2 H, m, quinoxalino H), 7.78 (1 H, t, *J* 1.8, aryl H_p), 7.79–7.84 (3 H, m, quinoxalino H and aryl H_p), 7.92–7.94 (2 H, m, aryl H_p), 7.94–7.96 (4 H, m, aryl H_o), 8.07 (2 H, d, *J* 1.8, aryl H_o), 8.10 (2 H, d, *J* 1.8, aryl H_o), 8.94 (1 H, dd, ^3J 5.0 and ^4J 1.6, β-pyrrolic H), 8.99–9.03 (3 H, m, β-pyrrolic H) and 9.05 (1 H, dd, ^3J 5.0 and ^4J 1.6, β-pyrrolic H); *m*/*z* (MALDI-TOF) 1211 (M + H requires 1211).

Method 2. [12-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]copper(II) **11c** (60.6 mg, 0.048 mmol) was demetallated using trifluoroacetic acid and concentrated sulfuric acid following the procedure described previously in this section to give 12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-porphyrin **17c** (54 mg, 93%).

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

Method 1. A solution of 7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin **17a** (221 mg, 0.182 mmol), sodium acetate (32.5 mg, 0.396 mmol) and palladium(II) chloride (128 mg, 0.721 mmol) in an acetic acid–chloroform mixture (2 : 1; 60 cm^3) was heated at reflux for 18 h. Ether (40 cm^3) was then added and the organic phase washed with water (4 × 40 cm^3), sodium carbonate solution (5%, 40 cm^3), brine (40 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was purified by dry-flash chromatography over silica (dichloromethane–light petroleum, 1 : 2) and the major red band collected and evaporated to dryness to give [7-nitro-

5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-b]porphyrinato]palladium(II) **12a** (235 mg, 98%) as a red amorphous powder, mp >300 °C (from dichloromethane–methanol) (Found: C, 75.2; H, 7.0; N, 7.15. $C_{82}H_{93}N_7O_2Pd$ requires C, 74.9; H, 7.1; N, 7.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2965, 2904, 2868, 1594, 1527 (NO_2), 1477, 1394, 1364, 1342 (NO_2), 1299, 1248, 1170, 1113, 1079, 1017, 948, 909 and 862; $\lambda_{max}(CHCl_3)/nm$ 346 (log ε 4.54), 407 sh (4.80), 442 (5.22), 514 (3.93), 547 (4.10) and 592 (4.44); δ_H(400 MHz; $CDCl_3$) 1.45 (18 H, s, *tert*-butyl H), 1.46 (18 H, s, *tert*-butyl H), 1.50–1.51 (36 H, m, *tert*-butyl H), 7.74–7.81 (6 H, m, quinoxalino H and aryl H_p), 7.87-7.90 (5 H, m, aryl $H_{o,p}$), 7.91 (1 H, t, *J* 1.8, aryl H_p), 7.97 (2 H, d, *J* 1.8, aryl H_o), 7.99 (2 H, d, *J* 1.8, aryl H_o), 8.74 and 8.76 (2 H, ABq, *J* 5.0, β-pyrrolic H), 8.80 (1 H, d, *J* 5.0, β-pyrrolic H), 8.88 (1 H, d, *J* 5.0, β-pyrrolic H) and 9.01 (1 H, s, 8-H); *m*/*z* (MALDI-TOF) 1314 (M + H requires 1315). The sample also contained approximately 9% of [8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino-[2,3-*b*]porphyrinato]palladium(II) **12b**. δ_H(400 MHz, $CDCl_3$, β-pyrrolic H region) 8.84 (d, *J* 5.0), 8.89 (d, *J* 5.1) and 9.18 (s).

Method 2. A solution of [2,3-dioxo-7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) **8a** (60.4 mg, 0.049 mmol) and 1,2-benzenediamine **9** (20.8 mg, 0.192 mmol) was stirred at room temperature for 30 min. The mixture was evaporated to dryness and the residue purified by chromatography over silica (dichloromethane–light petroleum, 1 : 2). The major red band was collected and evaporated to dryness to give [7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]palladium(II) **12a** (58 mg, 90%) as a red amorphous powder.

[12-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino [2,3-b]porphyrinato]palladium(II) 12c. A solution of 12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-b]porphyrin **17c** (130 mg, 0.107 mmol), sodium acetate (55.1 mg, 0.672 mmol) and palladium(II) chloride (53.4 mg, 0.301 mmol) in an acetic acid–chloroform mixture (2 : 1; 36 cm^3) was heated at reflux for 18 h. Ether (40 cm^3) was then added and the organic phase washed with water (4 × 40 cm^3), sodium carbonate solution (5%, 40 cm^3), brine (40 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was purified by chromatography over silica (dichloromethane–light petroleum, 1 : 2) and the major red band collected and evaporated to dryness to give [12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-b]porphyrinato]palladium(II) **12c** (132 mg, 94%) as a red amorphous powder, mp >300 °C (from dichloromethane–methanol) (Found: C, 74.8; H, 7.2; N, 7.2. $C_{82}H_{93}N_7O_2Pd$ requires C, 74.9; H, 7.1; N, 7.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2965, 2904, 2868, 1594, 1529 (NO_2), 1515, 1477, 1428, 1394, 1363, 1349 (NO_2), 1300, 1248, 1228, 1185, 1168, 1117, 1077, 1052, 1021, 958, 900 and 868; $\lambda_{max}(CHCl_3)/nm$ 302 (log ε 4.44), 346 (4.53), 411sh (4.73), 439sh (4.99), 457 (5.13), 509 (3.86), 547 (4.40) and 578 (4.01); δ_H(400 MHz; $CDCl_3$) 1.46–1.47 (36 H, m, *tert*-butyl H), 1.51 (18 H, s, *tert*-butyl H), 1.52 (18 H, s, *tert*-butyl H), 7.75 (1 H, t, *J* 1.8, aryl H_p), 7.76–7.84 (5 H, m, quinoxalino H and aryl H_p), 7.85–7.88 (4 H, m, aryl H_o), 7.90–7.92 (2 H, m, aryl H_p), 7.97–8.00 (4 H, m, aryl H_o), 8.73 (1 H, d, *J* 5.0, β-pyrrolic H), 8.83 (1 H, d, *J* 5.0, β-pyrrolic H), 8.84 (2 H, ABq, β-pyrrolic H) and 9.05 (1 H, s, 13-H); *m*/*z* (MALDI-TOF) 1314 (M + H requires 1315).

[8-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]palladium(II) 12b and [12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]palladium(II) 12c. A solution of a mixture of [2,3-dioxo-12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato] palladium(II) **8c** and [2,3-dioxo-8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorinato]palladium(II) **8b** (3 : 1) (61.4 mg, 0.049 mmol) and 1,2-benzenediamine **9** (10.8 mg, 0.100 mmol) was stirred at room temperature for 30 min. The mixture was evaporated to dryness and the residue purified by chromatography over silica (dichloromethane–light petroleum, 1 : 2). The major red band was collected and evaporated to dryness to give a mixture of [12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato] palladium(II) **12c** and [8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]palladium(II) **12b** (3 : 1) (63 mg, 97%) as a red amorphous powder which had a composite ^{1}H NMR spectrum of authentic samples.

Nitration of [5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]palladium(II) 15. A solution of [5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]-b]porphyrinato]palladium(II) **15** (202 mg, 0.159 mmol) in dichloromethane (15 cm^3) was treated with an aliquot of nitrogen dioxide in light petroleum (0.1 mol dm^{-3}; 0.04 equiv.) every 5 min until TLC analysis showed that none of the starting material remained. The crude product was purified by chromatography over silica (dichloromethane–light petroleum, 1 : 4) and the major red band collected and evaporated to dryness to give a mixture of [7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino-[2,3-*b*]porphyrinato]palladium(II) **12a**, [8-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*] porphyrinato]palladium(II) **12b** and [12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato] palladium(II) **12c** (169 mg, 82%). The ratio of the palladium(II) nitro-quinoxalino[2,3-*b*]porphyrin isomers, **12a** : **12b** : **12c**, was found to be 1.9 : 1 : 1.5 by integration of the resonances due to protons adjacent to the nitro group.

Spin-density calculation

The spin-density calculations wer performed using the Gaussian-03 package.[41] The B3LYP density-functional[42] was used in conjunction with the SDD[43] basis set for Zn and Pd as well as the 6-31G* basis set[44] for C, H, N, and O. All calculations were performed at optimized gas-phase geometries of the cations of molecules without aryl meso substituents.

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