Journal of Porphyrins and Phthalocyanines J. Porphyrins Phthalocyanines 2010; **14**: 481–493 DOI: 10.1142/S1088424610002318



# Azo-linked corner porphyrin systems: synthesis, crystal structures and spectroscopic investigation

## Bruno Bašić, John C. McMurtrie and Dennis P. Arnold\*<sup>0</sup>

Discipline of Chemistry, Faculty of Science and Technology, Queensland University of Technology, G.P.O. Box 2434, Brisbane 4001, Australia

Received 9 November 2009 Accepted 25 January 2010

> **ABSTRACT:** 1,2-bis[10,15-di(3,5-di-*tert*-butyl)phenylporphyrinatonickel(II)-5-yl]diazene was synthesised *via* copper-catalyzed coupling of aminated nickel(II) 5,10-diarylporphyrin ("corner porphyrin") and its X-ray crystal structure was determined. Two different crystals yielded different structures, one with the free *meso*-positions in a *trans*-like orientation, and the other with a *cis*-like disposition. The free *meso*-positions of the obtained dimer have been further functionalized while the synthesis of a zinc analog has so far been unsuccessful. The X-ray crystal structure of the dinitro derivative of the dinickel(II) azoporphyrin was determined, and the structure showed a *cis*-like disposition of the nitro groups.

KEYWORDS: azo bridge, azoporphyrin, corner porphyrin, crystal structure, dimer.

#### INTRODUCTION

Since the crystal structure of the light-harvesting antenna complex LH2 of *Rhodopseudomonas acidophila* was elucidated [1–3], efforts have been made to synthesize a diverse range of cyclic porphyrin oligomers (CPOs) with the aim of studying excitation energy transfer (EET) and creating analogs of natural light-harvesting antennae. However, CPOs have been investigated in other fields such as host-guest chemistry and single-molecule photochemistry [4].

While porphyrin systems linked by covalent bonds are the most robust, they are also difficult to make and so systems linked by metal coordination bonds, which rely to a large degree on the nitrogen atom-metal coordination bond, as well as systems involving non-covalent bonds, have also been explored [4–8]. Though the environment will influence all of these systems, the non-covalently linked porphyrins are more affected by solvents while porphyrin systems involving coordination bonds will be affected by coordinating solvents as well as by the presence of competing coordinating compounds.

The use of porphyrins as monomers for larger structures is not a new field. However, the investigation of linker groups, their properties and their overall effect on the resulting molecule is a developing area. The linker groups of special interest are those that do not interrupt the conjugation of the porphyrin macrocycle but rather extend the overall conjugation of the entire system. The first such conjugated porphyrin system was a butadiynelinked dimer [9]. Since then porphyrin systems that would offer the best electronic communication through their conjugated linkers have been investigated [4, 10-13]. The butadiyne and other linkers have been studied extensively, with numerous papers reporting interesting results with justified promise of potential in various fields [4, 13–19]. Theoretical work suggested that an azo linkage will provide the optimum degree of interporphyrin conjugation and thus quite possibly the best bridge for electronic communication between the porphyrins [17].

The Arnold group reported the copper-promoted synthesis of the first azoporphyrins from 5,10,15-triaryl substituted and 5,15-diaryl substituted porphyrins [20]. Here, we present an extension of that work to include the 5,10-diaryl substituted porphyrin (corner porphyrin). Our

<sup>&</sup>lt;sup>◊</sup>SPP full member in good standing

<sup>\*</sup>Correspondence to: Dennis P. Arnold, email: d.arnold@qut. edu.au, fax: +61 7-3138-1804



Fig. 1. Proposed azo-linked tetramers

objective was the synthesis of more ambitious azo-linked porphyrin systems. The initial goal was to synthesize an azo-linked dimer that would still have two meso-positions left available for further modification. We chose to use the corner porphyrin as our starting material. Though the synthesis of 5,10-DAP is harder than the synthesis of 5,15-DAP with notably lower yields, we felt that a successfully synthesized azo-linked dimer made of two corner porphyrin units would not only extend the family of known azo-linked compounds but would also allow us to explore a more diverse range of porphyrin systems. In particular, we are interested in preparing new CPOs. Furthermore, for the purposes of molecular electronics and nonlinear optics, we are interested in those CPOs in which ground-state electronic interaction between the linked porphyrins is substantial [21].

Inspired by work done elsewhere [4, 21] the research presented here aims towards the synthesis of cyclic azolinked tetramers (Fig. 1). Tetramer **A** would be the azo analog of the known butadiyne-linked cyclic porphyrin system [21] while **B** would be a system that uses both butadiyne and azo bridges, thus extending the synthesis possibilities for both linkers.

## **RESULTS AND DISCUSSION**

To approach the synthesis of tetramer **A**, we decided first to try the synthesis of an azo-linked dimer that would be further modified and then self-coupled to form the target compound. The synthesis of compounds **2**, **3** and **4** followed the methods used for the synthesis of analogous 5,15-diaryl substituted porphyrins [22]. All three compounds are obtained in good yields and the crude product of each can be used in subsequent steps. This is fortuitous as the recrystallization of **3** and particularly **4** has proved difficult due to high solubility of these compounds. Following the Cu(OAc)<sub>2</sub> method established by our group [20], compound **4** was successfully coupled to form the azo-bridged dimer **5** in 66% yield (Scheme 1). Aside from being the first azo-linked dimer made up of two corner porphyrin units, this dimer also has two free *meso*positions that could be further modified. Using the same  $AgNO_2/I_2$  method used for nitration of the monomer we attempted to nitrate the dimer. On a 5 mg scale the only product was the *meso* dinitrated dimer **6** in almost quantitative yield. However, the result was not reproducible when the scale was increased. The main outcome was the destruction of the dimer where, strangely enough, the unsubstituted Ni corner porphyrin **12** and the *meso* dinitrated monomer **13** were obtained together with some compound **6** and the mononitrated dimer **7**. This was the first indication that the azo link may not be as strong as we had thought it would be.

Although 6 was not available in great quantities we tried to reduce the nitro groups to amino groups using sodium borohydride and 10% palladium on carbon, mimicking the route in which 4 was obtained from 3. We considered the synthesis of an azo-linked dimer with amino groups on the remaining meso-positions a precursor to A as we further expected to induce the aminated dimer to self-couple. There was of course the possibility of creating an open oligomer rather than a closed cyclic tetramer system. However, we wished to investigate those linear systems, too, and explore reaction conditions that would give one but not the other. The result of the attempted reduction of the nitro groups was a complete loss of starting material in favour of unidentified non-porphyrinic compounds. Thus, once again we observed the azo-linked porphyrin dimer's apparent instability. Next, we tried to brominate the dimer using the same NBS method used for the bromination of monomer porphyrins [22]. We wanted to create a brominated dimer that would lend itself to the introduction of alkynyl groups. From there we thought tetramer **B** could be obtained through self-coupling as well as opening up various other substitution reactions. However, though 8



**Scheme 1.** Synthesis of azo-linked Ni corner porphyrin dimers: (i) 0.75 eq. I<sub>2</sub>, 1.5 eq. AgNO<sub>2</sub>, DCM/MeCN; (ii) Ni(acac)<sub>2</sub>, toluene 120 °C; (iii) 10% Pd on C, 25 eq. NaBH<sub>4</sub>, DCM/MeOH; (iv) 12 mol.% Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, 4 eq. pyridine, toluene 80 °C; (v) 1.5 eq. I2, 3 eq. AgNO<sub>2</sub>, DCM/MeCN; (vi) 2.5 eq. NBS, CHCl<sub>3</sub>/pyridine. Ar = 3,5-di-*tert*-butylphenyl

Compound		-			•		-		
	2-H	3-H	7-H	8-H	12-Н	13-Н	17-H	18-H	20-Н
5	9.27	10.15	10.08	8.99	8.73	8.71	8.83	9.01	9.71
6	8.95	9.88	9.98	9.40	9.11	8.79	8.67	8.65	N/A
8	8.90	9.91	9.97	9.90	9.35	8.71	8.63	8.61	N/A

was obtained, the yield was low and the reaction has not proven reproducible.

The <sup>1</sup>H NMR spectra of the azo compounds (5, 6 and 8) showed eight  $\beta$  peaks that were shifted significantly downfield (Table 1). The former is attributed to a lack of symmetry of the porphyrin macrocycles and the downfield shift to the presence of an electron-withdrawing group on the adjacent *meso*-positions.

The absorption spectra of the synthesized azo-linked dimers (Fig. 2) include a large split in the Soret band and red-shift of the Q bands. These features are commonly observed in porphyrin dimers linked with conjugated bridges and are also very similar to the features of the first azo-linked porphyrin dimer [20]. The overall red-shift of the absorption bands relative to other porphyrins is indicative of an efficient  $\pi$ -overlap between the porphyrin moieties [17].

Single crystals of **5** were grown from DCM/methanol, and the structures were solved by X-ray crystallographic analysis (Figs 3–5). For compound **5** two structures



Fig. 2. Electronic absorption spectra of azo-linked compounds: 5 (solid), 6 (dotted) and 7 (dashed)

were solved, namely **5a** and **5b**. The unsubstituted *meso*positions of the two porphyrin rings are in a *trans*-like relation to one another in **5a** and *cis*-like in **5b**. Pertinent geometric data for the porphyrin rings and their relative





**Fig. 3.** Crystal structure of **5a** shown from two different perspectives: (a) orthogonal to the mean planes of the porphyrin rings; (b) parallel to the mean planes. The side view (b) shows the distortion of the rings and the displacement of the planes of the rings with respect to each other. The porphyrin rings are ruffled but lie in parallel planes displaced by 2.35 Å



**Fig. 4.** Crystal structure of **5b** shown from two different perspectives: (a) orthogonal to the mean planes of the porphyrin rings; (b) parallel to the mean planes. The side view (b) shows the distortion of the rings and the displacement of the planes of the rings with respect to each other. The porphyrin rings are ruffled but lie in approximately parallel planes displaced by *ca.* 2.98 Å

conformational arrangements in each of the structures are provided in Table 3. All three structures bear resemblance to the first azo-bridged porphyrin structure [20].

In all three structures the porphyrin rings are significantly distorted from planarity. The *meso* carbon atoms

**Fig. 5.** Crystal structure of **6** shown orthogonal to the mean planes of the porphyrin rings. The two molecules (a) and (b) in the asymmetric unit of **6** both have the *cis*-like arrangement of the *meso* nitro groups

of the rings are farthest from the mean plane of the  $C_{20}N_4Ni$  porphyrin atoms in the arrangement described in the literature as "ruffled" [23]. The perpendicular distances of the *meso* carbon atoms from the  $C_{20}N_4Ni$  mean plane range between 0.319 Å and 0.778 Å across all the porphyrin rings in the three structures. These displacements are the best indicator of the extent of the distortion of the porphyrin. The coordination sphere (N<sub>4</sub>Ni) in each porphyrin is almost perfectly square planar. In each case the N<sub>4</sub>Ni plane is almost coincident with the mean  $C_{20}N_4Ni$  plane. The dihedral angles range between 0.62° and 1.47°. The maximum displacement for the nickel atoms from the mean plane of their respective  $C_{20}N_4Ni$ 

A key feature of interest in the structures is the relative orientation of the porphyrin rings with respect to each other. In 5a the unsubstituted meso carbon atoms (C5 and C5') are arranged in a *trans*-like fashion. In contrast to this the unsubstituted meso carbon atoms (C5 and C53) in **5b** and the nitro substituted *meso* carbon atoms (C5 and C53 in molecule 1 and C101 and C149 in molecule 2) of 6 are arranged in the *cis*-like position. Interestingly, the ruffling of porphyrin rings in the trans-like structure (5a) with an average  $C_{meso}$  displacement 0.40 Å is significantly less than that observed in the *cis*-like structures (**5b** and **6**) with an average  $C_{meso}$  displacement 0.56 Å for **5b** and 0.64 Å for **6**. Intuition based on intramolecular steric considerations suggests that the trans arrangement should be more favorable. However, the 3,5-di-tert-butylphenyl rings through which steric interference is possible are well separated in space with 11 Å

Complex	5a	5b	6		
Formula	$C_{98.5}H_{102}Cl_5N_{10}Ni_2$	$C_{96}H_{102}N_{10}Ni_2$	$C_{96}H_{100}N_{12}Ni_2O_4$		
Μ	1725.61	1513.30	1603.30		
Crystal system	triclinic	triclinic	triclinic		
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$		
<i>a</i> , Å	11.2769(5)	16.0280(9)	19.021(2)		
$b, \mathrm{\AA}$	12.4229(9)	17.4993(11)	22.330(2)		
c, Å	16.2387(9)	18.7205(11)	26.717(3)		
α, °	100.427(5)	114.691(2)	111.974(10)		
β, °	92.641(4)	95.295(2)	102.900(9)		
γ, °	97.123(5)	99.510(2)	96.223(9)		
$V, Å^3$	2214.6(2)	4628.2(5)	10023.6(19)		
$D_{\rm c}$ , g cm <sup>-3</sup>	1.294	1.086	1.062		
Ζ	1	2	4		
Color	purple/green	purple/green	purple		
Habit	prism	prism	prism		
Dimensions, mm	$0.68 \times 0.32 \times 0.14$	$0.10\times0.09\times0.04$	$0.14 \times 0.12 \times 0.03$		
$\mu(MoK\alpha), mm^{-1}$	0.629	0.454	0.426		
$T_{\min,\max}$	0.769, 1.000	0.824, 1.000	0.518, 1.000		
$N_{\rm ind} \left( R_{\rm int} \right)$	14643 (0.0451)	16316 (0.0591)	32722 (0.2113)		
$N_{\rm obs}$ - $(I > 2\sigma(I))$	8572	10541	6924		
$N_{ m var}$	534	979	919		
$R1^{a}$ , $wR2^{a}$	0.0720, 0.1659	0.0621, 0.2031	0.1345		
A, B	0.02, 5	0.08, 8	0.08, 1		
GoF	1.062	1.183	1.027		
$\Delta \rho_{min,max}$ , e <sup>-</sup> Å <sup>-3</sup>	~1.312, 1.001	~0.767, 1.083	~0.656, 0.947		

Table 2. Crystal data for 5a, 5b and 6

<sup>a</sup> Reflections with  $[I > 2\sigma(I)]$  considered observed.  $R1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$  for  $F_o > 2\sigma(F_o)$  and  $wR2_{(all)} = {\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]}^{1/2}$  where  $w = 1/[\sigma^2(F_o^2) + (\mathbf{A}P)^2 + \mathbf{B}P]$ ,  $P = (F_o^2 + 2F_c^2)/3$ .

between planes of 3,5-di-*tert*-butylphenyl rings and are thus unlikely to contribute significantly to steric instability in the *cis*-like arrangement. Interestingly, the azolinked porphyrin in the *trans*-like structure (**5a**) has porphyrin rings arranged such that their respective mean  $C_{20}N_4Ni$  planes are exactly co-planar and separated by approximately 2.35 Å. This was estimated by the perpendicular displacement of the Ni atom associated with one ring with the mean plane of the other. In the case of the *cis*-like structures there is a significant twist from co-planarity of the azo-bridged porphyrin rings with a 17.9° dihedral angle between  $C_{20}N_4Ni$  planes in **5b** and 22.93° and 22.13° in the two molecules of the asymmetric unit in **6**.

The occurrence of both the *trans*-like and *cis*-like forms of the molecules in different crystals clearly suggests that both forms exist in the solution phase. The *cis*like arrangement is required for creation of molecular squares and while the presence of the molecules in this configuration in crystals is not confirmation that it is the most favored arrangement, the fact that it can and does occur in crystals is strong evidence that it exists to some extent in solution and that the production of a molecular square is therefore possible.

The dihedral angles between the azo bridge (C-N=N-C) and the mean planes of the porphyrin rings are a measure of out-of-plane twist which, in turn, limits the potential for electronic communication. The *trans*-like structure **5a** has an out-of-plane twist of  $36.94^{\circ}$  which is virtually identical to that observed for the first azoporphyrin previously synthesized by the Arnold group [20]. There are two such measurements in **5b** and **6** resulting from the lack of molecular symmetry. In **5b**, the dihedral angles are  $30.65^{\circ}$  and  $42.31^{\circ}$ . In **6**, the angles are  $24^{\circ}$  and  $36^{\circ}$  for one molecule and  $23^{\circ}$  and  $38^{\circ}$  for the other. It is possible that the lower out-of-plane twist in **6** could lead to more efficient electronic communication.

Table 3. Geometric details for structures 5a, 5b and 6

Geometric parameter (Å or °)	5a	5b		6				
Porphyrin ring associated with	Ni1	Ni(1)	Ni(2)	Ni(1)	Ni(2)	Ni(3)	Ni(4)	
Ruffle	(Ni1')							
	0.319	0.439	0.602	0.674	0.633	0.640	0.778	
$C_{20}N_4Ni_{plane}$ - $C5_{meso}{}^a$			(C53)	(C5)	(C53)	(C101)	(C149)	
$C_{20}N_4Ni_{plane}$ - $C10_{meso}$ <sup>a</sup>	-0.369	-0.406	-0.614	-0.700	-0.444	-0.523	-0.666	
			(C58)	(C6)	(C58)	(C106)	(C154)	
C <sub>20</sub> N <sub>4</sub> Ni <sub>plane</sub> - C15 <sub>meso</sub> <sup>a</sup>	0.420	0.514	0.627	0.698	0.512	0.450	0.693	
			(C63)	(C15)	(C63)	(C111)	(C159)	
C <sub>20</sub> N <sub>4</sub> Ni <sub>plane</sub> - C20 <sub>meso</sub> <sup>a</sup>	-0.478	-0.575	-0.720	-0.733	-0.687	-0.614	-0.804	
			(C68)	(C20)	(C68)	(C116)	(C164)	
$\angle C_{20}N_4Ni_{plane}$ - $N_4Ni_{plane}^{\ b}$	0.92°	1.36°	0.62°	0.77°	$0.88^{\circ}$	1.47°	0.79°	
$C_{20}N_4Ni(a)_{plane}$ - $Ni(a)$ ( $\perp$ ) <sup>b</sup>	0.055	0.027	0.013	0.019	0.026	0.033	0.049	
$\angle C_{20}N_4Ni(a)_{plane}$ - $C_{20}N_4Ni(b)_{plane}$	0	17.90°		22.93°		22.13°		
$C_{20}N_4Ni(a)_{plane}$ - $Ni(b)$ ( $\perp$ ) <sup>d</sup>	2.351	2.794 (a = 1, b = 2)		3.169 (a = 1, b = 2)		3.318 (a = 3, b = 4)		
$C_{20}N_4Ni(b)_{plane}$ - $Ni(a)$ $(\perp)^d$	2.351	3.158 (a = 2, b = 1)		3.122 (a = 2, b = 1)		2.883 (a = 4, b = 3)		
$\angle C_{20}N_4Ni(a)_{plane}$ - CN=NC <sub>plane</sub> <sup>e</sup>	36.94°	42.31°		24.65°		38.34°		
$\angle C_{20}N_4Ni(b)_{plane}$ - CN=NC <sub>plane</sub> <sup>e</sup>	36.94°	30.65		36.15°		22.59°		

<sup>a</sup> The perpendicular distance of the respective *meso* carbon atoms from the mean plane of the porphyrin is indicative of the ruffled type [23] and degree of distortion from planarity. <sup>b</sup> The dihedral angles between the mean plane of the porphyrin and the mean plane of the coordination sphere combined with the perpendicular displacement of the Ni atom from that ring is indicative of the average distortion of the porphyrin with respect to the square planar coordination environment. <sup>c</sup> The dihedral angle between the mean planes of the two porphyrins in each azo-bridged molecule is a measure of the deviation from coplanarity of the two porphyrin components in each azo-bridged molecule. This is an estimate of the spatial displacement. <sup>e</sup> The dihedral angles between the porphyrin rings and the CN=NC atoms of the azo bridge are indicative of out-of-plane twist of the azo bridge connecting the two porphyrins. In general, the smaller this angle the greater the potential for electronic communication across the azo bridge.

We have also tried to synthesize zinc and free-base azo-linked dimers (Scheme 2). The Zn amino monomer 10 was made from 9 in very good yield but the copperpromoted self-coupling reaction yielded a non-porphyrinic material. The free-base aminated monomer 11 was created from 2 in good yield but the subsequent self-coupling gave only very little of the dimer which had copper in the porphyrin cores as well as some starting material with copper inserted. This was not unexpected as the conditions of the copper-catalyzed self-coupling reaction are similar to those needed to metalate the porphyrin with the copper. Interestingly, no free-base porphyrins were isolated even though only 30 mol.% of copper(II) acetate was used. Due to the paramagnetic nature of the copper <sup>1</sup>H NMR spectra were not obtained and the positive identification of the compounds was supported by MS and UV-vis analysis. These results led us to consider the possibility that the synthesis of the desired tetramers would have to use a route that did not include linking of preformed azo-linked dimers.

It should be briefly noted that compound **10** can also be obtained quantitatively from **11** and vice versa by metalation and acid-assisted demetalation, respectively.

In order to obtain A there was the option of attempting to synthesize 5,10-diamino substituted porphyrin and then using it to create the tetramer *via* the same reaction conditions used for the synthesis of the azo-linked dimer. The reason we did not go this way is we expected the diaminated porphyrin to be unstable and we needed a reliable route towards a 5,10-dinitro substituted porphyrin. Initially we tried to obtain it by modifying the  $AgNO_2/I_2$  method used for 2. However, that proved fruitless as we only ever obtained 2. We then turned to a different method of nitration using nitric acid [24]. After inserting nickel into 1 thus giving 12, 13 was obtained reliably and in very good yield by using 30% HNO<sub>3</sub> in chloroform. The compound proved to be very soluble and so the crude product (pure by <sup>1</sup>H NMR) was used to make 14 (Scheme 3). As we predicted, 14 was difficult to handle as it was very soluble and not very stable. A clear <sup>1</sup>H NMR spectrum was obtained only when the sample was cooled to -50 °C. The presence of amino groups was verified by ATR infrared spectrum while the MS analysis supported the conclusion of a successful synthesis. Compound 14 was then used to attempt synthesis of A via the route used for the synthesis of the azo-linked



Scheme 2. Synthesis of Zn aminoporphyrin 10 and free-base aminoporphyrin 11: (i)  $Zn(OAc)_2$ , chloroform 60 °C; (ii) 10% Pd on C, 10 eq. NaBH<sub>4</sub>, DCM/MeOH; (iii) 10% Pd on C, 4 eq. NaBH<sub>4</sub>, DCM/MeOH. Ar = 3,5-di-*tert*-butylphenyl



Scheme 3. Synthesis of Ni diaminoporphyrin 14: (i) Ni(acac)<sub>2</sub>, toluene 120 °C; (ii) 30% HNO<sub>3</sub>, CHCl<sub>3</sub>; (iii) 10% Pd on C, 4 eq. NaBH<sub>4</sub>, DCM/MeOH. Ar = 3,5-di-*tert*-butylphenyl

dimer, namely  $Cu(OAc)_2$  catalyzed coupling. Unfortunately, the attempts have not been successful and **A** has remained elusive. The reaction involving **14** resulted in loss of starting material in favor of very polar unidentified non-porphyrinic substances. As yet, we are unsure whether this is due to the instability of **14** or because **A** may simply not be viable. We have explored a range of approaches towards production of cyclic tetramer **B** with interesting outcomes and expect to report these experiments in the near future.

## EXPERIMENTAL

#### General

All reported synthetic work was performed at the Queensland University of Technology, Brisbane, Australia. All chemicals used were of analytical reagent grade and were purchased from Sigma-Aldrich. Solvents were evaporated under reduced pressure at 40 °C. Analytical TLC was performed using Merck Silica Gel 60 F254

plates. For preparative column chromatography, Merck silica gel (230-400 mesh) was used. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a Bruker Avance 400 MHz instrument. Samples were prepared in deuterated chloroform (CDCl<sub>3</sub>), unless stated otherwise. The chemical shifts are reported in ppm and referenced against the residual chloroform (CHCl<sub>3</sub>) peak at 7.26 ppm for <sup>1</sup>H NMR and CDCl<sub>3</sub> at 77.16 ppm for <sup>13</sup>C NMR. Coupling constants are given in Hz. The UV-visible spectra were recorded in dichloromethane (DCM) on a Varian Cary 50 instrument. Liquid Secondary Ion (LSI) and Electrospray Ionisation (ESI) mass spectra were recorded at the Organic Mass Spectrometry Facility, University of Tasmania, Hobart. LSIMS data were obtained on a Kratos ISQ double-focusing magnetic sector mass spectrometer using a direct insertion probe and fitted with an LSIMS ion source, using 10KV cesium ions as the primary beam, and *m*-nitrobenzyl alcohol as the liquid matrix. ESI mass spectra were obtained on a Thermo Electron LTQ Orbitrap mass spectrometer. Samples were dissolved in dichloromethane and then diluted 1/100 in methanol before being infused into the mass spectrometer at a flow rate of 50  $\mu$ L/min. A voltage of 4500 V was applied at the tip. The IR spectra were collected using a Nicolet 870 Nexus Fourier transform infrared (FTIR) system equipped with an attenuated total internal reflectance (ATR) accessory with a single-bounce diamond cell.

Reflection data for 5b were collected at 150(2) K using an APEX II-FR591 diffractometer employing graphite-monochromated Mo-Ka radiation generated from a rotating anode (0.71073 Å). Data integration and reduction were undertaken with SAINT and XPREP [25]. A multi-scan empirical absorption correction was applied using SADABS [26]. Reflection data for 5a and 6 were collected under the software control of CrysAlis CCD [27] at 173(2) K on an Oxford Diffraction Gemini Ultra diffractometer using Mo-Ka radiation generated from a sealed tube. Data reduction was performed using CrysAlis RED [27]. Multi-scan empirical absorption corrections were applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm, within CrysAlis RED [27]. Subsequent computations for all structures were carried out using the WinGX-32 graphical user interface [28].

The structures were solved by direct methods using SIR97 [29] and then refined with SHELXL-97 [30]. Ordered non-hydrogen atoms were refined anisotropically for 5b and 6. Hydrogen atoms attached to carbon atoms were included in idealized positions and refined using a riding model. All three structures are triclinic with symmetry  $P\overline{1}$ . Interestingly each one has a different Z value. In 5a the asymmetric unit comprises half of the azo-bridged dimer which has crystallographic inversion symmetry (Z = 1). The asymmetric unit in **5b** comprises one complete azo-bridged dimer (Z = 2) and in 6 the azo-bridged dimer comprises two full crystallographically distinct azo-bridged dimers (Z = 4). Crystal data and refinement details (presented left to right in order of decreasing symmetry) are reported in Table 2. Depictions of the molecular structures are provided in Figs 3–5.

#### Synthesis

2,5-bis(hydroxymethyl)pyrrole [31]. Potassium carbonate (62 g, 0.485 mol) was dissolved in deionized water (200 mL) in a 1 dm<sup>3</sup> round-bottomed flask. The solution was stirred in a cold water bath at 5 °C while being bubbled with argon for 30 min. Formalin (40%, 105 mL, 0.485 mol) and freshly distilled pyrrole (17 mL, 0.240 mol) were added. The resulting solution was bubbled with argon for a further 15 min and then the flask was sealed and shielded from light. The mixture was stirred for 7 days at 5 °C. The colorless solution was evaporated, leaving a white slurry. To this acetone (300 mL) was added. The potassium carbonate precipitated out and was filtered off and washed with acetone  $(3 \times 100)$ mL). To the collected solution anhydrous sodium sulfate (300 g) was added. The solution was shielded from light, sealed, and left in the fridge for 2 h. Sodium sulfate was

filtered off and the acetone evaporated, leaving behind a slightly orange oil. The oil was placed in the freezer. After one day white crystals formed. They were filtered off and washed with ice-cold acetone. The mother liquor was collected, the acetone evaporated and the oil stored in the freezer again. This process was repeated until the oil stopped yielding crystals. Yield 9.8% (32%). <sup>1</sup>H NMR (400 MHz; DMSO-d<sub>6</sub>):  $\delta_{\rm H}$ , ppm 10.52 (bs, 1H, NH), 5.77 (s, 2H,  $\beta$ -H), 4.76 (bs, 2H, OH), 4.33 (s, 4H, CH<sub>2</sub>).

Tripyrrane [31]. Deionized water (700 mL) was placed into a 1 dm<sup>3</sup> round bottomed flask. The flask was shielded from light and the water was stirred at 5 °C while being bubbled with argon for 30 min. 2,5-bis(hydroxymethyl) pyrrole (5 g, 0.039 mol) was added followed by pyrrole (26.9 mL, 0.39 mol) 10 min later. After 30 min the bubbling with argon was stopped and concentrated hydrochloric acid (0.5 mL) was added. The solution became a white emulsion that was stirred for a further 30 min. It was then neutralized with sodium bicarbonate (15 mL). The emulsion was stirred for a further 5 min. The product was extracted in DCM ( $3 \times 150$  mL). The solvent was removed and the oil was purified by column chromatography using DCM/TEA (100:1) as eluent. Collection of the desired fraction was monitored by TLC. The solvent was removed, leaving a yellow-white solid that was dried under vacuum and stored under argon in the freezer. Yield: 2.93 g (33%). <sup>1</sup>H NMR (400 MHz; DMSO-d<sub>6</sub>):  $\delta_{\rm H}$ , ppm 7.91 (bs, 2H, NH), 7.64 (bs, 1H, NH), 6.66 (m, 2H, 1,14-H), 6.14 (m, 2H, 2,13-H), 5.98 (bs, 2H, 3,12-H), 5.92 (m, 2H, 7,8-H), 3.90 (s, 4H, 5,5',10,10'-H).

5,10-bis(3,5-di-*tert*-butylphenyl)porphyrin (1) [21, 32]. To a 1 dm<sup>3</sup> round-bottomed flask DCM (300 mL) was added which was then bubbled with argon for 30 min. Tripyrrane (270 mg,  $1.20 \times 10^{-3}$  mol), followed by 3,5-di-*tert*-butylbenzaldehyde (524 mg,  $2.4 \times 10^{-3}$  mol), pyrrole (83  $\mu$ L, 1.2 × 10<sup>-3</sup> mol) and TFA (55  $\mu$ L,  $7.2 \times 10^{-4}$  mol) were added. The solution was stirred at room temperature for 3.5 h. DDQ (708 mg,  $3.13 \times 10^{-3}$ mol) was added and stirring continued for a further 30 min. The solution was neutralized with TEA (1 mL) and stirred for an additional 5 min. The solvent was evaporated, leaving a dark purple residue that was purified by column chromatography using DCM/hexane (1:2) as eluent. A single dark-red fraction was obtained. The solvent was evaporated once more, leaving a purple residue. It was recrystallized from DCM/methanol. The recrystallized product was dark-purple shiny needle-like crystals. Yield: 66 mg (8%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 10.22 (s, 2H, 15,20-H), 9.46 (s, 2H, 17,18-H), 9.35 (d, J 4.9 Hz, 2H, 2,13-H), 9.08 (d, J = 4.9 Hz, 2H, 3,12-H), 8.99 (s, 2H, 7,8-H), 8.10 (d, J = 2.0 Hz, 4H, o-H<sub>arvl</sub>), 7.82 (t, J = 2.0 Hz, 2H, p-H<sub>aryl</sub>), 1.56 (s, 36H, <sup>t</sup>Bu-H), -3.27 (bs, 2H, inner NH).

**10,15-bis(3,5-di***tert***-butylphenyl)-5-nitroporphyrin (2).** Compound **1** (357 mg,  $5.20 \times 10^{-4}$  mol) was dissolved in a DCM/acetonitrile solution (31.5 mL/31.5 mL) and stirred under argon for 10 min. The flask was shielded from light. Iodine (99 mg, 0.75 eq.,  $3.90 \times 10^{-4}$ mol) dissolved in DCM (12.5 mL) was added and the solution was stirred for 30 min. Silver nitrite (120 mg, 1.5 eq.,  $7.80 \times 10^{-4}$  mol) dissolved in acetonitrile (12.5 mL) was added. The starting material was consumed after 1.5 h. The solvents were evaporated, leaving a darkpurple solid which was redissolved in minimum amount of DCM and filtered through a cotton wool plug. The solvent was evaporated and the product recrystallized from DCM/methanol. The product was a grey-purple powder. Yield: 355 mg (93%), mp > 310 °C. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 10.22 (s, 1H, 20-H), 9.47 (d, J = 5.3Hz, 1H, 3-H), 9.41 (d, J = 5.3 Hz, 1H, 2-H), 9.35 (d, J = 5.2 Hz, 1H, 7-H), 9.27 (d, J = 5.0 Hz, 1H, 18-H), 9.02 (d, J = 5.0 Hz, 1H, 17-H), 9.00 (d, J = 5.2 Hz, 1H, 8-H), 8.91 (d, J = 5.3 Hz, 1H, 13-H), 8.84 (d, J = 5.3 Hz, 1H, 12-H), 8.05 (d, J = 1.8 Hz, 2H, o-H<sub>arvl</sub>), 8.02 (d, J= 1.8 Hz, 2H, o-H<sub>arvl</sub>), 7.83 (t, J = 1.8 Hz, 2H, p-H<sub>arvl</sub>), 1.54 (s, 18H, 'Bu-H), 1.53 (s, 18H, 'Bu-H), -2.71 (bs, 2H, inner NH). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta_{\rm C}$ , ppm 149.1, 148.9, 140.6, 140.0, 134.1, 133.7, 132.8, 132.2, 132.0, 131.0, 129.8, 129.6, 128.5, 127.5, 127.3, 125.9, 124.9, 121.7, 121.6, 107.2, 35.0, 31.7. UV-vis (DCM):  $\lambda_{max}$ , nm  $(\varepsilon, 10^3 \text{ M}^{-1} \text{ cm}^{-1})$  418 (149), 514 (9.16), 560 (7.80), 580 (6.45), 643 (4.31). MS (ESI): m/z 754.4098 (calcd. for  $C_{48}H_{53}N_5NaO_2 [M + Na]^+$  754.4097). IR (ATR): v, cm<sup>-1</sup> 1500s (NO<sub>2 asym</sub>), 1314s (NO<sub>2 sym</sub>).

[10,15-bis(3,5-di-tert-butylphenyl)-5-nitroporphy**rinato]nickel(II)** (3). Porphyrin 2 (354 mg,  $4.84 \times 10^{-4}$ mol) was dissolved in 15 mL of toluene and stirred. To this, Ni(acac)<sub>2</sub> (354 mg,  $1.38 \times 10^{-3}$  mol) was added. The mixture was refluxed for 2 h, after which the starting material was consumed. The product was purified by column chromatography using DCM/hexane (1:1) as eluent. A single red fraction was collected. The solvent was evaporated to give a red residue (yield: 382 mg (100%)) which was recrystallized from DCM/pentane to give a pale red powder. Yield: 218 mg (57%), mp > 310 °C.  $^{1}$ H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 9.84 (s, 1H, 20-H), 9.37 (d, J = 5.1 Hz, 1H, 3-H), 9.24 (d, J = 5.1 Hz, 1H, 7-H), 9.22 (d, J = 5.1 Hz, 1H, 2-H), 9.09 (d, J = 5.1 Hz, 1H, 18-H), 8.92 (d, J = 5.1 Hz, 1H, 8-H), 8.91 (d, J =5.1 Hz, 1H, 17-H), 8.81 (d, J = 5.1 Hz, 1H, 13-H), 8.78  $(d, J = 5.1 \text{ Hz}, 1\text{H}, 12\text{-H}), 7.85 (t, J = 2 \text{ Hz}, 2\text{H}, o\text{-H}_{arvl}),$ 7.83 (t, J = 2 Hz, 2H, o-H<sub>arvl</sub>), 7.75 (m, J = 1.9 Hz, 2H, *p*-H<sub>arvl</sub>), 1.48 (s, 18H, <sup>t</sup>Bu-H), 1.47 (s, 18H, <sup>t</sup>Bu-H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta_{\rm C}$ , ppm 149.1, 144.0, 143.8, 143.2, 143.0, 142.9, 142.7, 139.2, 139.1, 137.8, 137.5, 134.9, 134.4, 134.0, 133.5, 132.8, 132.3, 129.5, 128.7, 128.6, 126.3, 123.6, 123.0, 121.5, 106.5, 35.0, 31.7. UVvis (DCM):  $\lambda_{max}$ , nm ( $\epsilon$ , 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 411 (129), 528 (7.03), 565 (4.53). MS (ESI): m/z 810.3293, (calcd. for  $C_{48}H_{51}N_5NiNaO_2[M + Na]^+ 810.3294$ ). IR (ATR): v, cm<sup>-1</sup> 1498s (NO<sub>2 asym</sub>), 1314s (NO<sub>2 sym</sub>).

[5-amino-10,15-bis(3,5-di-*tert*-butylphenyl)porphyrinato]nickel(II) (4). Compound 3 (382 mg, 4.84  $\times 10^{-4}$  mol) was dissolved in a DCM/methanol solution (150 mL/150 mL) that was bubbled with argon for 10 min. Argon atmosphere was maintained and then 10% palladium on carbon (255 mg) was added, followed by stepwise addition of sodium borohydride (454 mg, 25 eq.,  $1.21 \times 10^{-3}$  mol). After 1.5 h the starting material was consumed. The solvent was evaporated and the residue filtered through a cotton wool plug after dissolving in DCM. The DCM solution was washed with water. The product was purified by column chromatography using DCM/hexane (1:1) as eluent. A single red fraction was obtained. The solvent was evaporated and the product was red/purple. Yield: 349 mg (95%). It was recrystallized from DCM/pentane. The product was a purple powder that is very soluble. Yield: 29 mg (8%), mp > 310 °C. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 9.36 s, 1H, 20-H), 9.09 (d, J = 4.9 Hz, 1H, 3-H), 9.01 (d, J = 4.9 Hz, 1H, 7-H), 8.88 (d, J = 4.9 Hz, 1H, 2-H), 8.85 (d, J = 4.9 Hz, 1H, 18-H), 8.61 (d, J = 4.9 Hz, 1H, 17-H), 8.59 (d, J = 4.9 Hz, 1H, 8-H), 8.57 (d, J = 5.1 Hz, 1H, 13-H), 8.51 (d, J = 5.1 Hz, 1H, 12-H), 7.78 (t, J = 2.0 Hz, 4H, o-H<sub>arvl</sub>), 7.67 (m, J = 2.0 Hz, 2H, p-H<sub>arvl</sub>), 5.81 (bs, 2H, NH<sub>2</sub>), 1.45 (s, 36H, 'Bu-H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta_{C}$ , ppm 149.0, 148.9, 145.0, 144.9, 141.5, 141.4, 141.0, 140.9, 140.8, 139.9, 133.2, 133.0, 132.7, 131.7, 131.1, 130.0, 129.2, 128.3, 128.2, 128.0, 124.1, 123.8, 120.8, 120.7, 120.5, 116.0, 104.2, 35.0, 31.5. UV-vis (DCM): λ<sub>max</sub>, nm (ε, 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 422 (160), 537 (9.79), 592 (9.96). MS (ESI): m/z 780.3542 (calcd. for C<sub>48</sub>H<sub>53</sub>N<sub>5</sub>NaNi [M + Na]<sup>+</sup> 780.3552). IR (ATR): v, cm<sup>-1</sup> 3392m, 1255m (NH<sub>2</sub>).

1,2-bis{[10,15-bis(3,5-di-tert-butylphenyl)porphyrinato]nickel(II)-5-yl}diazene (5). Porphyrin 4 (349 mg,  $4.60 \times 10^{-4}$  mol) was dissolved in 15 mL of toluene. To this copper(II) acetate (11 mg,  $5.52 \times 10^{-5}$  mol, 12 mol.%) and pyridine (150  $\mu$ L, 1.84 × 10<sup>-3</sup>, 4 eq) were added. The mixture was stirred at 80 °C for 2 h. The solution was washed with water and the product extracted into DCM. The solvent was evaporated and the product recrystallized from DCM/methanol. The product was an olive green powder. Yield: 230 mg (66%), mp > 310 °C. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 10.15 (d, J = 4.8Hz, 2H, 3,3'-H), 10.08 (d, *J* = 5.3 Hz, 2H, 7,7'-H), 9.71 (s, 2H, 20,20'-H), 9.27 (d, *J* = 4.8 Hz, 2H, 2,2'-H), 9.01 (d, J = 4.8 Hz, 2H, 18, 18'-H), 8.99 (d, J = 5.3 Hz, 2H,8,8'-H), 8.83 (d, J = 4.8 Hz, 2H, 17,17'-H), 8.73 (d, J =5.3 Hz, 2H, 12,12'-H), 8.71 (d, J = 5.3 Hz, 2H, 13,13'-H), 7.90 (d, J = 1.8 Hz, 4H, o-H<sub>arvl</sub>), 7.87 (d, J = 1.8 Hz, 4H, o-H<sub>arvl</sub>), 7.74 (m, J = 1.8 Hz, 4H, p-H<sub>arvl</sub>), 1.50 (s, 36H, 'Bu-H), 1.48 (s, 36H, 'Bu-H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta_{\rm C}$ , ppm 149.2, 149.0, 143.3, 143.2, 142.6, 142.5, 141.8, 141.5, 140.5, 140.4, 139.5, 139.4, 134.6, 134.2, 133.6, 133.5, 133.2, 132.9, 132.8, 132.2, 131.7, 128.6, 128.5, 128.4, 122.5, 122.4, 121.3, 106.0, 35.0, 31.7. UVvis (DCM):  $\lambda_{max}$ , nm ( $\epsilon$ , 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 402 (78.2), 487 (129), 738 (41.5). MS (LSI): m/z 1510.7024 (calcd. for C<sub>96</sub>H<sub>102</sub>N<sub>10</sub>Ni<sub>2</sub> [M]<sup>+</sup> 1510.6996). Crystals of **5** for X-ray data collection were grown by slow diffusion of methanol into a solution of the azo-linked porphyrin in DCM.

Crystals of **5a** and **5b** came from the same synthesis experiment. Structure 5a. The crystals, while not particularly small, diffracted relatively weakly. A reasonable dataset was obtained by long-frame collection time. The compound has 1 crystallographic symmetry and as such the asymmetric unit comprises half of one molecule. Contained within the asymmetric unit are dichloromethane molecules at two positions: one (comprising atoms C49, Cl1-2) modelled with occupancy 0.75 and the other (comprising atoms C50, Cl3) disordered around a  $\overline{1}$  site with occupancy for each position modelled at 0.5. Structure **5b.** The crystals were very small and relatively weakly diffracting (limited data with resolution better than 1 Å). The asymmetric unit comprises one complete molecule. The tert-butyl groups associated with C27 and C79 were modelled with disordered components 0.55:0.45 and 0.65:0.35 for positions A and B, respectively. There are solvent-accessible voids in the structure but there was no evidence of occupation of these voids by solvent.

1,2-bis{[15,20-bis(3,5-di-tert-butylphenyl)-10nitroporphyrinato]nickel(II)-5-yl}diazene (6). Dimer 5 (29 mg,  $1.91 \times 10^{-5}$  mol) was dissolved in DCM/ acetonitrile solution (2.3 mL/0.7 mL) and stirred under argon for 10 min. The flask was shielded from light. Iodine (7.3 mg, 1.5 eq.,  $2.86 \times 10^{-5}$  mol) dissolved in DCM (0.8 mL) was added and the solution stirred for 30 min. Silver nitrite (8.8 mg, 3 eq.,  $5.73 \times 10^{-4}$  mol) dissolved in acetonitrile (0.8 mL) was added. The starting material was consumed after 1 h. The solvents were evaporated. The dark-red solid was redissolved in minimum amount of DCM and filtered through a cotton wool plug. The compound was purified by two chromatography columns using DCM/hexane (1:1) as eluent. The product was a red/brown sticky powder. Yield: 15.2 mg (49%). It was recrystallized from DCM/methanol. Yield: 5.6 mg (18%), mp > 310 °C. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 9.98 (d, J = 4.8 Hz, 2H, 7,7'-H), 9.88 (d, J = 4.8 Hz, 2H, 3,3'-H), 9.40 (d, J = 4.8 Hz, 2H, 8,8'-H), 9.11 (d, J =4.8 Hz, 2H, 12,12'-H), 8.95 (d, *J* = 4.8 Hz, 2H, 2,2'-H), 8.79 (d, J = 4.8 Hz, 2H, 13,13'-H), 8.67 (d, J = 4.5 Hz, 2H, 17,17'-H), 8.65 (d, J = 4.5 Hz, 2H, 18,18'-H), 7.84 (d, J = 1.8 Hz, 4H, o-H<sub>arvl</sub>), 7.80 (d, J = 1.8 Hz, 4H, o-H<sub>arvl</sub>), 7.75 (t, J = 1.8 Hz, 4H, p-H<sub>arvl</sub>), 1.48 (s, 72H, <sup>t</sup>Bu-H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta_{\rm C}$ , ppm 149.2, 149.1, 143.3, 143.2, 142.6, 142.5, 141.8, 141.5, 140.5, 140.4, 139.5, 139.4, 134.6, 134.2, 133.5, 133.3, 132.9, 132.8, 132.3, 131.7, 128.6, 128.5, 128.4, 122.5, 122.4, 121.3, 106.0, 35.0, 31.7. UV-vis (DCM):  $\lambda_{max}$ , nm ( $\epsilon$ , 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 403 (54.9), 498 (74.6), 716 (26.0). MS (LSI): m/z 1600.6674 (calcd. for  $C_{96}H_{100}N_{12}Ni_2O_4$  [M]<sup>+</sup> 1600.6697). IR (ATR): v, cm<sup>-1</sup> 1479s (NO<sub>2 asym</sub>), 1370s (NO<sub>2 sym</sub>). Crystals for X-ray data collection were grown by slow diffusion of methanol into a solution of the azo-linked porphyrin in DCM. Structure 6. The crystals of this structure were very small and poorly formed. In almost all cases the crystals were clearly twinned and unusable for data collection. The crystals were also structurally unstable after removal from the mother liquor prior to cooling for data collection. The best dataset obtainable was characterized by very weak diffraction to about 1.1 Å and possible nonmerohedral twinning. Despite this it was possible to obtain a solution for the structure that shows very reasonable atom positions and molecular structure. The asymmetric unit comprises two full molecules. There are solventaccessible voids but the low data quality and resulting noisy difference map made it impossible to identify any particular solvents. Refinement was problematic and the final model has been refined isotropically for all atoms except Ni. Geometric restraints were applied to tert-butyl groups but proper convergence could not be achieved. The structure is presented herein despite the aforementioned shortcomings in the data because the molecular structure is very reasonable and indicates clearly both the presence and relative orientation of the meso-positioned nitro groups as well as the relative orientations of the azo-bridged porphyrin rings.

1-{[15,20-bis(3,5-di-tert-butylphenyl)-10-nitroporphyrinato]nickel(II)-5-yl}-2-{[10,15-bis(3,5-di-tertbutylphenyl)porphyrinato]nickel(II)-5-yl}diazene (7). Dimer 5 (100 mg,  $6.60 \times 10^{-5}$ ), was dissolved in DCM/ acetonitrile solution (12 mL/4 mL) and stirred under argon for 10 min. The flask was shielded from light. Iodine (21 mg, 1.25 eq.,  $8.27 \times 10^{-5}$  mol) dissolved in DCM (4 mL) was added and the solution stirred for 30 min. Silver nitrite (25 mg, 2.5 eq.,  $1.62 \times 10^{-4}$  mol) dissolved in acetonitrile (4 mL) was added. The starting material was consumed after 1 h. The solvents were evaporated. The dark-red solid was redissolved in minimum amount of DCM and filtered through a cotton wool plug. The compound was purified by two chromatography columns using DCM/hexane (1:2) as eluent. Two products were isolated. The first was compound 7. The second was compound 6. Both were red/brown sticky powders. They were recrystallized from DCM/methanol. Yield: 11 mg (10%) and 8 mg (7%) respectively. Data for  $\mathbf{6}$  can be found above. Data for 7 follow. mp > 310 °C. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 10.11 (d, J = 4.8 Hz, 1H, 3'-H), 10.06 (d, J = 4.8 Hz, 1H, 7'-H), 10.04 (d, J = 4.8 Hz, 1H, 18'-H), 9.95 (d, J = 4.8 Hz, 1H, 7-H), 9.72 (s, 1H, 20'-H), 9.43 (d, J = 4.8 Hz, 1H, 8'-H), 9.28 (d, J = 4.8 Hz, 1H, 2'-H), 9.15 (d, J = 4.9 Hz, 1H, 3-H), 9.01 (d, J = 4.8Hz, 1H, 17'-H), 9.00 (d, J = 5.0 Hz, 1H, 12-H), 8.96 (d, *J* = 4.8 Hz, 1H, 8-H), 8.83 (d, *J* = 5.0 Hz, 1H, 13-H), 8.82 (d, J = 4.9 Hz, 1H, 2-H), 8.73 (d, J = 4.8 Hz, 1H, 17-H),8.71 (d, J = 4.8 Hz, 1H, 18-H), 8.70 (d, J = 4.8 Hz, 1H, 18-H)12'-H), 8.67 (d, J = 4.8 Hz, 1H, 13'-H), 7.90 (d, J = 1.8Hz, 2H, o-H<sub>arvl</sub>), 7.88 (t, J = 1.8 Hz, 4H, o-H<sub>arvl</sub>), 7.83 (d, J = 1.8 Hz, 2H,  $o-H_{arvl}$ ), 7.76 (m, J = 1.8 Hz, 4H,  $p-H_{arvl}$ ), 1.50 (s, 72H, 'Bu-H). UV-vis (DCM):  $\lambda_{max}$ , nm ( $\epsilon$ , 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 410 (77.6), 497 (109), 731 (39.9). MS (LSI): m/z 1558.0 (calcd. for C<sub>96</sub>H<sub>10</sub>N<sub>11</sub>Ni<sub>2</sub>O<sub>2</sub> [M]<sup>+</sup> 1555.6847). IR (ATR): v, cm<sup>-1</sup> 1480s (NO<sub>2 asym</sub>), 1369s (NO<sub>2 sym</sub>).

1,2-bis{[10-bromo-15,20-bis(3,5-di-tert-butylphenyl)porphyrinato]nickel(II)-5-yl}diazene (8). Dimer 5  $(5 \text{ mg}, 3.30 \times 10^{-6} \text{ mol})$  was dissolved in 1.5 mL of chloroform. The solution was stirred and NBS (2 mg, 2.5 eq,  $8.25 \times 10^{-6}$ ) was added, followed by pyridine (20 µL,  $2.49 \times 10^{-4}$  mol). After 30 min the starting material was consumed and the reaction was quenched with acetone. The solvent was evaporated and the residue washed with methanol through a cotton wool plug. The product was extracted from the plug in DCM. The solvent was removed and the product dried. It was a dark red/brown powder residue. Yield: 2.3 mg (39%), mp > 310 °C.  $^{1}$ H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 9.97 (d, J = 5.0 Hz, 2H, 7,7'-H), 9.91 (d, J = 4.9 Hz, 2H, 3,3'-H), 9.60 (d, J = 5.0 Hz, 2H, 8,8'-H), 9.35 (d, *J* = 5.0 Hz, 2H, 12,12'-H), 8.90 (d, J = 4.9 Hz, 2H, 2,2'-H), 8.71 (d, J = 5.0 Hz, 2H, 13,13'-H), 8.63 (d, J = 4.4 Hz, 2H, 17,17'-H), 8.61 (d, J = 4.4 Hz, 2H, 18,18'-H), 7.84 (d, J = 2.1 Hz, 4H, $o-H_{arvl}$ , 7.80 (d, J = 2.1 Hz, 4H,  $o-H_{arvl}$ ), 7.73 (t, J = 2.1Hz, 4H, p-H<sub>arvl</sub>), 1.48 (s, 72H, <sup>t</sup>Bu-H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>): δ<sub>c</sub>, ppm 149.3, 149.2, 144.1, 142.8, 142.5, 141.9, 141.1, 140.5, 140.4, 139.0, 138.8, 135.1, 135.0, 134.3, 133.9, 133.5, 133.4, 133.2, 132.7, 132.6, 130.9, 128.7, 128.5, 128.3, 123.5, 122.5, 121.2, 103.8, 35.0, 31.7. UV-vis (DCM):  $\lambda_{max}$ , nm (intensity ratio) 413 (2.7), 495 (3.4), 761 (1.0). MS (LSI): m/z 1666.5135 (calcd. for  $C_{96}H_{100}Br_2N_{10}Ni_2[M]^+$  1666.5206).

[10,15-bis(3,5-di-tert-butylphenyl)-5-nitroporphy**rinato**]**zinc**(**II**) (9). Porphyrin 2 (50 mg,  $6.83 \times 10^{-5}$  mol) was dissolved in 5 mL of chloroform and stirred. To this  $Zn(OAc)_2$  (50 mg, 2.28 × 10<sup>-4</sup>) in 1 mL of methanol was added. The mixture was refluxed at 60 °C. After 20 min the starting material was consumed. The solution was washed with water and the product was extracted in DCM. The solvent was evaporated and the product was dark brown/green. Yield: 54 mg (100%). It was recrystallized from chloroform/pentane. The residue was a dark brown/ green sticky powder. Yield: 50 mg (91%), mp > 310 °C. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub> with pyridine-d<sub>5</sub>):  $\delta_{\rm H}$ , ppm 10.19 (s, 1H, 20-H), 9.41 (d, J = 4.8 Hz, 1H, 3-H), 9.39 (d, J = 4.8 Hz, 1H, 2-H), 9.36 (d, J = 4.8 Hz, 1H, 7-H),9.34 (d, J = 4.8 Hz, 1H, 18-H), 9.14 (d, J = 4.8 Hz, 1H, 17-H), 9.12 (d, *J* = 4.8 Hz, 1H, 8-H), 9.06 (d, *J* = 4.6 Hz, 1H, 12-H), 9.01 (d, J = 4.6 Hz, 1H, 13-H), 8.09 (d, J = 2.0 Hz, 2H, o-H<sub>arvl</sub>), 8.07 (d, J = 2.0 Hz, 2H, o-H<sub>arvl</sub>), 7.86 (t, J = 2.0 Hz, 2H, p-H<sub>arvl</sub>), 1.57 (s, 18H, <sup>t</sup>Bu-H), 1.56 (s, 18H, <sup>t</sup>Bu-H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub> with pyridine-d<sub>5</sub>): δ<sub>c</sub>, ppm 151.3, 150.7, 150.2, 150.1, 150.0, 148.5, 145.5, 145.4, 141.6, 141.4, 134.4, 133.7, 133.6, 132.8, 132.0, 131.2, 129.7, 129.6, 129.1, 128.0, 126.4, 125.3, 121.0, 106.9, 35.0, 31.7. UV-vis (DCM):  $\lambda_{max}$ , nm ( $\epsilon$ , 10<sup>3</sup> M<sup>-1</sup>. cm<sup>-1</sup>) 417 (378), 546 (27.8), 586 (19.2). MS (LSI): *m/z* 794.4847 (calcd. for  $C_{48}H_{52}N_5O_2Zn [M + H]^+$  794.3407). IR (ATR): v, cm<sup>-1</sup> 1510s (NO<sub>2 asym</sub>), 1333s (NO<sub>2 sym</sub>). The reaction was repeated successfully on a 170 mg scale.

[5-amino-10,15-bis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) (10). Porphyrin 9 (45 mg, 5.65  $\times$  10<sup>-5</sup> mol) was dissolved in a DCM/methanol solution (18 mL/18 mL) that was bubbled with argon for 10 min. Argon atmosphere was maintained and then 10% palladium on carbon (30 mg) was added, followed by stepwise addition of sodium borohydride (21 mg, 10 eq.,  $5.65 \times 10^{-4}$  mol). After 10 min the starting material was consumed. The solvent was evaporated and the residue filtered through a cotton wool plug after dissolving in DCM. The DCM solution was washed with water and the product extracted. The solvent was removed and the product was purified by column chromatography using DCM/pyridine (100:1) as eluent. A single green/blue fraction was isolated. The solvent was evaporated and the product was green/purple. Yield: 41 mg (85%). It was recrystallized from chloroform/pentane. The product was a green powder. Yield: 22 mg (46%), mp > 310 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> with pyridine-d<sub>5</sub>):  $\delta_{\rm H}$ , ppm 9.61 (s, 1H, 20-H), 9.23 (d, J = 4.4 Hz, 1H, 3-H), 9.14 (d, J =4.4 Hz, 1H, 7-H), 9.05 (d, J = 4.4 Hz, 1H, 2-H), 9.01 (d, J= 4.8 Hz, 1H, 18-H), 8.70 (d, J = 4.8 Hz, 1H, 17-H), 8.67 (d, J = 4.4 Hz, 1H, 8-H), 8.66 (d, J = 4.8 Hz, 1H, 12-H),8.61 (d, J = 4.8 Hz, 1H, 13-H), 7.98 (d, J = 2.0 Hz, 2H,  $o-H_{arvl}$ ), 7.96 (d, J = 2.0 Hz, 2H,  $o-H_{arvl}$ ), 7.73 (t, J = 2.0Hz, 1H, p-H<sub>arvl</sub>), 7.71 (t, J = 2.0 Hz, 1H, p-H<sub>arvl</sub>), 6.35 (bs, 2H, NH<sub>2</sub>), 1.52 (s, 18H, 'Bu-H), 1.51 (s, 18H, 'Bu-H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub> with pyridine-d<sub>5</sub>):  $\delta_c$ , ppm 153.0, 149.0, 148.8, 148.4, 148.2, 148.1, 147.4, 142.6, 142.4, 140.0, 139.7, 132.6, 132.0, 131.6, 131.0, 130.9, 129.8, 129.6, 129.4, 128.8, 123.1, 122.4, 122.3, 120.3, 120.1, 116.6, 105.1, 35.0, 31.6. UV-vis (DCM): λ<sub>max</sub>, nm  $(\epsilon, 10^3 \text{ M}^{-1}.\text{cm}^{-1})$  425 (473), 556 (7.40), 5.95 (10.2), 623 (17.4). MS (ESI): m/z 764.3681 (calcd. for  $C_{48}H_{54}N_5Zn$  $[M + H]^+$  764.3671). IR (ATR): v, cm<sup>-1</sup> 3302b, 1236m  $(NH_2)$ . The reaction was repeated successfully on a 100 mg scale.

Attempted synthesis of 1,2-bis{[10,15-bis(3,5-di*tert*-butylphenyl)porphyrinato]zinc(II)-5-yl}diazene. Porphyrin 10 (88 mg,  $1.15 \times 10^{-4}$  mol) was dissolved in 7 mL of toluene. To this copper(II) acetate (3 mg,  $1.37 \times 10^{-5}$  mol, 12 mol.%) and pyridine (37 µL, 4 eq.,  $4.59 \times 10^{-3}$  mol) were added. The mixture was stirred at 80 °C and the starting material was consumed after 3 h. The dimer was not formed. The main products were non-porphyrinic compounds, as shown by <sup>1</sup>H NMR spectroscopy. The residue was purified by column chromatography. Only one porphyrin was isolated, which was found by NMR spectroscopy to be the unsubstituted Zn corner porphyrin monomer.

**5-amino-10,15-bis(3,5-di-***tert***-butylphenyl)por-phyrin (11).** Porphyrin **2** (25 mg,  $3.41 \times 10^{-5}$  mol) was dissolved in a DCM/methanol solution (10 mL/10 mL) that was bubbled with argon for 10 min. Argon atmosphere was maintained and then 10% palladium on carbon (18 mg) was added followed by a stepwise addition of sodium borohydride (5 mg, 4 eq.,  $1.36 \times 10^{-4}$  mol). After 10 min the starting material was consumed. The solvent was evaporated and the residue filtered through a cotton wool plug after dissolving in DCM. The DCM solution was washed with water and the product extracted. The

solvent was removed and the product was purified by column chromatography using DCM/TEA (100:1) as eluent. A single violet fraction was isolated. The solvent was evaporated and the product was green/purple. Yield: 22 mg (91%). It was recrystallized from chloroform/pentane as purple crystals. Yield: 2 mg (8%), mp > 310 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 9.67 (s, 1H, 20-H), 9.19 (d, J = 4.6 Hz, 1H, 3-H), 9.07 (d, J = 4.6 Hz, 1H, 7-H), 9.04 (d, J = 4.6 Hz, 1H, 2-H), 9.01 (d, J = 4.6 Hz, 1H, 18-H), 8.68 (d, J = 4.6 Hz, 1H, 17-H), 8.62 (d, J = 5.0 Hz, 1H, 12-H), 8.60 (d, J = 4.6 Hz, 1H, 8-H), 8.58 (d, J = 5.0 Hz, 1H, 13-H), 7.98 (d, J = 2.0 Hz, 2H, o-H<sub>arvl</sub>), 7.97 (d, J = 2.0 Hz, 2H, o-H<sub>arvl</sub>), 7.77 (t, J = 2.0 Hz, 1H,  $p-H_{arvl}$ , 7.74 (t, J = 2.0 Hz, 1H,  $p-H_{arvl}$ ), 6.39 (bs, 2H, NH<sub>2</sub>), 1.53 (s, 18H, <sup>t</sup>Bu-H), 1.52 (s, 18H, <sup>t</sup>Bu-H), -1.13 (bs, 2H, inner NH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$ , ppm 149.0, 148.6, 141.6, 140.7, 132.5, 132.0, 130.8, 129.9, 129.5, 129.3, 128.3, 122.2, 121.9, 121.7, 120.9, 120.7, 115.9, 104.5, 35.0, 31.7. UV-vis (DCM):  $\lambda_{max}$ , nm  $(\epsilon, 10^3 \text{ M}^{-1} \text{.cm}^{-1})$  421 (308), 534 (9.52), 572 (20.2), 615 (6.01), 675 (16.6). MS (ESI): m/z 702.4533 (calcd. for  $C_{48}H_{56}N_5$  [M + H]<sup>+</sup> 702.4536). IR (ATR): v, cm<sup>-1</sup> 3360b, 1245s (NH<sub>2</sub>). The reaction was repeated successfully on a 50 mg scale.

Attempted synthesis of 1,2-bis[10,15-bis(3,5-di-*tert*butylphenyl)porphyrin-5-yl]diazene. Porphyrin 11 (25 mg,  $3.56 \times 10^{-5}$  mol) was dissolved in 5 mL of toluene. To this copper(II) acetate (2 mg,  $1.00 \times 10^{-5}$  mol, 30 mol.%) and pyridine (6 µL, 4 eq., 7.41 ×  $10^{-5}$  mol) were added. The mixture was stirred at 80 °C and the starting material was consumed after 3 h. The solution was washed with water and the product extracted into DCM. The residue was purified by column chromatography. The target compound was not achieved. The main products were non-porphyrinic compounds. The main porphyrin product was the copper analog of the target compound. Yield: 4 mg (5%). UV-vis (DCM):  $\lambda_{max}$ , nm (intensity ratio) 400 (3.3), 484 (4.3), 700 (1.0), 753 (1.1). MS (ESI): *m/z* 1521.6996 (calcd. for C<sub>96</sub>H<sub>102</sub>Cu<sub>2</sub>N<sub>10</sub> [M]<sup>+</sup> 1521.6915).

[5,10-bis(3,5-di-tert-butylphenyl)porphyrinato] nickel(II) (12) [21]. Porphyrin 1 (200 mg, 2.91 × 10<sup>-4</sup> mol) was dissolved in 12 mL of toluene and stirred. To this Ni(acac)<sub>2</sub> (200 mg, 7.78 × 10<sup>-4</sup> mol) was added. The mixture was refluxed for 2 h after which the starting material was consumed. The product was purified by column chromatography using DCM/hexane (1:1) as eluent. A single red fraction was collected. The solvent was evaporated and the product was recrystallized from DCM/methanol to give shiny purple crystals. Yield: 203 mg (94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 9.93 (s, 2H, 15,20-H), 9.29 (s, 2H, 17,18-H), 9.20 (d, *J* = 4.6 Hz, 2H, 2,13-H), 8.99 (d, *J* = 4.6 Hz, 2H, 3,12-H), 8.90 (s, 2H, 7,8-H), 7.93 (d, *J* = 1.8 Hz, 4H, *o*-H<sub>aryl</sub>), 7.77 (t, *J* = 1.8 Hz, 2H, *p*-H<sub>aryl</sub>), 1.51 (s, 36H, 'Bu-H).

[15,20-bis(3,5-di-*tert*-butylphenyl)-5,10-dinitroporphyrinato]nickel(II) (13). Compound 12 (25 mg,  $3.36 \times 10^{-5}$  mol) was dissolved in chloroform (10 mL) and stirred. To this 30% HNO<sub>3</sub> (3 mL) was added. The starting material was consumed within 20 min. The reaction mixture was diluted with water (20 mL). The organic layer was separated and washed with saturated sodium bicarbonate solution (20 mL) and water (20 mL) before being dried over anhydrous potassium carbonate. The organic layer was decanted and the solvent removed. The compound was purified by column chromatography using DCM/ hexane (1:1) as eluent. A single red powder compound was isolated. Yield: 26 mg (94%), mp > 310 °C.  $^{1}$ H NMR  $(400 \text{ MHz}, \text{CDCl}_3)$ :  $\delta_H$ , ppm 9.32 (s, 2H, 7,8-H), 9.15 (d, J = 5.0 Hz, 2H, 3,12-H), 8.89 (d, J = 5.0 Hz, 2H, 2,13-H), 8.76 (s, 2H, 17,18-H), 7.78 (d, J = 1.8 Hz, 4H, o-H<sub>arvl</sub>), 7.76 (t, J = 1.8 Hz, 2H, p-H<sub>arvl</sub>), 1.47 (s, 36H, <sup>t</sup>Bu-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$ , ppm 149.0, 144.5, 143.4, 138.3, 138.2, 137.4, 135.9, 134.2, 131.3, 129.3, 129.1, 128.6, 125.5, 122.0, 35.0, 31.3. UV-vis (DCM): λ<sub>max</sub>, nm  $(\epsilon, 10^3 \text{ M}^{-1}.\text{cm}^{-1})$  426 (96.0), 536 (11.6). MS (LSI): m/z833.3322 (calcd. for  $C_{48}H_{51}N_6NiO_4$  [M + H]<sup>+</sup> 833.3325). IR (ATR): v, cm<sup>-1</sup> 1510s (NO<sub>2 asym</sub>), 1345s (NO<sub>2 sym</sub>).

[5,10-diamino-15,20-bis(3,5-di-tert-butylphenyl) porphyrinato]nickel(II) (14). Compound 13 (20 mg,  $2.39 \times 10^{-5}$  mol) was dissolved in DCM/methanol solution (5 mL/5 mL) that was bubbled with argon for 10 min. Argon atmosphere was maintained and 10% palladium on carbon (13 mg) was added, followed by addition of sodium borohydride (3.6 mg, 4 eq.,  $9.56 \times 10^{-5}$  mol). There was an immediate change of color from wine red to emerald green. The starting material was consumed within 1 min. The solvent was evaporated and the residue filtered through a cotton wool plug after dissolving in DCM. The DCM solution was washed with water and the product extracted. The solvent was removed to leave a green powder residue. Yield: 18 mg (95%), mp >  $310 \degree$ C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, -50 °C): δ<sub>H</sub>, ppm 8.71 (s, 2H, 7,8-H), 8.61 (bs, 2H, 3,12-H), 8.27 (bs, 4H, 2,13,17,18-H), 7.70 (bs, 4H, o-H<sub>arvl</sub>), 7.58 (bs, 2H, p-H<sub>arvl</sub>), 5.57 (bs, 4H, NH<sub>2</sub>), 1.42 (s, 36H, <sup>t</sup>Bu-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): unobtainable due to broadness of peaks. UV-vis (DCM):  $\lambda_{max}$ , nm (intensity ratio) 430 (9.8), 614 (1.0). MS (LSI): m/z 772.3763 (calcd. for C<sub>48</sub>H<sub>54</sub>N<sub>6</sub>Ni [M]<sup>+</sup> 772.3763). IR (ATR): v, cm<sup>-1</sup> 3375m, 1281m (NH<sub>2</sub>).

Attempted synthesis of Ni azo-linked cyclic tetramer (A). Porphyrin 14 (8 mg,  $1.03 \times 10^{-5}$  mol) was dissolved in 4 mL of toluene. To this copper(II) acetate (1 mg,  $5.00 \times 10^{-6}$  mol, 50 mol.%) and pyridine ( $1.7 \mu$ L, 2 eq.,  $2.06 \times 10^{-5}$  mol) were added. The mixture was stirred at 80 °C and the starting material was consumed after 1 hour. The solution was washed with water and the product extracted into DCM. The residue was purified by column chromatography. The target compound was not achieved. The main products were non-porphyrinic compounds.

#### Acknowledgements

We thank the Australian Research Council for financial support through Discovery Grant DP0663774, Prof. K.-i. Sugiura for collaboration on the corner porphyrin synthesis and the Crystal Structure Analysis Facility, University of Sydney, for single-crystal X-ray data collection of **5b**. B.B. thanks the Queensland University of Technology for post-graduate scholarships and the School of Physical and Chemical Sciences for continuing support.

## **Supporting information**

Crystallographic data for **5a**, **5b** and **6** have been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition numbers 753463-753465. Copies can be obtained on request, free-of-charge, *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

## REFERENCES

- McDermott G, Prince SM, Freer AA, Hawthornthwaite-Lawless AM, Papiz MZ, Cogdell RJ and Isaacs NW. *Nature* 1995; **374**: 517–521.
- Koepke J, Hu X, Muenke C, Schulten K and Michel H. *Structure* 1996; 4: 581–597.
- Roszak AW, Howard TD, Southall J, Gardiner AT, Law CJ, Isaacs NW and Cogdell RJ. *Science* 2003; 302: 1969–1972.
- Nakamura Y, Aratani N and Osuka A. Chem. Soc. Rev. 2007; 36: 831–845.
- Burrell AK, Officer DL, Plieger PG and Reid DCW. *Chem. Rev.* 2001; **101**: 2751–2796.
- Iengo E, Zangrando E and Alessio E. Eur. J. Inorg. Chem. 2003; 2371–2384.
- Würthner F, You C-C and Saha-Möller CR. *Chem.* Soc. Rev. 2004; **33**: 133–146.
- 8. Satake A and Kobuke Y. *Tetrahedron* 2005; **61**: 13–41.
- Arnold DP, Johnson AW and Mahendran M. Perkin Trans. 1 1978; 366–370.
- Kato A, Sugiura K-i, Miyasaka H, Tanaka H, Kawai T, Sugimoto M and Yamashita M. *Chem. Lett.* 2004; 33: 578–579.
- Nakamura Y, Aratani N, Shinokubo H, Takagi A, Kawai T, Matsumoto T, Yoon ZS, Kim DY, Ahn TK, Kim D, Muranaka A, Kobayashi N and Osuka A. J. Am. Chem. Soc. 2006; **128**: 4119–4127.
- 12. Anderson HL. Chem. Commun. 1999: 2323–2330.

- 13. Hoffmann M, Wilson CJ, Odell B and Anderson HL. Angew. Chem. Int. Ed. 2007; 46: 3122–3125.
- 14. Anderson HL. Inorg. Chem. 1994; 33: 972–981.
- 15. Kuebler SM, Danning RG and Anderson HL. J. Am. *Chem. Soc.* 2000; **122**: 339–347.
- Screen TEO, Thorne JRG, Denning RG, Bucknall DG and Anderson HL. J. Am. Chem. Soc. 2002; 124: 9712–9713.
- Screen TEO, Blake IM, Rees LH, Clegg W, Borwick SJ and Anderson HL. *Perkin Trans.* 1 2002; 320–329.
- Drobizhev M, Stepanenko Y, Dzenis Y, Karotki A, Rebane A, Taylor PN and Anderson HL. J. Am. Chem. Soc. 2004; 126: 15352–15353.
- Balaz M, Collins HA, Dahlstedt E and Anderson HL. Org. Biomol. Chem. 2009; 7: 874–888.
- 20. Esdaile LJ, Jensen P, McMurtrie JC and Arnold DP. Angew. Chem. Int. Ed. 2007; **46**: 2090–2093.
- 21. Sugiura K-i, Fujimoto Y and Sakata Y. Chem. Commun. 2000; 1105–1106.
- 22. Arnold DP, Bott RC, Eldridge H, Elms FM, Smith G and Zojaji M. *Aust. J. Chem.* 1997; **50**: 495–503.
- 23. Senge MO. Chem. Commun. 2006; 243-256.
- 24. Wyrębek P and Ostrowski S. J. Porphyrins Phthalocyanines 2007; **11**: 822–828.
- Bruker-Nonius APX, SAINT and XPREP. Area detector control and data integration and reductions software. Bruker-Nonius Analytical X-ray Instruments Inc. 2006, Madison, Wisconsin, USA.
- Sheldrick GM. SADABS Empirical Absorption Correction Software 1990–2003, University of Göttingen Germany.
- 27. Oxford Diffraction Ltd., *CrysAlis CCD and CrysAlis RED* 2007, Abingdon, Oxforshire, England.
- 28. Farrugia LJ. J. Appl. Crystallogr. 1999; **32**: 837–838.
- Altomare A, Burla MC, Camalli M, Cascarano GL, Giocovazzo C, Guagliardi A, Moliterni AGC, Polidori G and Spagna SJ. J. Appl. Crystallogr. 1999; 32: 115–119.
- 30. Sheldrick GM. SHELXL-97 Programs for Crystal Structure Analysis 1997, University of Göttingen, Germany.
- Taniguchi S, Hasegawa H, Yanagiya S, Tabeta Y, Nakano Y and Takahashi M. *Tetrahedron* 2001; 57: 2103–2108.
- Hatscher S and Senge MO. *Tetrahedron Lett.* 2003;
   44: 157–160.

Copyright of the works in this Journal is vested with World Scientific Publishing. The article is allowed for individual use only and may not be copied, further disseminated, or hosted on any other third party website or repository without the copyright holder's written permission.