Expansion of the porphyrin π-system: stepwise annelation of porphyrin β,β′-pyrrolic faces leading to trisquinoxalinoporphyrin†

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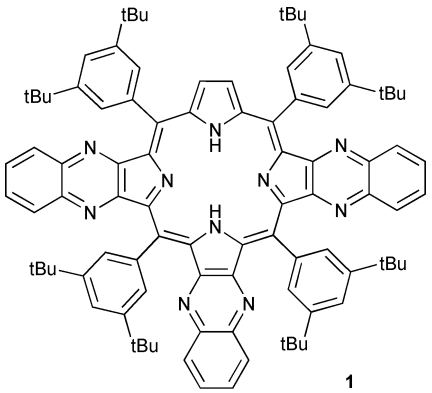
Lateral extension of the porphyrin π-electron system by ring annelation of β,β′-pyrrolic faces is reported. Three separate syntheses of trisquinoxalinoporphyrin **1**, differing in the sequence in which pyrrolic rings are elaborated, are reported. The most efficient pathway converts readily accessible zinc(II) corner bisquinoxalinoporphyrin **7** into **1** in five steps in 47% yield overall. Routes to **1** are also established from linear bisquinoxalinoporphyrin **8** and quinoxalinoporphyrin **10**. The ring annelation process involves a nitration, reduction, photooxidation sequence to establish α-dione functionality that is reacted with 1,2-diaminobenzene. The ^{1}H NMR spectrum of **1** reveals that it exists predominantly as a single *trans*-tautomer in which the two inner hydrogens reside on the nitrogens of the unsubstituted pyrrolic ring and its opposite quinoxalino-fused pyrrolic ring. Each of the synthetic routes established in this study could have use in elaboration of more complex oligoporphyrin arrays.

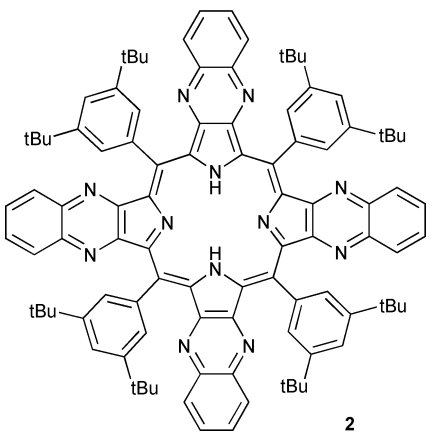
Introduction

Porphyrinoid macrocycles appear in many naturally occurring redox systems and they have many functional properties that make them attractive for use in emerging technologies. The redox and photoactive functions performed by porphyrins in nature establish the paradigm for molecular electronics and show that porphyrins may be useful components of rationally designed molecular electronic devices and new artificial light-harvesting systems.

Porphyrins are essentially planar macrocycles with extensive π-systems.[1] In addition, a porphyrin ring has a diameter of ~1 nm and so is well-suited as a building block for the construction of devices 5–10 nm in size, thought necessary in first generation 'molecular electronics'.[2] For new materials and molecular electronic circuit applications, it is desirable to have multiple-connector building blocks. The porphyrin periphery with its four pyrrolic rings arranged on a square matrix has a geometry that allows construction of molecular arrays based on a square grid motif. Up to four connections can be made through π-system annelation of each of the pyrrolic rings. Additionally, expansion of the π-system of the porphyrin offers a means to modulate the redox and photophysical properties of the macrocycle.[3–10] This is also the case with related phthalocyanines and porphyrazines.[6,11,12]

Recently, we presented an efficient synthetic protocol for stepwise elaboration of the pyrrolic faces of a porphyrin. This strategy was demonstrated by synthetic routes to trisquinoxalinoporphyrin **1** and tetrakisquinoxalinoporphyrin **2** starting from a porphyrin-2,3,7,8-tetraone.[4]





Herein we explore three other synthetic sequences to trisquinoxalinoporphyrin **1** by further elaboration of corner

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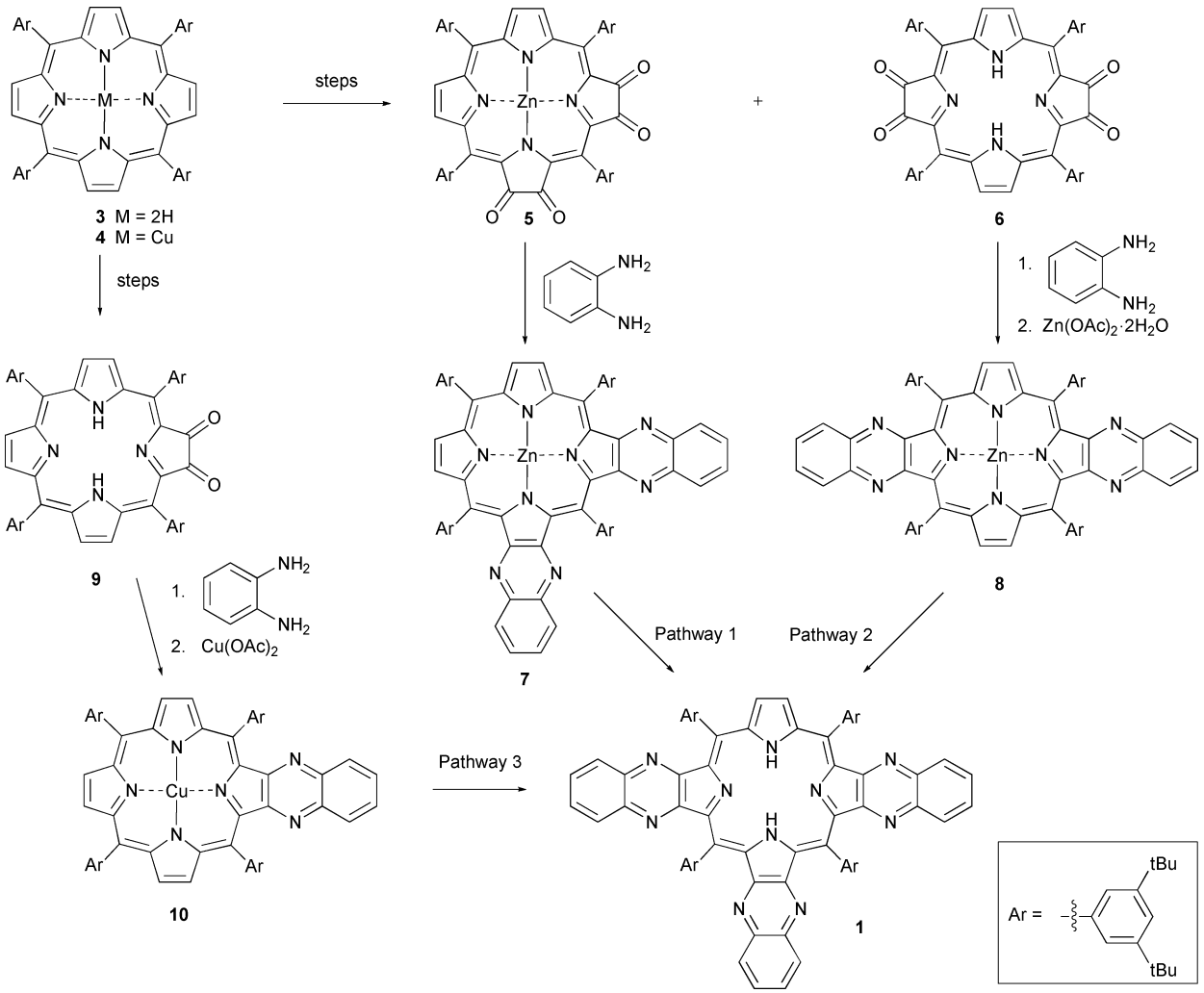
† Electronic supplementary information (ESI) available: Variable-temperature NMR spectra of trisquinoxalinoporphyrin **1**, NOESY spectra of 7,18-dinitroporphyrin **24a** and full details of infrared spectra of all new compounds are given. See DOI: 10.1039/b901338e



Scheme 1 Three pathways to the trisquinoxalinoporphyrin **1** and to more elaborated oligoporphyrin systems when the fused quinoxalino groups are replaced by tetraazaanthracene-bridged porphyrin units.

bisquinoxalinoporphyrin **7**, linear bisquinoxalinoporphyrin **8** and quinoxalinoporphyrin **10** (Scheme 1), compounds that have been prepared from the parent porphyrin **3** in earlier studies.[13,14] These compounds can also be regarded as model systems for terminal (compound **10**) and interior components (compounds **7** and **8**) of extended oligomeric porphyrins, where fused quinoxalines are replaced by tetraazaanthracene-bridged porphyrin units.

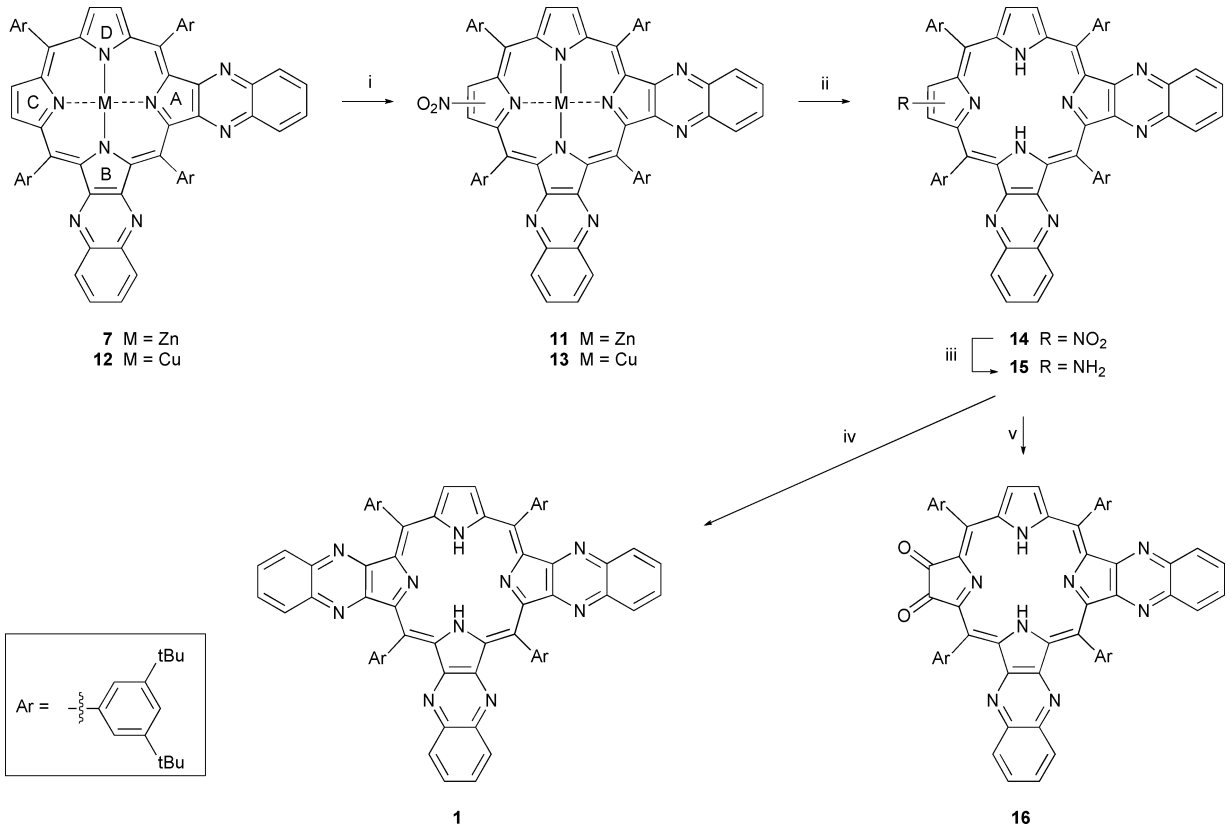
Results and discussion

The synthetic strategy undertaken in this work was to further functionalise metallated quinoxalinoporphyrin and bisquinoxalinoporphyrins that were obtained from 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin **3** *via* its copper(II) chelate **4** (Scheme 1).

The starting materials for the sequences were prepared by reported methods.[4,13–15] Thus dinitration of porphyrin **4** followed by demetallation and reduction to a mixture of diaminoporphyrins, photooxidation and partial metallation with zinc(II) afforded free-base porphyrin-2,3,12,13-tetraone **6** and a mixture of zinc(II) 7-amino and 8-aminoporphyrin-2,3-diones.[15] The latter compounds were smoothly photo-oxidised to corner zinc(II) porphyrin-2,3,7,8-tetraone[13,15] **5**, which upon reaction with 1,2-diaminobenzene afforded the corner zinc(II) bisquinoxalinoporphyrin **7**. The overall yield of **7** for the seven steps from **3** was 40%.[13] Treatment of tetraone **6** with 1,2-diaminobenzene and then $Zn(OAc)_2{\cdot}2H_2O$ gave linear zinc(II) bisquinoxalinoporphyrin **8** in 18% from **3**.[13] Copper(II) quinoxalinoporphyrin **10** was prepared in 65% overall yield by nitration of **4** to give the corresponding 2-nitroporphyrin, followed by demetallation and reduction to 2-aminoporphyrin, and photooxidation to the 2,3-dione[16] **9**, which was reacted with 1,2-diaminobenzene and remetallated.[14,17]

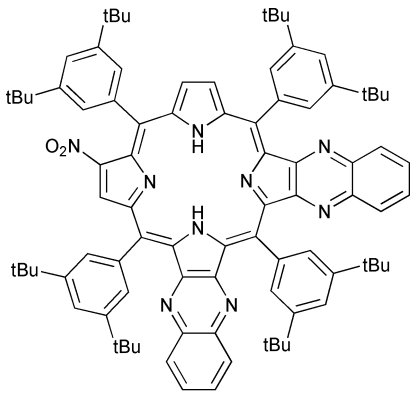
Synthesis of trisquinoxalinoporphyrin 1 from metallated corner bisquinoxalinoporphyrins 7 and 12 (Pathway 1)

The first pathway (Scheme 2) requires functionalisation of the C-ring (equivalent to the D-ring by symmetry) of a corner bisquinoxalinoporphyrin. For nitration at a porphyrin β-pyrrolic position the use of copper(II) chelates is usually preferred because of the high selectivity of the reaction but in

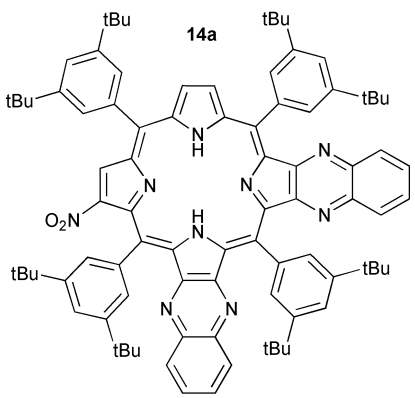


Scheme 2 Pathway 1, *Reagents and conditions*: (i) NO_2 in light petroleum, CH_2H_2; (ii) HCl, CH_2Cl_2; (iii) $SnCl_2{\cdot}2H_2O$ in HCl–Et_2O; (iv) O_2, hν and 1,2-diaminobenzene in CH_2Cl_2.

more π-expanded porphyrins, as in this case, the zinc(II) chelate can also be used.[4,18] As the corner zinc(II) bisquinoxalinoporphyrin **7** was readily available in fewer steps than the copper(II) chelate it was used directly.



14a



14b

Nitration of zinc chelate **7** afforded an inseparable mixture of zinc(II) 12- and 13-nitro-bisquinoxalinoporphyrins **11** in 83% yield (Scheme 2). Demetallation of **11** and chromatography of the product afforded the free-base corner 13-nitro-bisquinoxalinoporphyrin **14a** in 26% yield and the corner 12-nitro-bisquinoxalinoporphyrin **14b** in 63% yield. Analogous reactions (with almost equivalent yields) occur on the corresponding corner zinc(II) 5,10,15,20-tetraphenyl-bisquinoxalinoporphyrin, and X-ray crystal structure analysis of the analogue of compound **14a** confirms the assignment of the structure. Buttressing by the quinoxaline groups makes the 12-position sterically more accessible than the 13-position; this effect is discussed further below.

As both isomers, **14a** and **14b**, afford the same α-dione **16**, batches of the mixture were used in the subsequent steps. Free-base corner 12- and 13-nitro-bisquinoxalinoporphyrins **14** were reduced to afford the corresponding corner 12- and 13-amino-bisquinoxalinopophyrins **15**. The aminoporphyrins **15** have significant double bond character across the C12–C13 bond and were smoothly photooxidised in the presence of 1,2-diaminobenzene for five hours to give **1** in 64% yield presumably by way of corner bisquinoxalinoporphyrin-12,13-dione **16** (Scheme 2). Indeed, the corner bisquinoxalinoporphyrin-12,13-dione **16** was isolated in 32% yield when the sequence was carried out without the addition of 1,2-diaminobenzene. Singlet oxygen is the oxidant and the porphyrin is able to directly catalyse its formation. The lower

yield of isolated dione **16** is attributed to its instability under the photooxidation conditions and to the formation of undesirable side products. We have previously reported the formation of porphyrin-lactone and a macrocyclic anhydride upon further oxidation of 5,10,15,20-tetraphenylporphyrin-2,3-dione.[19] Clearly, trapping the dione **16** as it is formed by reaction with 1,2-diaminobenzene is beneficial. The overall yield of **1** by pathway 1 was 47% over four steps.

The ^{1}H NMR spectrum of **1** showed clearly the C_{2v} symmetry of the molecule and indicated that its tautomeric equilibrium is skewed to almost completely favour the *trans*-tautomer in which the two inner hydrogens reside on the nitrogens of the unsubstituted pyrrolic ring and its opposite quinoxalino-fused pyrrolic ring (as drawn in Scheme 1). This is shown by appearance of the resonances of the inner NH hydrogens as two one-proton broad singlets at −0.44 and −0.36 ppm and a single resonance for the β-pyrrolic protons (variable-temperature NMR spectra of **1** are given in the ESI†). By decreasing the temperature to 230 K, ^4J coupling (J = 1.8 Hz) was detected between the β-pyrrolic protons and the more downfield of the inner NH resonances of **1**. Irradiation of this resonance collapsed the resonance of the β-pyrrolic protons to a sharp singlet.

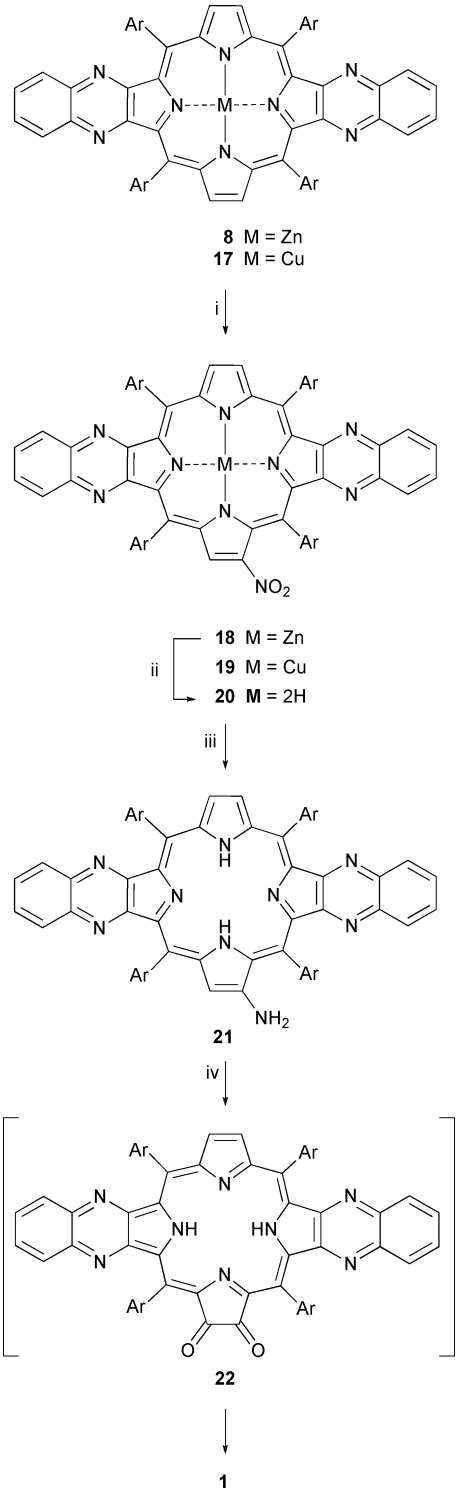
In the preferred tautomer of trisquinoxalinoporphyrin **1**, the β,β′-pyrrolic positions of rings that are protonated on the inner nitrogens form part of the 18-atom 18-π-electron aromatic delocalisation pathway. The non-protonated A- and C-rings both have a fused quinoxaline which is able to have a greater share of the electron density across the β,β′-pyrrolic positions.

The corner copper(II) bisquinoxalinoporphyrin **12** was also used as a primary precursor, and it has been found that upon nitration, the corner copper(II) 12- and 13-nitro-bisquinoxalinoporphyrins **13** were obtained in 97% yield (Scheme 2). Demetallations of compounds **13** were successfully achieved by stirring them in a refluxing mixture of dichloromethane, concentrated sulfuric acid and trifluoroacetic acid for three days. Chromatography of the products gave corner 13- and 12-nitro-bisquinoxalinoporphryins, **14a** and **14b**, in 16% and 52% yield, respectively. Again, the 12-nitro isomer predominated. The overall yield of nitro-bisquinoxalinoporphyrins **14** using copper chelate **6** is comparable to that obtained from the zinc chelate **7**, despite the harsher demetallation conditions required.

Pathway 1 (Scheme 2) is a very efficient route for preparing trisquinoxalinoporphyrin **1** in good overall yield that should be easy to scale-up to afford **1** in gram quantities.

Synthesis of trisquinoxalinoporphyrin 1 from the zinc(II) linear bisquinoxalinoporphyrin 8 (Pathway 2)

The second pathway requires functionalisation of the B-ring of a linear bisquinoxalinoporphyrin. Isomers will not arise in this pathway because of the symmetry of the starting material in which all four β-pyrrolic positions that are available for reaction are equivalent. Reactions on two metallated linear bisquinoxalinoporphyrins **8** and **17** were investigated. Nitration of the linear zinc(II) bisquinoxalinoporphyrin **8** afforded the linear zinc(II) 7-nitro-bisquinoxalinoporphyrin **18** in 74% yield (Scheme 3). Acidic demetallation of **18** gave the linear 7-nitro-bisquinoxalinoporphyrin **20** in 93% yield.



Scheme 3 Pathway 2, *Reagents and conditions*: (i) NO_2 in light petroleum, CH_2H_2; (ii) HCl, CH_2Cl_2; (iii) $SnCl_2{\cdot}2H_2O$ in HCl–Et_2O; (iv) O_2, hν and 1,2-diaminobenzene in CH_2Cl_2.

Reduction of **20** afforded the linear 7-amino-bisquinoxalinoporphyrin **21**, which was photooxidised in the presence of 1,2-diaminobenzene for five hours to afford **1** in 20% yield.

Photooxidation is the problematic step. Compound **21** is predominately the tautomer shown (evinced by ^4J couplings between the inner NHs and the β-pyrrolic groups) and thus the C7–C8 bond has substantial aromatic character as it is part of the 18-atom 18-π-electron aromatic delocalisation pathway. Photooxidation of aminoporphyrins involving singlet oxygen occurs much more readily and in better yield when the amino group is attached to an isolated double bond on the porphyrin periphery rather than to one involved in the aromatic delocalisation pathway. Despite these difficulties, linear 7-amino-bisquinoxalinoporphyrin **21** is an important building block in its own right and has been used to create chiral cavities and dendrimers as will be reported separately.

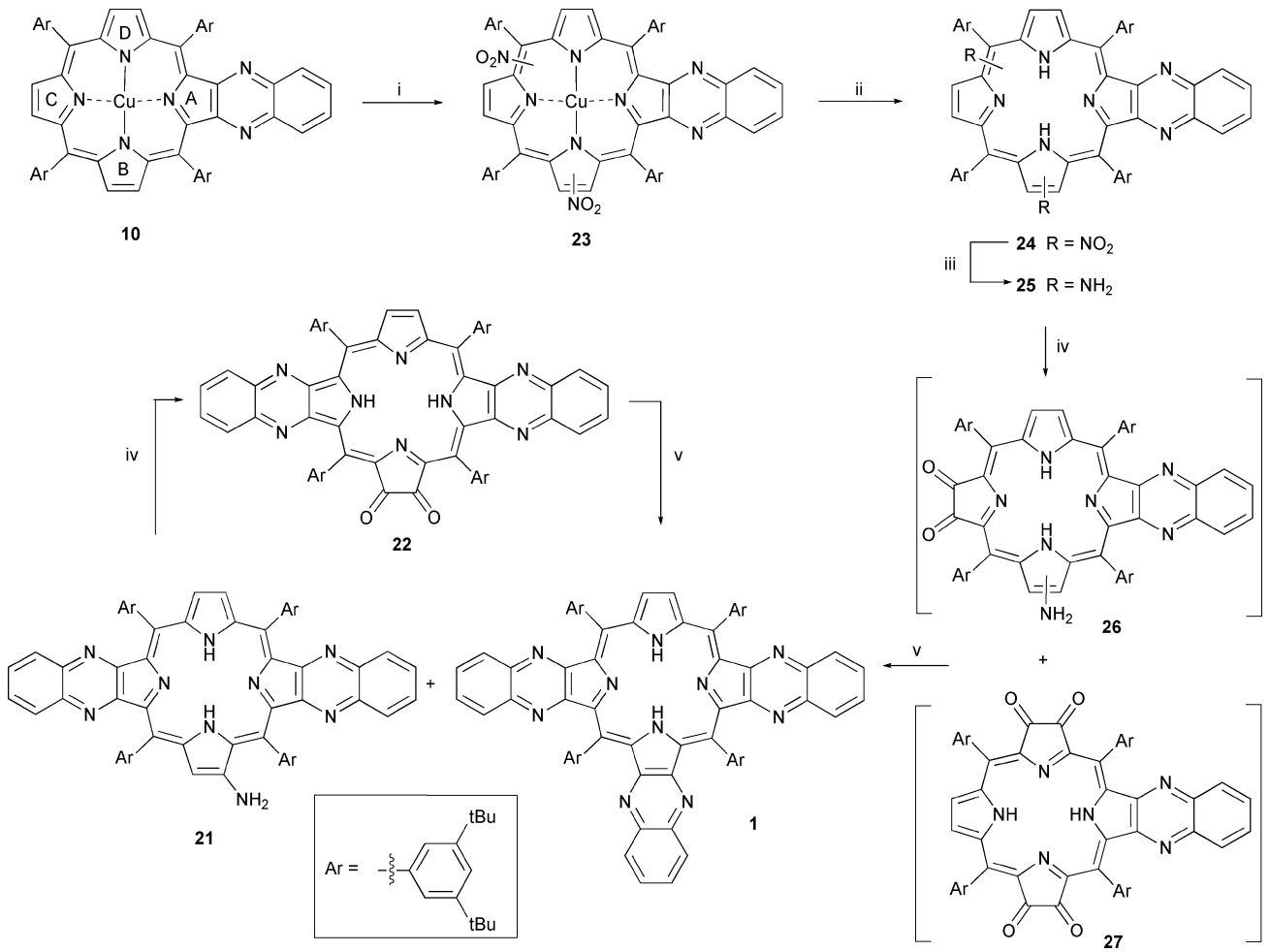
The linear bisquinoxalinoporphyrin-7,8-dione **22** is an intermediate in the conversion of aminoporphyrin **21** into **1** (Scheme 3) and was also made independently and reacted with 1,2-diaminobenzene to give **1** (see Scheme 4). The overall yield of **1** from zinc(II) linear bisquinoxalinoporphyrin **8** by pathway 2 was 14%.

Use of the copper(II) chelates in this sequence failed. Nitration of linear copper(II) bisquinoxalinoporphyrin **17** afforded the linear copper(II) nitro-bisquinoxalinoporphyrin **19** in 92% yield but it could not be demetallated even with TFA–sulfuric acid mixtures (Scheme 3).

Synthesis of trisquinoxalinoporphyrin 1 from the copper(II) quinoxalinoporphyrin 10 (Pathway 3)

In order to synthesise trisquinoxalinoporphyrin **1** it is necessary to elaborate two pyrrolic rings of a quinoxalinoporphyrin. This was achieved by nitration of copper(II) quinoxalinoporphyrin **10** using nitrogen dioxide to give a mixture of the copper(II) dinitroquinoxalinoporphyrins **23** in 87% yield (Scheme 4). The mixture of dinitro-quinoxalinoporphyrins **23** was demetallated by stirring with concentrated sulfuric acid for 15 min to afford free-base dinitroquinoxalinoporphyrins **24** in 97% yield. Examination of the ^{1}H NMR spectrum of the regioisomers **24** showed no resonance patterns that would indicate dinitration of the same pyrrolic ring. This observation is in accord with studies of the dinitration of copper(II) 5,10,15,20-tetraphenylporphyrin in which all the possible isomers except the 2,3-dinitroporphyrin were obtained.[20] Hence all the dinitroquinoxalinoporphyrin isomers formed will lead to trisquinoxalinoporphyrin **1** and the mixture was carried forward.

The dinitroquinoxalinoporphyrins **24** were stirred with tin(II) chloride dihydrate to give the diamino-quinoxalinoporphyrins **25**, which were photooxidised to an inseparable mixture of



Scheme 4 Pathway 3, *Reagents and conditions*: (i) NO_2 in light petroleum, CH_2H_2; (ii) H_2SO_4, CH_2Cl_2; (iii) $SnCl_2{\cdot}2H_2O$ in HCl–Et_2O; (iv) O_2, hν, CH_2Cl_2; (v) 1,2-diaminobenzene, CH_2Cl_2.

7- and 8-aminoquinoxalinoporphyrin-12,13-diones **26** and quinoxalinoporphyrin-7,8,17,18-tetraone **27** (Scheme 1).

The mixture of aminoporphyrin-dione **26** and porphyrin-tetraone **27** was condensed with 1,2-diaminobenzene to give the linear 7-amino-bisquinoxalinoporphyrin **21** in 6% yield and the trisquinoxalinoporphyrin **1** in 10% yield. This product has arisen from annelation of the B- and D-rings of **10** (as labelled in Scheme 2). The residual amino-bisquinoxalinoporphyrin **26** could also be converted into **1**. Compound **26** was subjected to prolonged photooxidation to afford the bisquinoxalinoporphyrin-dione **22** in 23% yield; products of over-oxidation were also observed, a consequence of the dione **22** being more susceptible to oxidation than the starting amino-bisquinoxalinoporphyrin **26**. It is probable that the photooxidation reaction would have gone better on the corresponding zinc(II) chelate of **26** which has increased bond order of the C7–C8 bond which would allow a shorter reaction time, thereby reducing the possibility of over-oxidation.[15,19] The dione **22** was reacted with 1,2-diaminobenzene to give **1** in 77% yield. This product has arisen from annelation of the B- and C-rings of **10**.

The formation of intermediates **26** and **27** has direct analogy to the results obtained by photooxidation of a mixture of free-base 2,*x*-diamino-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrins which gives the corresponding 7- and 8-amino-porphyrin-2,3-diones and the porphyrin-2,3,12,13-tetraone **6**.[15]

Dione units shift the tautomeric equilibrium of free-base porphyrins to greatly favour the *trans*-tautomer in which the inner hydrogens do not reside on the nitrogen of the α-diketopyrrolic ring. This also imposes double bond character on the β,β′-pyrrolic bond opposite it and aromatic character to the β,β′-pyrrolic bond in adjacent pyrrolic rings. An amino group situated on a double bond is photooxidised much more readily than one situated on an aromatic bond.[15,17,21–23] A fused quinoxalino group also shifts the position of tautomeric equilibrium (to a lesser extent) in the same way[18] but is greatly out-competed by a dione unit when they are in competition in adjacent pyrrolic rings. The formation of intermediates **26** and **27** can be readily understood as arising from the initial influence of the quinoxalino group and then the dominance of the first formed dione (or precursor keto-imine) in controlling bond order and subsequent reactivity at the second amino site.

The overall yield of **1** from **10** following Pathway 3 was 9% in five steps. This sequence showed that **1** can be synthesised from the copper(II) quinoxalinoporphyrin **10** by functionalisation of two additional pyrrolic rings through nitration and eventual conversion of each to an α-diketopyrrolic ring.

Careful column chromatography of a batch of the regioisomers **24** over silica (1 : 3 dichloromethane–light petroleum over 48 hours) allowed isolation of 1 part 7,18-dinitroquinoxalinoporphyrin **24a** from 4 parts of other dinitroquinoxalinoporphyrin regioisomers.

The C_{2v} symmetry of dinitroporphyrin **24a** was apparent in its ^{1}H NMR spectrum and the substitution pattern was confirmed by NOESY studies which showed a through space connectivity between H(8) (δ_H 8.89), the H$_o$ of the aryl at the 10-position (δ_H 8.02) and H(12) (δ_H 8.66) (Fig. 1 and ESI†). A NOESY interaction is also seen between the β-pyrrolic protons and one of the two *tert*-butyl signals.

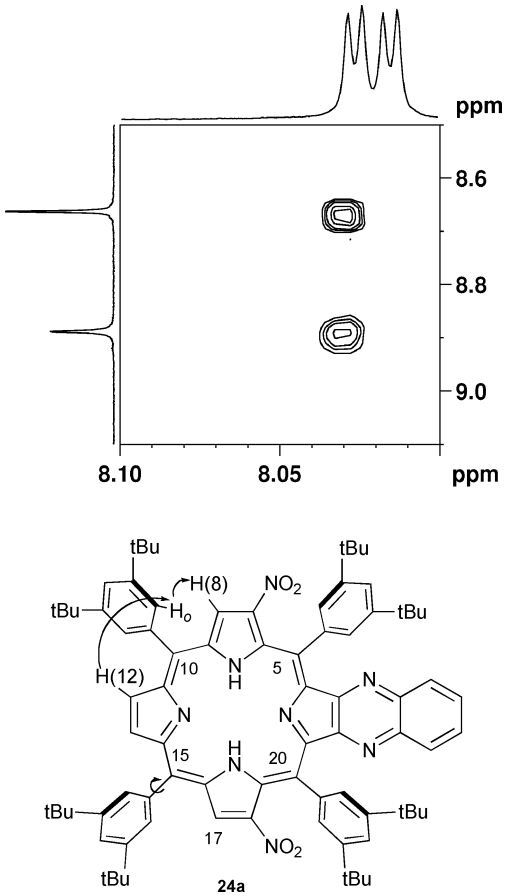


Fig. 1 Through-space connectivity of H(8)–H$_o$–H(12) seen in partial NOESY spectra of 7,18-dinitroporphyrin **24a**.

The amount of the 7,18-dinitroquinoxalinoporphyrin **24a** obtained is about three times more than expected on statistical grounds alone. Previously, mono-nitration of **9** gave 7-nitro > 12-nitro > 8-nitro in the ratio 5 : 3 : 1.5, largely the result of the 7-position being more accessible for nitration due to the quinoxalino group restricting rotation of the 5- and 20-aryl groups and buttressing these aryls into a more orthogonal arrangement to the porphyrin plane on a time average than the 10- and 15-aryl groups.[18] The formation of 7,18-dinitroquinoxalinoporphyrin **24a** in moderate yield in this work can reasonably be accounted for as being due to the same effect.

Conclusions

Three different routes are used to prepare trisquinoxalinoporphyrin **1** by further functionalisation and annelation of pre-formed porphyrins. Starting from corner zinc(II) bisquinoxalinoporphyrin **7** or linear zinc(II) bisquinoxalinoporphyrin **8**, functionalisation of only one additional ring was required. Corner zinc(II) bisquinoxalinoporphyrin **7** is converted into **1** in 47% overall yield over four steps (Scheme 2); corner copper(II) bisquinoxalinoporphyrin **12** was also converted to **1** by this route. Linear zinc(II) bisquinoxalinoporphyrin **8** is converted into **1** in 14% overall yield over four steps (Scheme 3). Functionalisation of two rings is required to convert copper(II) quinoxalinoporphyrin

10 into **1** and this was achieved in 9% over five steps (Scheme 4). Each synthetic route established in this work could have use in elaboration of more complex oligoporphyrin arrays.

The major determinate of yield was the ease with which photooxidation steps in each sequence proceeded and this was related to bond order effects. As with simpler aminoporphyrin systems photooxidation proceeds best when there is substantial double bond character on the bond to be oxidised. In a free-base compound when the bond to be oxidised has essentially aromatic character the bond order can be increased by conversion to a metalloporphyrin derivative.[22] The aminoporphyrins all acted as singlet oxygen sensitisers and addition of rose bengal was not required for porphyrin-dione formation.

Studies underway in our laboratories show that free-base trisquinoxalinoporphyrin **1** and metallated derivatives have second harmonic properties in non-linear optical experiments and they show important incoherent photon up-conversion by triplet–triplet annihilation. These studies will be reported elsewhere.

In addition, the methodology developed for the synthesis of **1** establishes protocols that will be of use in the construction of T-junction molecular assemblies, grids and compounds of possible application in molecular electronics and photonics. Synthesis of such compounds is also underway in our laboratories.

Experimental

General procedures

General procedures were the same as those described elsewhere.[18]

Synthesis of trisquinoxalinoporphyrin 1 from metallated corner bisquinoxalinopophyrin (Pathway 1, Scheme 2)

{12- and 13-Nitro-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-bisquinoxalino[2,3-b′:7,8-b″]porphyrinato}zinc(II) **11**. {5,10,15,20-Tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]-porphyrinato}zinc(II)[13] **7** (0.822 g, 0.618 mmol) was dissolved in CH_2Cl_2 (750 ml) and treated with a solution of nitrogen dioxide in light petroleum (1 M), added portion-wise with stirring until the nitration was complete by TLC analysis. The crude mixture was purified by column chromatography over silica (CH_2Cl_2–light petroleum 3 : 2). The front running green band was collected to give a mixture of {12- and 13-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]-porphyrinato}zinc(II) **11** (0.725 g, 83%) as a black shiny microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation (CH_2Cl_2–MeOH); (Found: C, 73.28; H, 6.96; N, 8.57. $C_{88}H_{95}N_9O_2Zn + CH_2Cl_2$ requires C, 73.16; H, 6.69; N, 8.63%); (HR-ESI-FT/ICR found: $[M + H]^+$ 1374.7070. $C_{88}H_{96}N_9O_2Zn$ requires 1374.6973); $\nu_{max}(CHCl_3)/cm^{-1}$ 3022s, 2963s, 1523m (NO_2), 1363s (NO_2); $\lambda_{max}(CHCl_3)/nm$ 343 (log ε 4.62), 401sh (4.65), 424 (4.83), 465 (4.88), 491 (5.12), 555sh (3.82), 599 (4.34), 639 (3.99); δ_H(400 MHz; $CDCl_3$) 1.45 (s, *t*-butyl H), 1.47 (s, *t*-butyl H), 1.482 (s, *t*-butyl H), 1.483 (s, *t*-butyl H), 1.522 (s, *t*-butyl H), 1.523 (s, *t*-butyl H), 7.76 (t, *J* 1.8 Hz, H_p), 7.78–7.94 (m, quinoxaline H, H_o, H_p), 8.01 (d, *J* 1.8 Hz, H_o), 8.02–8.03 (m, H_o, H_p), 8.78 and 8.829 (ABq, *J* 4.7 Hz, β-pyrrolic H), 8.832 and 8.87 (ABq, *J* 4.8 Hz, β-pyrrolic H), 8.98 (s, β-pyrrolic H), 9.10 (s, β-pyrrolic H); *m*/*z* (ESI) 1374.9 ($[M + H]^+$ requires 1374.7).

{12- and 13-Nitro-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-bisquinoxalino[2,3-b′:7,8-b″]porphyrinato}copper(II) **13**. {5,10,15,20-Tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]-porphyrinato}copper(II)[13] **12** (206 mg, 0.155 mmol) was dissolved in CH_2Cl_2 (125 ml) and treated with a solution of nitrogen dioxide in light petroleum (1 M), added portion-wise with stirring until nitration was complete. The crude mixture was purified by column chromatography over silica (CH_2Cl_2–light petroleum 1 : 2). The front running band was collected to give a mixture of {12- and 13-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]-porphyrinato}copper(II) **13** (207 mg, 97%) as a green microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation (CH_2Cl_2–MeOH); (Found: C, 75.77; H, 6.99; N, 8.75. $C_{88}H_{59}CuN_9O_2 + CH_3OH$ requires C, 76.01; H, 7.10; N, 8.96%); (HR-ESI-FT/ICR found: $[M + H]^+$ 1373.6887. $C_{88}H_{95}CuN_9O_2$ requires 1373.6918); $\nu_{max}(CHCl_3)/cm^{-1}$ 3017s, 2964s, 2904m, 1527m (NO_2), 1363s (NO_2); $\lambda_{max}(CHCl_3)/nm$ 309sh (log ε 4.57), 342 (4.68), 389sh (4.56), 421 (4.81), 459sh (4.88), 482 (5.08), 585 (4.28), 629 (4.13); *m*/*z* (ESI) 1373.9 ($[M + H]^+$ requires 1373.7).

12- and 13-Nitro-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-bisquinoxalino[2,3-b′:7,8-b″]porphyrins **14b** *and* **14a**

Method 1: demetallation of zinc(II) corner 12- and 13-nitro-bisquinoxalinoporphyrin **11**. A solution of {12- and 13-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]porphyrinato}zinc(II) **11** (610 mg, 0.443 mmol) in CH_2Cl_2 (140 ml) was stirred with hydrochloric acid (140 ml, 8 M) for 20 min, then poured onto ice (200 g). When the ice melted the organic phase was separated, washed with water (200 ml), sodium carbonate solution (10%, 2 × 250 ml) and water (200 ml), dried over anhydrous sodium sulfate, filtered and the filtrate evaporated to dryness. The crude mixture was purified by chromatography over silica (CH_2Cl_2–light petroleum 1 : 2). The front running green band was collected and the solvent was removed to give 13-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]-porphyrin **14a** (150 mg, 26%) as a green microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation (CH_2Cl_2–MeOH); (Found: C, 77.48; H, 7.43; N, 9.23. $C_{88}H_{97}N_9O_2 + 3CH_3OH$ requires C, 77.58; H, 7.80; N, 8.95%); (HR-ESI-FT/ICR found: $[M + H]^+$ 1312.7854. $C_{88}H_{98}N_9O_2$ requires 1312.7838); $\nu_{max}(CHCl_3)/cm^{-1}$ 3325w (NH), 3021s, 3008w, 2964s, 2928m, 1507m (NO_2), 1362s (NO_2); $\lambda_{max}(CHCl_3)/nm$ 311sh (logε 4.37), 344 (4.56), 389sh (4.54), 421 (4.72), 457sh (4.83), 482 (5.03), 562 (4.00), 610 (4.09), 629 (4.09), 689 (3.89); δ_H(400 MHz; $CDCl_3$) −0.51 (2 H, br s, inner NH), 1.44 (18 H, s, *t*-butyl H), 1.49 (36 H, s, *t*-butyl H), 1.53 (18 H, s, *t*-butyl H), 7.74–7.79 (4 H, m, quinoxaline H, aryl H), 7.82–7.84 (1 H, m, quinoxaline H), 7.87–7.98 (12 H, m, quinoxaline H, H_o, H_p), 8.01 (1 H, t, *J* 1.8 Hz, H_p), 8.07 (2 H, d, *J* 1.7 Hz, H_o), 8.74 and 8.79 (2 H, ABq, *J* 4.8 Hz, β-pyrrolic H), 8.92 (1 H, s, β-pyrrolic H); *m*/*z* (ESI) 1312.9 ($[M + H]^+$ requires 1312.8).

The second green band was collected and the solvent removed to give 12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]porphyrin **14b** (366 mg, 63%) as a green microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation (CH_2Cl_2–MeOH); (Found: C, 78.59; H, 7.43; N, 9.40. $C_{88}H_{97}N_9O_2$ + $2CH_3OH$ requires C, 78.51; H, 7.69; N, 9.16%); (HR-ESI-FT/ICR found: $[M + H]^+$ 1312.7845. $C_{88}H_{98}N_9O_2$ requires 1312.7838); $\nu_{max}(CHCl_3)/cm^{-1}$ 3326w (NH), 3026s, 3014w, 2864s, 1524w (NO_2), 1363m (NO_2); $\lambda_{max}(CHCl_3)$/nm 314sh (log ε 4.46), 342 (4.57), 385sh (4.56), 421 (4.75), 455sh (4.89), 477 (5.06), 560 (4.10), 599 (4.14), 626 (4.07), 682 (3.77); δ_H(400 MHz; $CDCl_3$) −0.29 (2 H, br s, inner NH), 1.45 (18 H, s, *t*-butyl H), 1.48 (36 H, s, *t*-butyl H), 1.54 (18 H, s, *t*-butyl H), 7.74–7.78 (3 H, m, quinoxaline H, Hp), 7.82–7.88 (5 H, m, quinoxaline H, aryl H), 7.89 (2 H, d, *J* 1.8 Hz, H_o), 7.91–7.94 (5 H, m, quinoxaline H, H_o, H_p), 7.98 (2 H, d, *J* 1.7 Hz, H_o), 8.01 (1 H, t, *J* 1.8 Hz, H_p), 8.03 (2 H, d, *J* 1.9 Hz, H_p), 8.68 and 8.70 (2 H, ABq, *J* 4.8 Hz, β-pyrrolic H), 8.78 (1 H, s, β-pyrrolic H); *m*/*z* (ESI) 1312.9 ($[M + H]^+$ requires 1312.8).

Method 2: demetallation of copper(II) corner 12- and 13-nitro-bisquinoxalinoporphyrin **13**. A solution of {12- and 13-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino-[2,3-*b*′:7,8-*b*″]porphyrinato}copper(II) **13** (180 mg, 0.131 mmol) in CH_2Cl_2 (90 ml) was stirred and heated at 100 °C with trifluoroacetic acid (2 ml) and concentrated sulfuric acid (98%, 4.4 ml) for 3 days, then poured onto ice (50 g). When the ice melted the organic phase was separated, washed with water (200 ml), sodium carbonate solution (10%, 2 × 200 ml), water (200 ml), dried over anhydrous sodium sulfate, filtered and the filtrate evaporated to dryness. The crude mixture was purified by chromatography over silica (CH_2Cl_2–light petroleum; 1 : 2) to give two fractions. The first fraction gave 13-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]-porphyrin **14a** (28.0 mg, 16%) as a green microcrystalline solid, mp > 300 °C, which co-chromatographed with an authentic sample prepared by method 1. The second fraction gave 12-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]porphyrin **14b** (90.0 mg, 52%) as a green microcrystalline solid, mp > 300 °C, which co-chromatographed with an authentic sample prepared by method 1.

5,10,15,20-Tetrakis(3,5-di-tert-butylphenyl)trisquinoxalino-[2,3-b′:7,8-b″:12,13-b‴]porphyrin **1**. A solution of crude 12- and 13-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-bisquinoxalino[2,3-*b*′:7,8-*b*″]porphyrin **14** (0.593 g, 0.451 mmol) in a HCl–ether mixture (4 M, 40 ml) was stirred with tin(II) chloride dihydrate (0.441 g, 1.95 mmol) in the dark for 2 h. Work-up as before gave 12- and 13-amino-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]porphyrin **15**. The mixture was dissolved in CH_2Cl_2 (2 L) and photooxidised in the presence of 1,2-diaminobenzene (0.218 g, 2.02 mmol) for 5 h. Mass spectroscopy showed the presence of 12,13-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]porphyrin **16** as an intermediate. The solvent was removed under vacuum and the crude mixture purified by column chromatography over silica (CH_2Cl_2–light petroleum 1 : 3). The first dark green band was collected to give 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-trisquinoxalino[2,3-*b*′:7,8-*b*″:12,13-*b*‴]porphyrin **1** (0.398 g, 64%) as a green microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation ($CHCl_3$–MeOH); (Found: C, 81.42; H, 7.48; N, 9.93. $C_{94}H_{100}N_{10}$ + CH_3OH requires C, 81.39; H, 7.48; N, 9.99%); (ESI-HRMS found: $[M + H]^+$ 1369.816. $C_{94}H_{101}N_{10}$ requires 1369.821); $\nu_{max}(CHCl_3)/cm^{-1}$ 3346w (NH), 2962s, 2926s, 2856s, 1595s, 1576w, 1558w, 1545w, 1516w, 1506w, 1495w, 1487w, 1475m, 1466m, 1431w, 1393w, 1362s, 1352m, 1300m, 1248m, 1236m, 1204w, 1190w, 1173w, 1153m, 1136w, 1111s; $\lambda_{max}(CHCl_3)$/nm 307sh (logε 4.36), 345 (4.59), 390sh (4.71), 421 (4.87), 466 (4.83), 492 (4.94), 537sh (3.98), 576 (4.15), 608 (4.18), 629sh (4.00), 638 (4.01), 687 (3.30); δ_H(400 MHz; $CDCl_3$; 300 K) −0.44 (1 H, br s, inner NH), −0.36 (1 H, br s, inner NH), 1.46 (36 H, s, *t*-butyl H), 1.49 (36 H, s, *t*-butyl H), 7.71–7.75 (4 H, m, quinoxaline H), 7.77–7.80 (2 H, m, quinoxaline H), 7.82–7.85 (2 H, m, quinoxaline H), 7.87–7.89 (2 H, m, quinoxaline H), 7.89 (4 H, d, *J* 1.6 Hz, H_o), 7.92 (2 H, t, *J* 1.7 Hz, H_p), 7.94 (4 H, d, *J* 1.6 Hz, H_o), 7.95–7.99 (2 H, m, quinoxaline H), 8.02 (2 H, t, *J* 1.7 Hz, H_o), 8.76 (2 H, s, β-pyrrolic H); δ_H(400 MHz; $CDCl_3$; 230 K) −0.59 (1 H, s, inner NH), −0.52 (1 H, br s, inner NH), 1.40 (36 H, s, *t*-butyl H), 1.45 (36 H, s, *t*-butyl H), 7.76–7.80 (8 H, m, quinoxaline H), 7.88–7.95 (16 H, m, quinoxaline H, H_o, H_p), 8.82 (2 H, d, *J* 1.6 Hz, β-pyrrolic H); *m*/*z* (ESI) 1369.9 ($[M + H]^+$ requires 1369.8).

12,13-Dioxo-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)bisquinoxalino[2,3-b′:7,8-b″]porphyrin **16**. The above reactions were repeated on 12- and 13-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:7,8-*b*″]porphyrin **14** (48.4 mg, 0.0369 mmol) but without addition of 1,2-diaminobenzene. The solvent was removed under vacuum and the crude mixture was purified by column chromatography over silica (CH_2Cl_2–light petroleum 2 : 3). The front running orange band was collected and the solvent removed to give 12,13-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-bisquinoxalino[2,3-*b*′:7,8-*b*″]porphyrin **16** (15.2 mg, 32%) as a black microcrystalline solid, mp > 300 °C; (ESI-HRMS found: $[M + H]^+$ 1297.772. $C_{88}H_{97}N_8O_2$ requires 1297.773); $\nu_{max}(CHCl_3)/cm^{-1}$ 3354w (NH), 2964s, 2903m, 2866m, 1724s (CO), 1595m; $\lambda_{max}(CHCl_3)$/nm 352sh (logε 4.68), 404 (4.97), 464 (4.85), 530sh (4.47), 589sh (4.12), 684 (3.66), 710 (3.60), 760 (3.59); δ_H(400 MHz; $CDCl_3$) 0.15 (1 H, br s, inner NH), 0.19 (1 H, br s, inner NH), 1.43 (18 H, s, *t*-butyl H), 1.44 (18 H, s, *t*-butyl H), 1.47 (18 H, s, *t*-butyl H), 1.48 (18 H, s, *t*-butyl H), 7.65 (2 H, d, *J* 1.8 Hz, H_o), 7.70 (2 H, d, *J* 1.8 Hz, H_o), 7.71–7.93 (15 H, m, quinoxaline H, H_o, H_p), 8.00 (1 H, t, *J* 1.8 Hz, H_p), 8.33 and 8.55 (2 H, d of ABq, *J* 4.7, J_{NH} 1.9 Hz, β-pyrrolic H); *m*/*z* (ESI) 1296.9 (M^+ requires 1296.8).

Synthesis of trisquinoxalinoporphyrin 1 from metallated linear bisquinoxalinoporphyrin (Pathway 2, Scheme 3)

{7-Nitro-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)bisquinoxalino[2,3-b′:12,13-b″]porphyrinato}zinc(II) **18**. {5,10,15,20-Tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]-porphyrinato}zinc(II)[13] **8** (60.0 mg, 0.0451 mmol) was dissolved in CH_2Cl_2 (500 ml) and nitrated. The crude mixture

was purified by column chromatography over silica (CH_2Cl_2–light petroleum 3 : 2). The front running band was collected and the solvent was removed to give 7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]porphyrinato}zinc(II) **18** (46.0 mg, 74%) as a green shiny microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation ($CHCl_3$–MeOH); (Found: C, 74.30; H, 6.98; N, 8.74. $C_{88}H_{95}N_9O_2Zn$ + 1/2$CHCl_3$ requires C, 74.03; H, 6.70; N, 8.78%); (HR-ESI-FT/ICR found: $[M]^+$ 1373.6931. $C_{88}H_{95}N_9O_2Zn$ requires 1373.6890); $\nu_{max}(CHCl_3)/cm^{-1}$ 2964s, 2903m, 2866m, 1526m (NO_2), 1362s (NO_2); $\lambda_{max}(CHCl_3)$/nm 349 (logε 4.64), 403sh (4.73), 465 (5.30), 559 (3.88), 608 (3.93), 642sh (4.32); 659 (4.62) nm; δ_H(400 MHz; $CDCl_3$) 1.489 (18 H, s, *t*-butyl H), 1.493 (18 H, s, *t*-butyl H), 1.498 (18 H, s, *t*-butyl H), 1.501 (18 H, s, *t*-butyl H), 7.78–7.97 (20 H, m, quinoxaline H, H_o, H_p), 9.07–9.09 (2 H, m, tight ABq, β-pyrrolic H), 9.27 (1 H, s, β-pyrrolic H); *m*/*z* (ESI) (*m*/*z*): 1374.7 ($[M + H]^+$ requires 1374.7).

7-Nitro-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)bisquinoxalino[2,3-b′:12,13-b″]porphyrin **20**. A solution of {7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]-porphyrinato}zinc(II) **18** (46.0 mg, 0.0334 mmol) in CH_2Cl_2 (20 ml) was stirred with hydrochloric acid (20 ml, 8 M) for 20 min. After work-up the crude mixture was purified by chromatography over silica (CH_2Cl_2–light petroleum 1 : 1). The front running green band was collected and evaporated to give 7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-bisquinoxalino[2,3-*b*′:12,13-*b*″]porphyrin **20** (41.0 mg, 93%) as a green microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation ($CHCl_3$–MeOH); (Found: C, 79.08; H, 7.47; N, 9.52. $C_{88}H_{97}N_9O_2$ + CH_3OH requires C, 79.49; H, 7.57; N, 9.37%); (HR-ESI-FT/ICR found: $[M + H]^+$ 1312.7785. $C_{88}H_{98}N_9O_2$ requires 1312.7833); $\nu_{max}(CHCl_3)/cm^{-1}$ 3369w (NH), 2964s, 2905m, 1533m (NO_2), 1364m (NO_2); $\lambda_{max}(CHCl_3)$/nm 354 (logε 4.65), 423sh (4.93), 449 (5.37), 536 (4.21), 577 (4.05), 620 (4.05); 675 (3.99); δ_H(400 MHz; $CDCl_3$) −1.97 (1 H, d, *J* 1.8 Hz, inner NH), −1.92 (1 H, br s, inner NH), 1.48 (18 H, s, *t*-butyl H), 1.49 (36 H, s, *t*-butyl H), 1.50 (18 H, s, *t*-butyl H), 7.72–7.83 (8 H, m, quinoxaline H), 7.90 (1 H, t, *J* 1.8 Hz, H_p), 7.93–7.97 (7 H, m, H_o, H_p), 7.98 (2 H, d, *J* 1.8 Hz, H_o), 7.99 (2 H, d, *J* 1.8 Hz, H_o), 9.02 and 9.04 (2 H, d of ABq, *J* 4.9, J_{NH} 1.8 Hz, β-pyrrolic H), 9.17 (1 H, d, *J* 2.5 Hz, β-pyrrolic H); *m*/*z* (ESI) 1312.8 ($[M + H]^+$ requires 1312.8).

5,10,15,20-Tetrakis(3,5-di-tert-butylphenyl)trisquinoxalino[2,3-b′:7,8-b″:12,13-b‴]porphyrin **1**. A solution of 7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]porphyrin **20** (34.0 mg, 0.0259 mmol) in a HCl–ether mixture (4 M, 10 ml) was stirred with tin(II) chloride dihydrate (26.0 mg, 0.115 mmol) in the dark for 1.5 h. After work-up the 7-amino-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bis-quinoxalino[2,3-*b*′:12,13-*b*″]porphyrin **21** was obtained, which was then dissolved in CH_2Cl_2 (0.5 L) and photooxidised in the presence of 1,2-diaminobenzene (25.0 mg, 0.231 mmol) for 5 h. The solvent was removed and the crude mixture was purified by column chromatography over silica (CH_2Cl_2–light petroleum 1 : 3). The first dark green band was collected and the solvent was removed to give 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)trisquinoxalino[2,3-*b*′:7,8-*b*″:12,13-*b*‴]porphyrin **1** (7.0 mg, 20%) as a green microcrystalline solid, mp > 300 °C, which co-chromatographed with an authentic sample reported above.

Synthesis of {7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]porphyrinato}copper(II) 19. {5,10,15,20-Tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino-[2,3-*b*′:12,13-*b*″]porphyrinato}copper(II)[13] **17** (100 mg, 0.0752 mmol) was dissolved in CH_2Cl_2 (300 ml) and nitrated. The crude mixture was purified by column chromatography over silica ($CHCl_3$–light petroleum 1 : 2). The front running band was collected to give {7-nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]porphyrinato}copper(II) **19** (95.0 mg, 92%) as a green shiny microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation ($CHCl_3$–MeOH); (Found: C, 75.85; H, 6.88; N, 9.06. $C_{88}H_{95}CuN_9O_2$ + CH_3OH requires C, 76.01; H, 7.10; N, 8.96%); (HR-ESI-FT/ICR found: $[M + H]^+$ 1373.7017. $C_{88}H_{96}CuN_9O_2$ requires 1373.6983); $\nu_{max}(CHCl_3)/cm^{-1}$ 2964s, 2903m, 2866m, 1522w (NO_2), 1362s (NO_2); $\lambda_{max}(CHCl_3)$/nm 349 (logε 4.70), 398sh (4.67), 461 (5.25), 550 (3.90), 626 (4.21), 660 (4.47) nm; *m*/*z* (ESI) 1373.8 ($[M + H]^+$ requires 1373.7).

Synthesis of trisquinoxalinoporphyrin 1 from the copper(II) quinoxalinoporphyrin 3 (Scheme 4, Pathway 3)

{Dinitro-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)quinoxalino[2,3-b′]porphyrinato}copper(II) isomers **23**. {5,10,15,20-Tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*′]porphyrinato}copper(II)[14] **10** (1.61 g, 1.31 mmol) was dissolved in CH_2Cl_2 (300 ml) and nitrated as above. The reaction was followed by TLC analysis which showed the initial formation of nitro-5,10,15,20-tetrakis-(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*′]porphyrinato}copper(II). When none of the mononitro adducts remained, the solution was evaporated to dryness and the resultant product was subjected to chromatography over silica (CH_2Cl_2–light petroleum 1 : 2). The major band yielded {dinitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*′]porphyrinato}copper(II) isomers **23** (1.50 g, 87%) as a shiny purple microcrystalline solid (recrystallisation from CH_2Cl_2–MeOH), mp > 300 °C; (Found: C, 74.2; H, 7.2; N, 8.6. $C_{82}H_{92}CuN_8O_4$ + CH_3OH requires C, 73.9; H, 7.2; N, 8.3%); (HR-ESI-FT/ICR found: $[M + H]^+$ 1316.6660. $C_{82}H_{93}CuN_8O_4$ requires 1316.6615); $\nu_{max}(CHCl_3)/cm^{-1}$ 2985s, 2905s, 2868s, 1530s (NO_2), 1363s (NO_2); λ_{max} ($CHCl_3$)/nm 344 (log ε 4.50), 385sh (4.43), 457 (5.09), 574 (4.08), 535sh (3.83), 623 (4.13); *m*/*z* (ESI) 1316.9 ($[M + H]^+$ requires 1316.7).

Dinitro-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)quinoxalino[2,3-b′]porphyrin isomers **24**. A solution of {dinitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*′]porphyrinato}-copper(II) isomers **23** (1.50 g, 1.14 mmol) in CH_2Cl_2 (50 ml) was stirred with concentrated sulfuric acid (98%, 6.5 ml) for 15 min. After work-up the crude mixture was passed through a plug of silica (CH_2Cl_2–light petroleum 1 : 1) to afford dinitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino-[2,3-*b*′]porphyrin isomers **24** (1.39 g, 97%) as a green

microcrystalline solid (recrystallisation from a CH_2Cl_2–MeOH solution), mp > 300 °C; (Found: C, 77.65; H, 7.7; N, 8.9. $C_{82}H_{94}N_8O_4$ + CH_3OH requires C, 77.4; H, 7.7; N, 8.7%). (HR-ESI-FT/ICR found: $[M + H]^+$ 1255.7462. $C_{82}H_{95}N_8O_4$ requires 1255.7471). $\nu_{max}(CHCl_3)/cm^{-1}$ 3369w (NH), 3006s, 3000s, 2965s, 2868m, 1533m (NO_2), 1363s (NO_2); $\lambda_{max}(CHCl_3)/nm$ 347 (logε 4.46), 394sh (4.48), 457 (5.11), 550 (4.01), 609 (3.99), 692 (3.72); δ_H(400 MHz; $CDCl_3$) −2.14 (s, inner NH), −2.03 (s, inner NH), −1.96 (s, inner NH), −1.94 (s, inner NH), −1.88 (s, inner NH), −1.80 (s, inner NH), −1.24 (s, inner NH), 1.47–1.50 (m, *t*-butyl H), 1.52–1.55 (m, *t*-butyl H), 7.75–8.07 (m, quinoxaline H, H_o, H_p), 8.10 (t, *J* 2.0 Hz, H_p), 8.12 (d, *J* 1.8 Hz, H_o), 8.62–9.17 (m, β-pyrrolic H); *m*/*z* (ESI) 1255.8 ($[M + H]^+$ requires 1255.7).

Isolation of 7,18-dinitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*′]porphyrin 24a. Dinitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*′]porphyrin isomers **24** (1.39 g, 1.107 mmol) were further fractionated by chromatography over silica (CH_2Cl_2–light petroleum 1 : 3) to give two fractions. The first fraction was an inseparable mixture of the 7,12-, 7,13-, 7,17-, 8,12-, 8,13- and 8,17-dinitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*′]-porphyrin **24b** (1.14 g, 79%). The second fraction gave 7,18-dinitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino-[2,3-*b*′]porphyrin **24a** (0.250 g, 21%) as a green microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation (CH_2Cl_2–MeOH); (HR-ESI-FT/ICR found: $[M + H]^+$ 1255.7433. $C_{82}H_{95}N_8O_4$ requires 1255.7471); $\nu_{max}(CHCl_3)/cm^{-1}$ 3323w (NH), 3016s, 2965s, 2905m, 1526m (NO_2), 1363s (NO_2); $\lambda_{max}(CHCl_3)/nm$ 352 (logε 4.34), 451 (5.03), 562sh (3.79), 604 (3.90), 695 (3.79), 726sh (3.74); δ_H(400 MHz; $CDCl_3$) −0.95 (2 H, br s, inner NH), 1.48 (36 H, s, *t*-butyl H), 1.54 (36 H, s, *t*-butyl H), 7.78–7.83 (4 H, m, quinoxaline H), 7.84 (2 H, t, *J* 1.7 Hz, H_p), 7.87 (2 H, t, *J* 1.7 Hz, H_p), 8.01 (4 H, d, *J* 1.7 Hz, H_o), 8.02 (4 H, d, *J* 1.8 Hz, H_o), 8.66 (2 H, s, β-pyrrolic H), 8.89 (2 H, s, β-pyrrolic H); *m*/*z* (ESI) 1255.8 ($[M + H]^+$ requires 1255.7).

5,10,15,20-Tetrakis(3,5-di-tert-butylphenyl)trisquinoxalino-[2,3-b′:7,8-b″:12,13-b‴]porphyrin **1**. A solution of dinitro-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*′]porphyrins **24** (1.38 g, 1.10 mmol) in a HCl–ether mixture (4 M, 150 ml) was stirred with tin(II) chloride dihydrate (2.5 g, 11.1 mmol) in the dark for 3 h. Work-up of the reaction mixture afforded diamino-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*′]-porphyrin isomers **25**. The mixture **25** was dissolved in CH_2Cl_2 (2 L) and photooxidised for 2 h. The residue afforded an inseparable mixture of amino-quinoxalinoporphyrin-dione **26** [*m*/*z* (MALDI-TOF) 1211.3 ($[M + H]^+$ requires 1210.8)] and quinoxalinoporphyrin-tetraone **27** [*m*/*z* (MALDI-TOF) 1226.2 ($[M + H]^+$ requires 1225.7)]. The reaction products and 1,2-diaminobenzene (810 mg, 7.49 mmol) in CH_2Cl_2 (60 ml) were stirred for 20 min. The solvent was removed and the crude mixture was purified by column chromatography over silica ($CHCl_3$–light petroleum 1 : 1). The front running brown band was collected and gave a linear 7-amino-5,10,15,20-tetrakis-(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]porphyrin **21** (90 mg, 6%) as a brown microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation ($CHCl_3$–MeOH); (HR-ESI-FT/ICR found: $[M+H]^+$ 1282.8047. $C_{88}H_{100}N_9$ requires 1282.8098); $\nu_{max}(CHCl_3)/cm^{-1}$ 3492w (NH_2), 3376w (NH), 3024m, 2960s, 2927s, 2871s, 1609w, 1594m, 1549m, 1463s, 1361m; $\lambda_{max}(CHCl_3)/nm$ 349 (logε 4.54), 408 (4.96), 464 (5.17), 546 (4.22), 587 (3.82), 619 (4.03), 677 (4.26); δ_H(400 MHz; $CDCl_3$) −2.77 (1 H, d, *J* 2.0 Hz, inner NH), −2.02 (1 H, s, inner NH), 1.48 (18 H, s, *t*-butyl H), 1.49 (54 H, s, *t*-butyl H), 4.81 (2 H, br s, amine H), 7.70–7.75 (5 H, m, quinoxaline H), 7.78–7.84 (3 H, m, quinoxaline H), 7.92 (1 H, t, *J* 1.8 Hz, H_p), 7.93–7.98 (8 H, m, H_o, H_p), 8.01 (1 H, t, *J* 1.8 Hz, H_p), 8.02 (2 H, d, *J* 1.7 Hz, H_p), 8.06 (1 H, d, *J* 2.4 Hz, β-pyrrolic H), 8.96 (1 H, dd, A of ABq, *J* 4.8, J_{NH} 1.8 Hz, β-pyrrolic H) and 9.00 (1 H, dd, B of ABq, *J* 4.8, J_{NH} 1.8 Hz, β-pyrrolic H); *m*/*z* (ESI) 1282.9 ($[M + H]^+$ requires 1282.8); (*m*/*z*) (MALDI-TOF) 1282.7 ($[M + H]^+$ requires 1282.8).

The second green band was collected to give 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)trisquinoxalino[2,3-*b*′:7,8-*b*″:12,13-*b*‴]porphyrin **1** (150 mg, 10%) as a green microcrystalline solid, mp > 300 °C, which co-chromatographed with an authentic sample prepared previously.

Synthesis of 7,8-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]chlorin 22. The 7-amino-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]porphyrin **21** (17.0 mg, 0.0133 mmol), isolated in the previous procedure, was dissolved in CH_2Cl_2 (500 ml) and subjected to further photoirradiation for 4 h. The reaction was monitored by TLC analysis, and when no starting material remained the solvent was removed under vacuum and the residue was purified by chromatography over silica ($CHCl_3$–light petroleum 1 : 1). The major red brown band was collected and evaporated to yield 7,8-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]-chlorin **22** (4.0 mg, 23%) as a black microcrystalline solid, mp > 300 °C. An analytically pure sample was obtained by recrystallisation (CH_2Cl_2–acetonitrile); (ESI-HRMS found: $[M+H]^+$ 1297.774. $C_{88}H_{97}N_8O_2$ requires 1297.773); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400w (NH), 3024s, 3017s, 3012w, 3004w, 2961s, 2929s, 2858m, 1725s (CO), 1598s; $\lambda_{max}(CHCl_3)/nm$ 348 ((logε 4.45), 405 (4.59), 454sh (4.48), 495sh (4.23), 532 (4.22), 620 (3.59), 677 (3.72), 767 (3.47); δ_H(400 MHz; $CDCl_3$) 1.37 (36 H, s, *t*-butyl H), 1.41 (36 H, s, *t*-butyl H), 4,49 (2 H, br s, inner NH), 7.43 (4 H, d, *J* 1.7 Hz, H_o), 7.55–7.58 (4 H, m, quinoxaline H), 7.60–7.66 (8 H, m, quinoxaline H, H_o), 7.75 (2 H, t, *J* 1.7 Hz, H_p), 7.79 (2 H, t, *J* 1.8 Hz, H_p), 7.81 (2 H, s, β-pyrrolic H); *m*/*z* (ESI) 1297.7 ($[M+H]^+$ requires 1297.8).

Conversion of 7,8-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]chlorin 22 to 1. 7,8-Dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bisquinoxalino[2,3-*b*′:12,13-*b*″]porphyrin **22** (11.0 mg, 8.48 μmol) and 1,2-diaminobenzene (43.0 mg, 0.397 mmol) in CH_2Cl_2 (10 ml) were stirred at room temperature for 1 min. The solvent was removed under vacuum and the crude mixture was passed through a plug of silica (CH_2Cl_2–light petroleum 1 : 1). The front running green band was collected and evaporated to dryness to give 5,10,

15,20-tetrakis(3,5-di-*tert*-butylphenyl)trisquinoxalino[2,3-*b*′:7,8-*b*″:12,13-*b*‴]porphyrin **1** (9.0 mg, 77%) as a green microcrystalline solid, mp > 300 °C, which co-chromatographed with an authentic sample prepared in the previous procedure.

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