Bis-porphyrin arrays. Part 3.† The synthesis of model bis-porphyrin dimers and an electrochemical study

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We have successfully synthesised *exo* and *endo* diphenylacetylene linked bis-porphyrin dimers. We found that the *exo*-bis-porphyrin dimer could be easily prepared in good yield whilst the *endo*-dimer was harder to form due to the steric constraints of the *meso*-substituents. Electrochemical studies indicated that the porphyrin centred reductions of the bis-porphyrin dimers were dominated by the bis-porphyrin moieties. We found that the first four one-electron reductions of the *exo*- and *endo*-bis-porphyrin dimers occurred at similar potentials. Finally, at more negative potentials the bis-porphyrin dimers were reduced further which significantly changed the subsequent oxidation processes. This is thought to be due to a conformational change in the molecule which causes a change in orbital density in the "excited state".

Introduction

Porphyrin arrays have been assembled using covalent bonds[1] and metal complexation.[2] Porphyrin arrays in which the porphyrins are connected *via* conjugated bridges have tended to use either *meso*- or β-pyrrolic linking points. We have been working towards a new class of porphyrin array in which both the β-pyrrolic and *meso*-positions on a single porphyrin are utilised. In particular, our aim was to link bis-porphyrins where the two porphyrins are joined at the β-pyrrolic position with a tetraazaanthracene bridge. Such bis-porphyrin arrays are of interest as charge transport layers in light-emitting diodes or as materials for photovoltaics because the joining of the bis-porphyrins should alter their processing properties and, if a conjugated link is used, the electronic properties of the bis-porphyrins may also be modulated. We chose a diphenylacetylene link as this has been successfully used in simple porphyrin systems.[3] To prepare *meso*-connected bis-porphyrin dimers with a phenylacetylene bridge it was necessary to make bis-porphyrins which were functionalised at a *meso*-position. To this end, we have reported the synthesis of bis-porphyrins with a single *meso*-halophenyl moiety, which could be used in palladium catalysed couplings, with the other *meso*-positions carrying solubilising 3,5-di-*tert*-butylphenyl groups.[4] In this paper we describe the preparation of two isomeric bis-porphyrin dimers and present a preliminary study on their redox properties.

Results and discussion

In our report on the synthesis of asymmetric bis-porphyrins one of the problems was the separation of the desired asymmetric bis-porphyrin from symmetric bis-porphyrin by-products of similar polarity.[4] Separation was achieved by chelating copper into the less polar porphyrin-α-dione which gave bis-porphyrins with zero, one or two metals chelated. The three bis-porphyrins could then be easily separated by chromatography over silica as the chelated metal atoms enhanced the difference in polarity of the bis-porphyrins. However, one of the difficulties encountered in that work was that, although the copper could be removed, the yield of the corresponding free-base bis-porphyrin was not high. Therefore, in this study we chose to use nickel instead of copper, as nickel porphyrins also tend to be less polar than their free-base counterparts. As nickel is diamagnetic the products can be easily analysed by NMR spectroscopy. The second change to our reported route was to replace the bromophenyl derivative with the iodophenyl group to allow for efficient palladium catalysed couplings.

The method of porphyrin-α-dione synthesis provided two possible mono(4′-iodophenyl)porphyrin-α-diones, (*exo*) (Scheme 1) or (*endo*) (Scheme 2), in which the iodophenyl is away from or flanking the porphyrin-α-dione respectively.[5] These two porphyrin-α-diones could in turn give rise to bis-porphyrins with distinctly different geometries.

The mono(4′-iodophenyl)porphyrin-α-diones were more polar than the symmetric porphyrin-α-dione **2**. Therefore, for ease of separation of the bis-porphyrins **5** and **9** the symmetric nickel chelated porphyrin-α-dione **3** was required. Nickel porphyrin-α-dione **3** was made in an 86% yield by heating at reflux a solution of the free-base porphyrin-α-dione **2**[6] and excess nickel acetate tetrahydrate in DMF for 0.5 hours.

The synthesis of the mononickel *exo*-(4′-iodophenyl)bis-porphyrin **5** was achieved by reacting a solution of the *exo*-(4′-iodophenyl)porphyrin-α-dione **1** with a small excess of benzene-1,2,4,5-tetraamine tetrahydrochloride in pyridine heated at reflux for 1 h. The porphyrin diamino-quinoxaline intermediate was then condensed with the nickel porphyrin-α-dione **3** by heating the reaction mixture at reflux for a further 16 hours. Purification was straightforward, and the mononickel *exo*-(4′-iodophenyl)bis-porphyrin **5** was isolated in an 81% yield. The dinickel bis-porphyrin **4** and free-base bis(4′-iodophenyl)bis-porphyrin **6** were isolated in 9 and 7% yields respectively. In addition, the excess of nickel porphyrin-α-dione **3** was returned. There are two possible isomers of bis-porphyrin **6**, the *trans*-isomer as illustrated in Scheme 1 and the *cis*-isomer which has the 4′-iodophenyl groups on the same side of the bis-porphyrin. There is no reactivity difference which would mark out either isomer as the favoured product, however we believe that we only formed and isolated the *trans*-isomer. Evidence for this comes from the ^{1}H NMR of **5** and **6**. The bridge protons of **5** are observed as two singlets at 8.57 and 8.65 ppm respectively. If **6** was the *cis*-isomer then we would also expect to see two singlets for the bridge protons, but instead, we only see one singlet in the ^{1}H NMR. Although this is consistent with the C_2
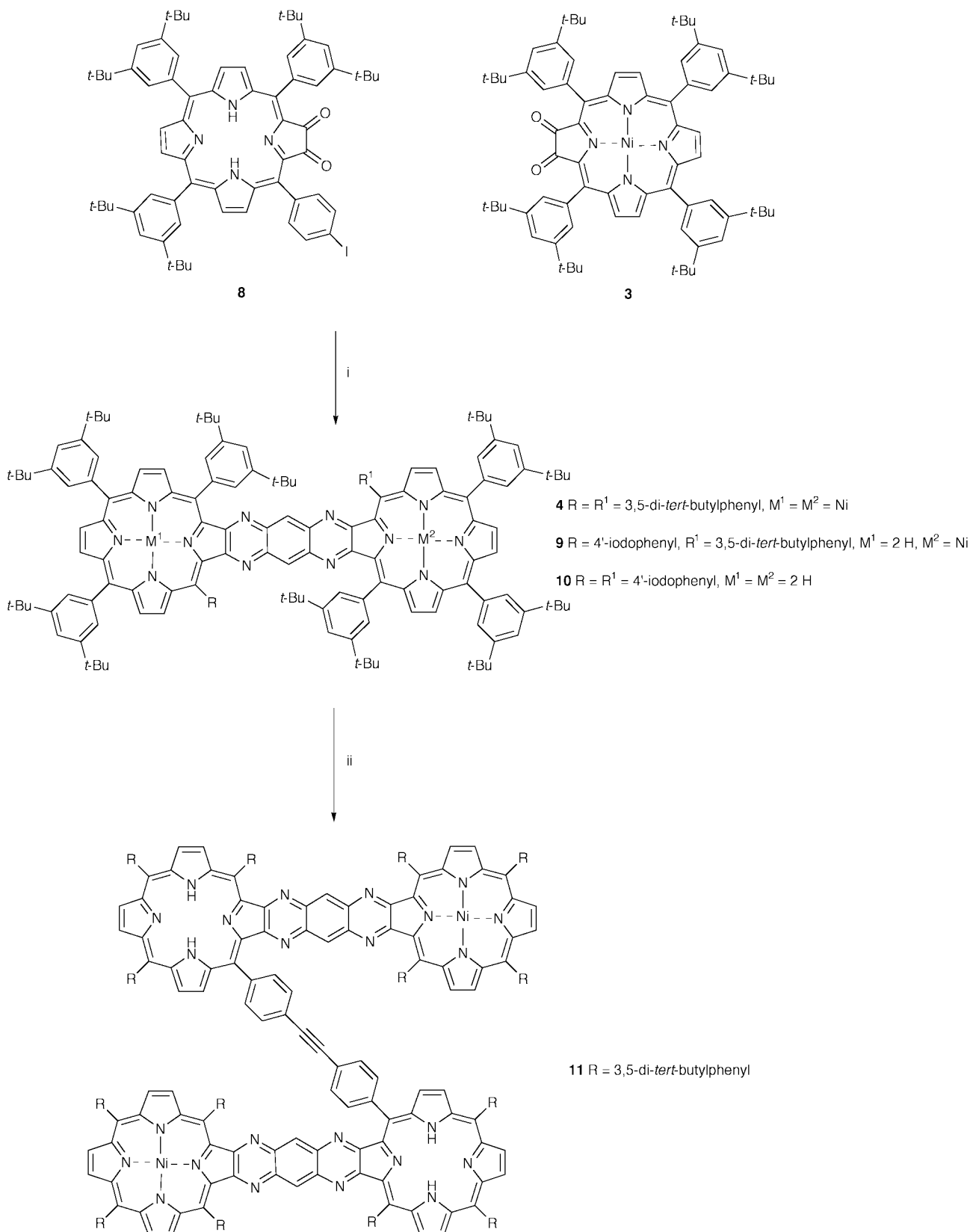
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† For Part 2, see ref. 4.
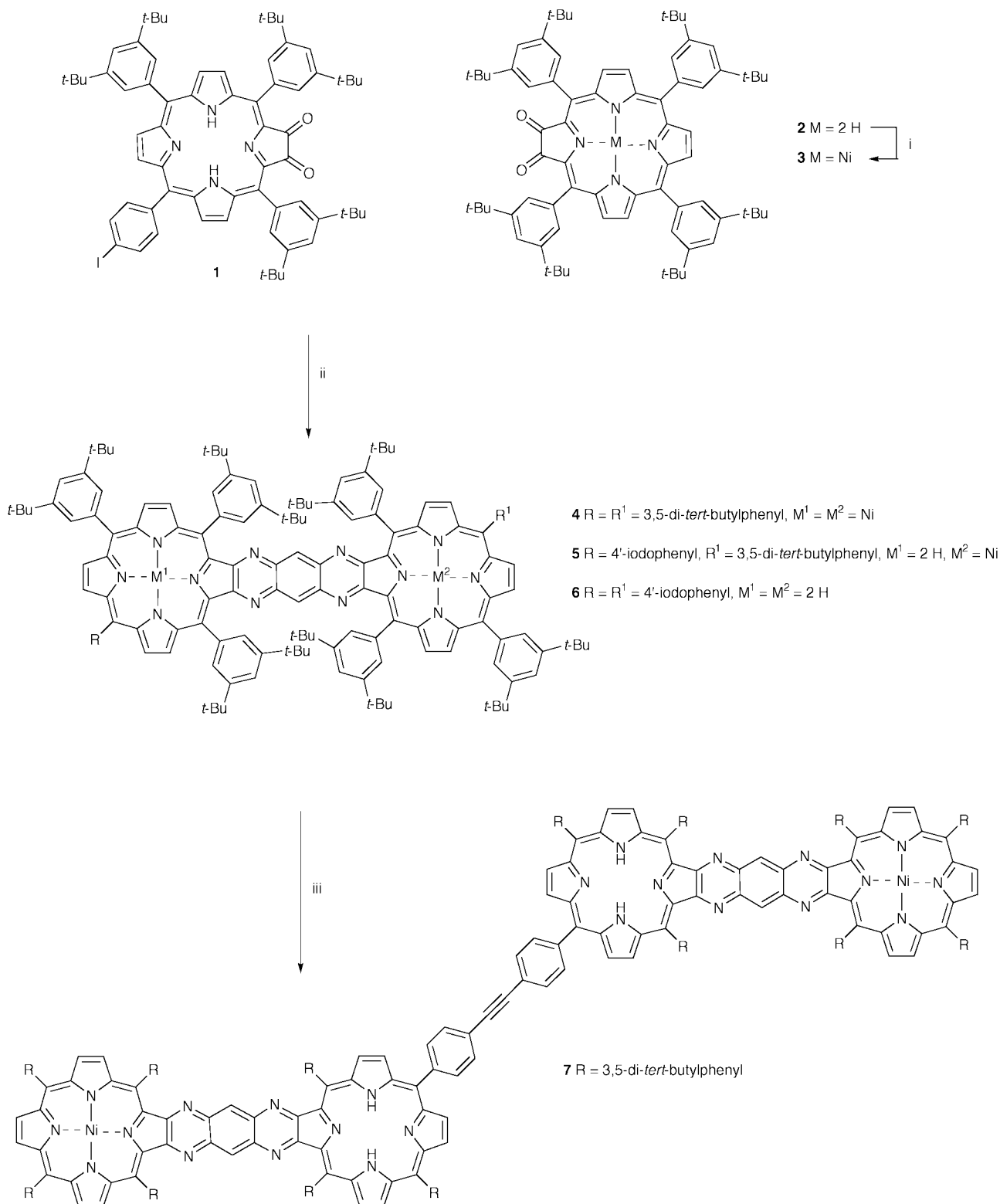
Scheme 1 *Reagents and conditions*: i, Ni(OAc)₂·4H₂O, DMF, Δ; ii, pyridine, benzene-1,2,4,5-tetraamine tetrahydrochloride, Ar, Δ then second porphyrin-α-dione, Ar, Δ; iii, bis(tri-*n*-butylstannyl)acetylene, Pd(OAc)₂, PPh₃, Et₃N, Δ.

symmetry of the illustrated *trans*-isomer, we do not know why it is the only isomer isolated.

The alternative *endo*-isomer, the mononickel (4′-iodophenyl)-bis-porphyrin **9**, was prepared by a similar method. A solution of the free-base *endo*-(4′-iodophenyl)porphyrin-α-dione **8** and a small excess of benzene-1,2,4,5-tetraamine tetrahydrochloride in pyridine was heated at reflux for 1 h. The porphyrin diamino-quinoxaline intermediate was then condensed with nickel porphyrin-α-dione **3** under the same conditions but for 9.5 hours. Purification was again straightforward, giving the mono-nickel iodophenylbis-porphyrin **9** in a 43% yield, the dinickel

bis-porphyrin **4** in a 10% yield, and the free-base bis(iodo-phenyl)bis-porphyrin **10** in a 41% yield. The excess nickel porphyrin-α-dione **3** was returned. Unlike the free-base *exo*-bis(4′-iodophenyl)bis-porphyrin **6** the free-base *endo*-bis(4′-iodophenyl)bis-porphyrin **10** was isolated as a 1:1 mixture of the *cis*- and *trans*-isomers. This was clearly seen by ¹H NMR where there were overlapping sets of absorptions of the *cis*- and *trans*-isomers. The ratio could be determined from the clearly differentiated signals assigned to the protons of one half of the 4′-iodophenyl AA′BB′ system for each isomer which were at 8.27 and 8.34 ppm. It might have been thought that in this case
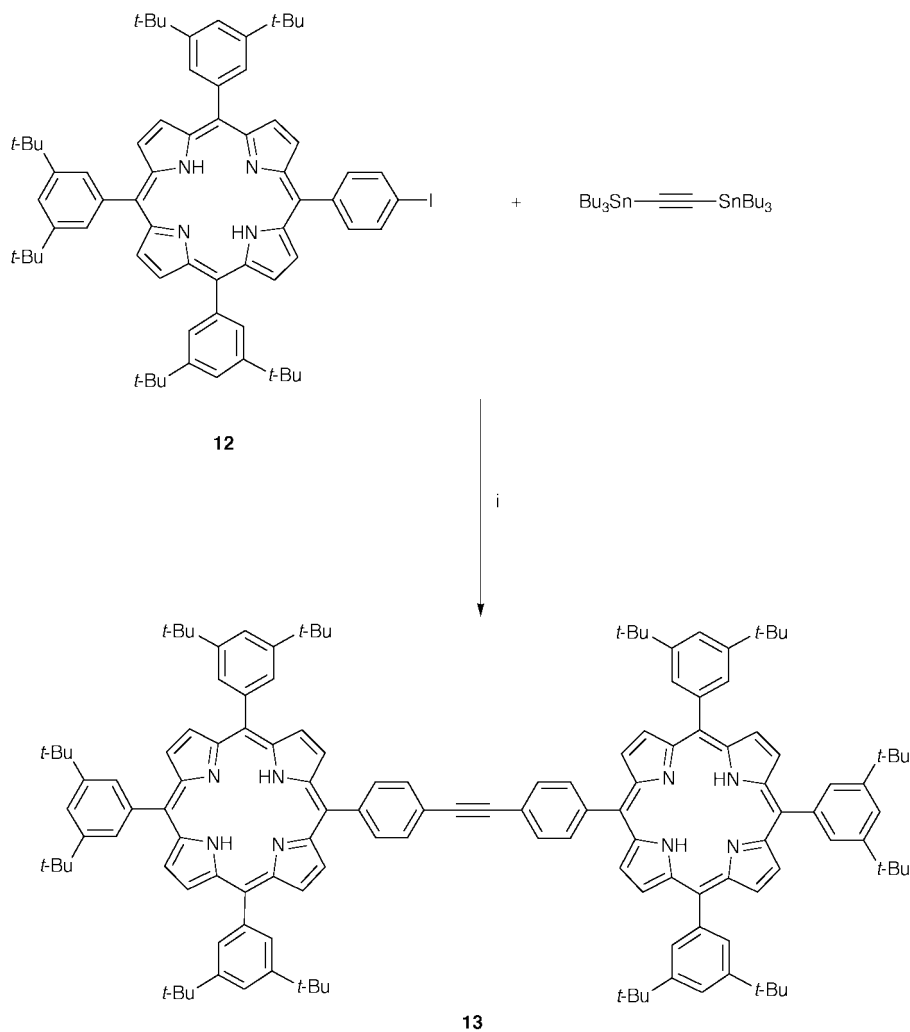
Scheme 2 *Reagents and conditions*: i, pyridine, benzene-1,2,4,5-tetraamine tetrahydrochloride, Ar, Δ then second porphyrin-α-dione, Ar, Δ; ii, bis(tri-*n*-butylstannyl)acetylene, Pd(OAc)₂, PPh₃, Et₃N, Δ.

there would be different steric demands on the formation of the two isomers, but that appears from this result not to be the case. The relatively high yield of **10** compared with **6**, where the overall steric demand of two iodophenyl and two 3,5-di-*tert*-butylphenyl groups in **10** would be less than that for four 3,5-di-*tert*-butylphenyl groups in **6**, is consistent with the results showing that less sterically demanding porphyrin-α-diones,

when used in the first condensation step, give less of the desired asymmetric bis-porphyrin.[7]

The final step in the synthesis of the two bis-porphyrin arrays illustrated in Schemes 1 and 2 was to join the bis-porphyrins together using palladium catalysed Stille couplings. The coupling of the *exo*-(4′-iodophenyl)bis-porphyrin **5** to form the *exo*-bis-porphyrin dimer was achieved by reaction with bis-

t-Bu   t-Bu

t-Bu

NH   N

N   HN

t-Bu

I

t-Bu   t-Bu

12

+   Bu₃Sn———SnBu₃

i

t-Bu   t-Bu   t-Bu   t-Bu

t-Bu   t-Bu

N   HN   N   HN

NH   N   NH   N

t-Bu   t-Bu

t-Bu   t-Bu   t-Bu   t-Bu

13

Scheme 3   *Reagents and conditions*: i, bis(tri-*n*-butylstannyl)acetylene, Pd(OAc)₂, PPh₃, Et₃N, Δ.

(tri-*n*-butylstannyl)acetylene, in the presence of palladium(II) acetate and triphenylphosphine in triethylamine heated at reflux for 3 hours. On purification the *exo*-bis-porphyrin dimer **7** was isolated in a 76% yield. The structure of **7** was confirmed by its MALDI mass spectra, which showed an isotopic distribution of molecular ions which corresponded well to the calculated distribution for the molecular formula of **7**. In addition, the ¹H NMR of **7**, although complicated, was consistent with the C_2 symmetry of the molecule.

By using the *endo*-(4′-iodophenyl)bis-porphyrin **9** it was possible to make a similar *endo*-bis-porphyrin dimer **11**. The bis-porphyrin **9** was reacted under the same conditions used for the preparation of **7** and this gave **11** in a 10% yield. We believe that the low yield of **11** compared to that of **7** is due to the steric hindrance in the approach of the two *endo*-bis-porphyrins in the coupling reaction. The (4′-iodophenyl)bis-porphyrin **9** was returned in an 11% yield. As in the case of the *exo*-bis-porphyrin dimer **7**, the MALDI mass spectrum of **11** showed an isotopic distribution of molecular ions consistent with the molecular formula and as expected this corresponded to that observed for **7**. The ¹H NMR was also consistent with the symmetry of **11**.

The final porphyrin dimer required in this study was **13** (Scheme 3) which was to be used as a model for the electrochemical studies of the diphenylacetylene bridged porphyrins in the bis-porphyrin dimers. Dimer **13** was prepared by reacting free-base iodophenylporphyrin **12** with bis(tri-*n*-butylstannyl)-acetylene in the presence of a palladium(II) acetate–triphenylphosphine catalyst in triethylamine heated at reflux for 3 hours. Under these conditions the free-base porphyrin dimer **13** was formed in a yield of 84%.

All the porphyrin dimers produced were highly soluble in chloroform and dichloromethane which suggests that extending the dimers to polymers may give rise to materials which are solution processable.

Electronic properties

We have carried out an initial study on the electronic properties of the bis-porphyrin dimers using cyclic voltammetry. These bis-porphyrin dimers can be considered to consist of two porphyrin chromophores; namely a tetraazaanthracene bridged bis-porphyrin which comprises one nickel and one free-base porphyrin, and a *meso*-diphenylacetylene linked porphyrin dimer containing two free-base porphyrins. Electrochemical studies on both these systems have been reported. Porphyrins normally undergo two one-electron reductions (to form a radical anion and then a dianion) and two one-electron oxidations (to form a radical cation and subsequently a dication). If two porphyrins within a porphyrin array are in electronic communication then the reduction or oxidation of one porphyrin ring can affect the redox properties of the second porphyrin ring. In our case two one-electron reductions are clearly observed for the single porphyrin **14** (Fig. 1a). However, for bis-porphyrin **15** four quasi-reversible one-electron porphyrin centred reductions are observed (Fig. 1b).[8] This suggests that there is moderate electronic communication between the two porphyrin rings in the bis-porphyrin. In addition, there is a further reduction at a more negative potential which at first sight appears to be only partially chemically reversible (Fig. 1c) as the oxidation of the reduced species has a smaller current than the reduction. However, in conjunction with this extra reduction the oxidation
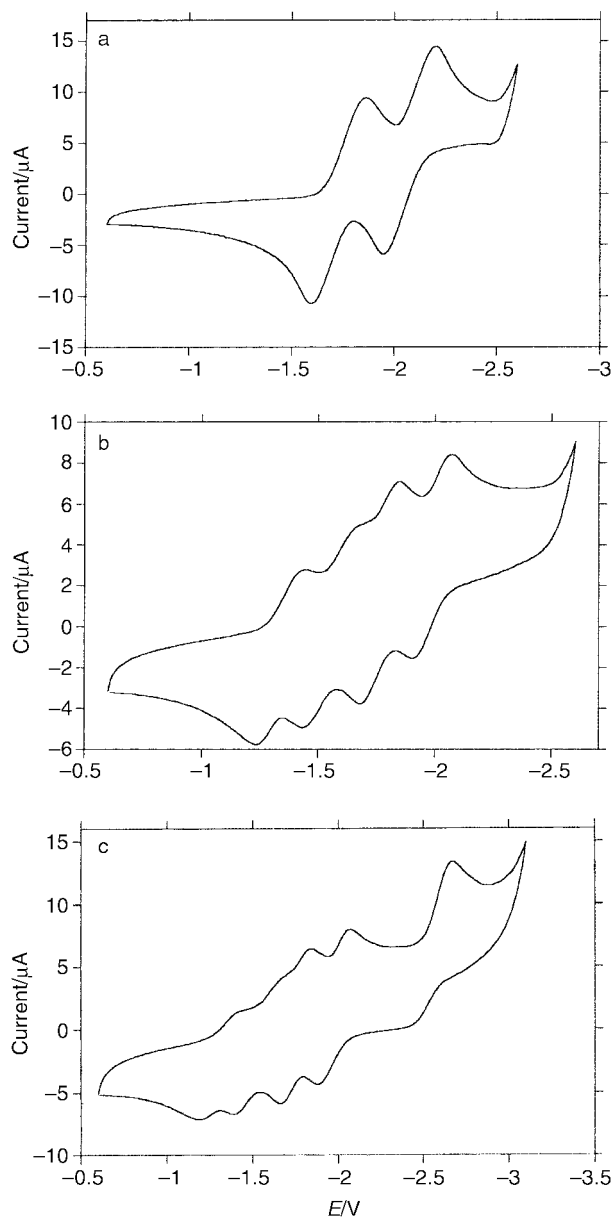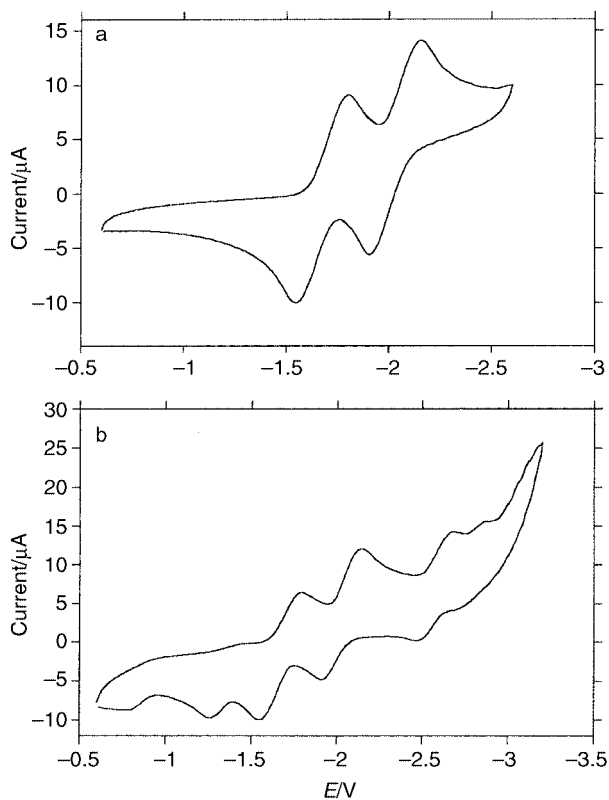
Fig. 1 Cyclic voltammograms of **14** (a), and **15** (b) and (c).

Table 1[a] Reduction potentials found in cyclic voltammetry studies

Comp.	Conc./mM	Type[b]	E_{pa}/V[c]	E_{pc}/V[d]	$E_{1/2}$/V
14	1.1	r1	−1.59	−1.86	−1.73
		r2	−1.95	−2.21	−2.08
12	0.46	r1	−1.58	−1.81	−1.70
		r2	−1.92	−2.16	−2.04
16	0.53	r1	−1.68	−1.88	−1.78
		r2	−2.17	−2.38	−2.28
15	0.43	r1	−1.24	−1.45	−1.35
		r2	−1.43	−1.70	−1.56
		r3	−1.68	−1.85	−1.77
		r4	−1.90	−2.08	−1.99
		r5	—	−2.67	—
7	0.34	r1	−1.16	−1.39	−1.28
		r2	−1.43	−1.72	−1.58
		r3	−1.74	−1.94	−1.84
		r4	−2.07	−2.25	−2.16
		r5	—	−2.74	—
11	0.15	r1	−1.14	−1.42	−1.28
		r2	−1.42	−1.74	−1.58
		r3	−1.74	−1.96	−1.85
		r4	−2.10	−2.30	−2.20
		r5	−2.47	−2.68	−2.58
		r6	—	−2.89	—
13	0.47	r1	−1.55	−1.80	−1.68
		r2	−1.90	−2.15	−2.03
		r3	−2.46	−2.68	−2.57
		r4	—	−2.87	—
5	0.34	r1	−1.21	−1.36	−1.29
		r2	−1.49	−1.66	−1.58
		r3	−1.75	−1.92	−1.84
		r4	−2.08	−2.25	−2.17
		r5	−2.48	−2.73	−2.61
		r6		−2.93	—

[a] Scan rate = 500 mV s^{-1}. [b] r1 First reduction; r2 second reduction, *etc.* [c] E_{pa} Peak anodic potential. [d] E_{pc} Peak cathodic potential

the orbital energies. A similar argument could be used to explain the minor changes in the cyclic voltammogram for **15** after the fifth reduction. This would be consistent with work on diphenylacetylene porphyrin arrays which suggests that a conformational change could explain enhanced conjugation observed between the π-electron systems of the porphyrin rings and the bridging diphenylacetylene group in the excited state.[9] It may be that a similar change occurs after the fourth reduction of our diphenylacetylene linked dimer.

Given that the bis-porphyrin dimers have nickel chelated into two of the constituent porphyrin rings, the next step in the study was to determine the effect of nickel on the porphyrin redox processes. The model compound we chose to use was *exo*-bis-porphyrin **5**. The 4-iodophenyl group was found to have no effect on the porphyrin reduction potentials with **14** and **12** having essentially the same reduction potentials. In contrast, chelation of nickel to **12**, giving **16**, moved the two porphyrin reductions to slightly more negative potentials and increased the separation between the potentials of the two reductions (Table 1). The second reduction appears to be less chemically reversible as its corresponding oxidation peak on the return sweep of potential is significantly smaller than the reduction peak at 500 mV s^{-1}. This was confirmed by using a faster scan rate (2000 mV s^{-1}) and under these conditions the oxidation of the reduced species became chemically reversible. The nickel porphyrin **16** also had a chemically reversible oxidation.

The mononickel bis-porphyrin **5** was found to have four chemically reversible one-electron reductions of the porphyrin rings (Fig. 3a). The reduction couples for **5** ($\Delta E_{1,2} = 290$ mV and $\Delta E_{3,4} = 330$ mV; scan rate: 500 mV s^{-1}) are more widely separated than in the case of the free-base bis-porphyrin **15** ($\Delta E_{1,2} = 210$ mV and $\Delta E_{3,4} = 220$ mV) with the larger separations indicating stronger electronic coupling between the porphyrin rings. When the switching potential was lowered to

peaks of the one-electron reductions appear to change their relative intensities. The chemical reversibility of the five reduction processes was confirmed by multiple scans which showed no diminution in the current. In contrast, neither **14** nor **15** had chemically reversible oxidations under the conditions we used.

The oxidative electrochemistry of a porphyrin dimer similar to **13** with mesitylene as opposed to 3,5-di-*tert*-butylphenyl *meso*-substituents has been reported.[9] The porphyrin dimer was shown to have two two-electron oxidations indicating that the two porphyrins with the diphenylacetylene bridge were not in electronic communication. We have studied the reduction processes of **13** and found that on reduction the porphyrin dimer shows two two-electron quasi-reversible porphyrin centred reductions which are at similar potentials (Table 1) to the single porphyrin. This indicates that up to the tetraanion there is no communication between the two porphyrin rings (Fig. 2a). However, when more negative potentials were used, $E_\lambda = -3.2$ V, then the reduction processes become more complex with two further reversible reductions observed (E_{pc} (r3) = −2.68 V and E_{pc} (r4) = −2.87 V) and the oxidations on the return sweep of potential are changed dramatically (Fig. 2b). This may be due to the structure of the porphyrin dimer rearranging to form an extended planar π-system over the two porphyrin rings to accommodate the extra electrons, which in turn would change

$E_\lambda = -3.6$ V (Fig. 3b) two further reductions were seen (E_{pc} (r5) $= -2.73$ and E_{pc} (r6) $= -2.93$ V) and the oxidations of the reduced species on the return sweep of potential are quite different from those observed when $E_\lambda = -2.6$ V (Fig. 3a). In particular, the oxidation at $E_{pa} = -1.2$ V has more current density than would be expected for removal of a single electron, which again suggests that the reduced species may be undergoing a change in electronic structure as discussed for **13** and **15**. In addition, mononickel bis-porphyrin **5** has one partially chemically reversible oxidation.
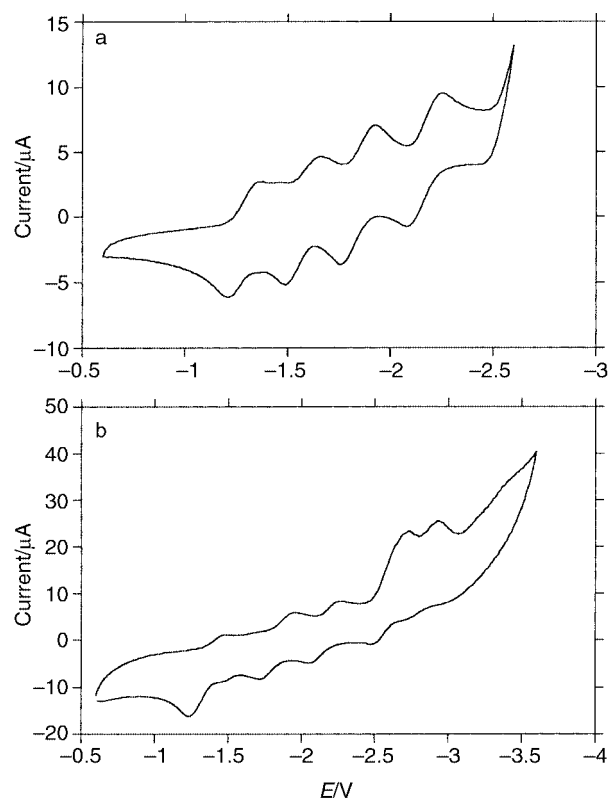

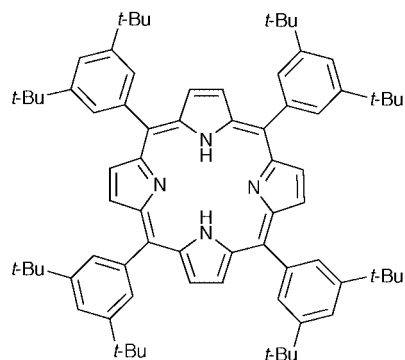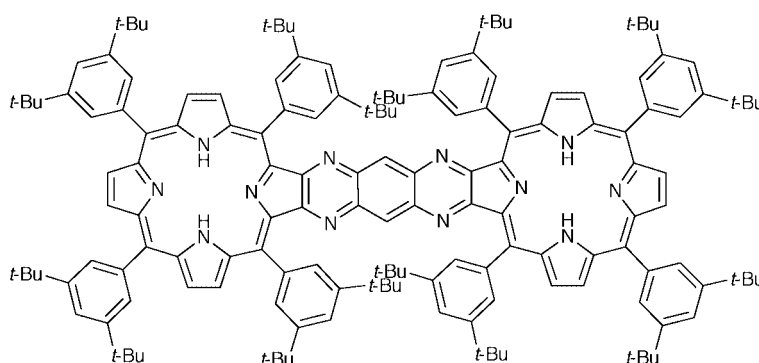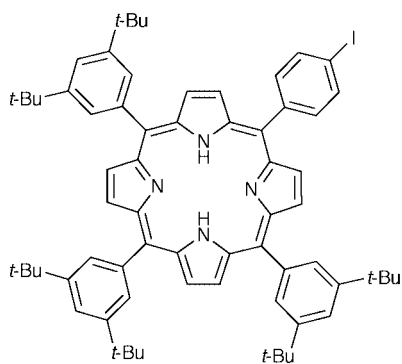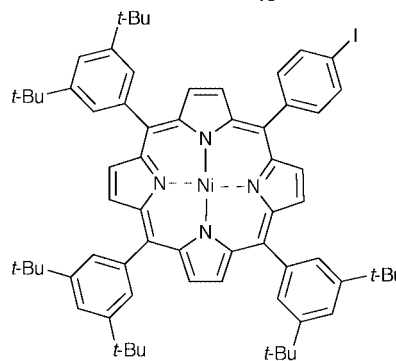Fig. 2 Cyclic voltammograms of **13** (a) and (b).

Fig. 3 Cyclic voltammograms of **5** (a) and (b).
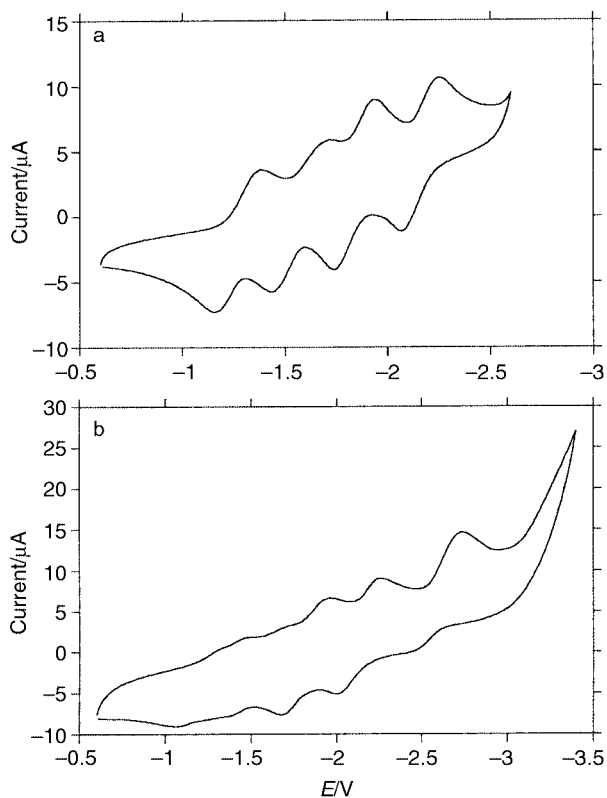

14

15

12

16

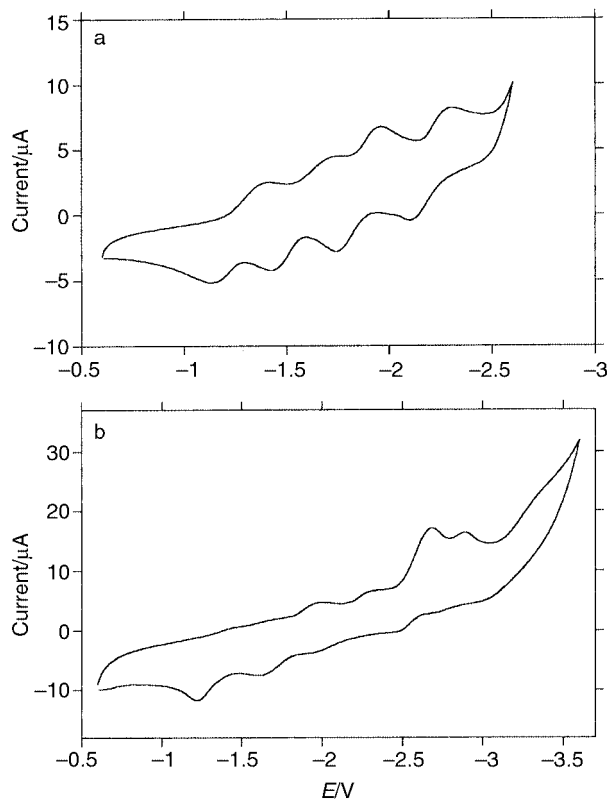**Fig. 4** Cyclic voltammograms of **7** (a) and (b).

Fig. 5 Cyclic voltammograms of **11** (a) and (b).

From the results observed for **5** and **13** we might expect that the electrochemistry of bis-porphyrin dimers **7** (*exo*) and **11** (*endo*) should be the same as that of the mono-nickel bis-porphyrin **5** at low switching potentials as there is no electronic through-bond communication between the two porphyrin rings across the diphenylacetylene bridge. When **7** and **11** were studied at a low switching potential they were found to have four chemically reversible two-electron reductions (Figs. 4a and 5a)

at the same potentials as **5** (Table 1). However, unlike bis-porphyrin **5**, which shows two further reductions at more negative potentials, the *exo*-bis-porphyrin dimer **7** shows only one further broad reduction peak ($E_{pc} = -2.74$ V) (Fig. 4b) reminiscent of the free-base porphyrin **15**. In contrast, the *endo*-bis-porphyrin dimer **11** shows two further reductions (Fig. 5b), as observed in the mononickel bis-porphyrin **5** (Fig. 3b). These results show that there was only a minor effect in having the two bis-porphyrins covalently linked on the electrochemical properties and only when very negative switching potentials were used.

Conclusions

We have successfully synthesised *exo* and *endo* diphenylacetylene linked bis-porphyrin dimers. We found that the *exo*-bis-porphyrin dimer could be formed easily and in good yield whilst the *endo*-dimer was harder to form due to the steric constraints of the *meso*-substituents. The two bis-porphyrin dimers were found to have good solubility. The electrochemical studies indicated that the porphyrin centred redox properties of the dimers were dominated by the bis-porphyrin moieties. We found that the redox properties of both *exo*- and *endo*-dimers were essentially the same at low switching potentials. Finally, at more negative potentials the cyclic voltammograms of the porphyrin dimers, bis-porphyrins, and bis-porphyrin arrays showed further reductions which disrupt the oxidation pattern on the return sweep of potential. This was thought to be due to conformational changes in the molecule.

Experimental

Measurements

^{1}H NMR spectra were recorded on a Bruker AM-500 (500 MHz) or a Varian Gemini 200 (200 MHz) spectrometer. Infrared spectra were recorded using KBr discs with either a Perkin-Elmer 781 or Paragon 1000 infrared spectrometer. UV-visible spectra were recorded on Perkin-Elmer UV-visible spectrometers (Lambda 2 or Lambda 14P) in either spectrophotometric grade chloroform or dichloromethane. For the free-base porphyrins the dichloromethane was filtered through a plug of potassium carbonate immediately before use. The absorption spectra of the porphyrin-α-diones all had a broad absorption, relative to the other absorption peaks, at long wavelengths. The absorption whilst broad often showed a number of minor features. ε values are given in dm^3 mol^{-1} cm^{-1}. Fast atom bombardment (FAB) mass spectra (m/z) were recorded on a VG Autospec spectrometer. Atmospheric pressure chemical ionization (APCI) mass spectra were recorded on a VG Platform spectrometer. Major peaks are listed with intensities quoted as percentages of the base peak. Due to the combination of metal chelation, halogen substituents, and size of molecules the molecular weight observed by mass spectroscopy generally appeared as a complex isotopic cluster around the expected parent ion. In these cases we have quoted the most abundant peak for each compound. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. We found that although the compounds did not melt, some partially decomposed on heating. This was observable by analysis with thin-layer chromatography which showed the presence of more than one compound after heating. Therefore, these melting points are quoted as decomposition below the highest temperature measured. Microanalyses were performed in either the Dyson Perrins Laboratory or the Inorganic Chemistry Laboratory, Oxford. All solvents for recrystallization were distilled before use. Dichloromethane and dimethyl sulfoxide were dried over calcium hydride and freshly distilled before use. Tetrahydrofuran was dried over sodium wire and freshly distilled before use. Light petroleum refers to the fraction of

boiling point 60–80 °C and ether refers to diethyl ether. Thin layer chromatography was performed on glass micro plates coated with silica GF$_{254}$, or with Merck aluminium plates coated with silica gel 60 F$_{254}$. Preparative layer chromatography was performed using glass plates coated with silica gel GF$_{254}$ with a concentration band. Column chromatography was performed using silica gel (flash) C60, 40–60. Where solvent mixtures are used, the proportions are given by volume. Electrochemistry was performed using an EG&G Princeton Applied Research potentiostat/galvanostat model 263A. All measurements were made at room temperature on samples dissolved in freshly distilled tetrahydrofuran, with 0.1 M tetra-n-butylammonium tetrafluoroborate as the electrolyte. The tetrahydrofuran was distilled from sodium wire and benzophenone under nitrogen, and then distilled from lithium aluminium hydride under argon. The electrolyte was purified by recrystallisation from an ethyl acetate–ether mixture, dried under vacuum, and stored over P$_2$O$_5$. The solutions were deoxygenated with argon. A glassy carbon working electrode, platinum wire counter electrode, and Ag/AgCl/NaCl (sat) reference electrode were used. The ferricenium/ferrocene couple was used as standard,[10] and the ferrocene was purified by recrystallisation from ethanol and then dried under vacuum and stored over P$_2$O$_5$. All the electrochemical experiments were carried out at 500 mV s^{-1} unless stated otherwise. In all cases three cycles were run except for Figs. 1a and 3a where five were run. In all cases the final cycle is illustrated in the Figure.

[2,3-Dioxo-5,10,15,20-tetrakis(3″,5″-di-$tert$-butylphenyl)-chlorinato]nickel(II) 3

A mixture of free-base porphyrin-α-dione 2 (420 mg, 0.384 mmol) and nickel(II) acetate tetrahydrate (344 mg, 1.38 mmol) in N,N-dimethylformamide (30 cm^3) was heated at reflux for 30 min and allowed to cool. Water (30 cm^3) was added to precipitate the product, which was collected by filtration and washed with methanol. The filtrate was also collected, the solvent completely removed, and the residue purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2:3) as eluent. Dione 3 was isolated as a green solid (382 mg, 86%), mp >300 °C [Found: C, 78.98; H, 8.07; N, 4.88; m/z (FAB) 1150.7 (100%). C$_{76}$H$_{90}$N$_4$O$_2$Ni requires C, 79.36; H, 7.89; N, 4.87%; M, 1150.3]; v_{max}(KBr disc)/cm^{-1} 1723 (C=O); λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 415 (4.97), 487 (4.31), and 717 (3.71); δ_H(500 MHz; CDCl$_3$) 1.38 and 1.43 (72 H, 2 × s, t-butyl H), 7.35 (4 H, d, $J_{4',2'} = J_{4',6'} = 2.0$ Hz, C(2′) H and C(6′) H), 7.58 (2 H, dd, $J_{2',4'} = J_{6',4'} = 2.0$ Hz, C(4′) H), 7.67 (2 H, dd, $J_{2',4'} = J_{6',4'} = 2.0$ Hz, C(4′) H), 7.69 (4 H, d, $J_{4',2'} = J_{4',6'} = 1.79$ Hz, C(2′) H and C(6′) H), 8.21 and 8.40 (4 H, ABq, $J_{AB} = 5.0$ Hz, C(2) H, C(3) H, C(12) H, and C(13) H), and 8.26 (2 H, s, C(7) H and C(8) H).

exo-(4′-Iodophenyl)heptakis(3″,5″-di-$tert$-butylphenyl)bis-porphyrin nickel(II) 5

A solution of exo-(4′-iodophenyl)porphyrin-α-dione 1 (111 mg, 0.100 mmol) and benzene-1,2,4,5-tetraamine tetrahydrochloride (34 mg, 0.12 mmol) in dry, deoxygenated pyridine (2.7 cm^3) was heated at reflux under argon for 1 h. The solution was then transferred under argon to a flask containing 3 (197 mg, 0.171 mmol). The first reaction flask was rinsed with pyridine (1.5 cm^3) and this was transferred to the reaction mixture under argon. The reaction mixture was then heated at reflux under argon for a further 16 h and allowed to cool. Dichloromethane (25 cm^3) was added, and the solution was washed with water (3 × 25 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (1:4 to 1.5:3.5) as eluent and four bands were collected. Octakis(3′,5′-di-$tert$-butylphenyl)bis-porphyrin dinickel(II) 4 was isolated as a brown solid (19 mg,

9%), mp >300 °C [Found: C, 79.67; H, 7.33; N, 6.91; m/z (MALDI) 2367.4 (100%). C$_{158}$H$_{182}$N$_{12}$Ni$_2$ requires C, 80.19; H, 7.75; N, 7.10%; M, 2366.6]; λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 428 (5.36), 450 (5.36), 514sh (4.82), 534 (4.86), and 666 (4.36); δ_H(500 MHz; CDCl$_3$) 1.47 and 1.48 (144 H, 2 × s, t-butyl H), 7.70 (4 H, dd, $J_{2',4'} = J_{6',4'} = 2.0$ Hz, C(4′) H), 7.73 (8 H, d, $J_{4',2'} = J_{4',6'} = 2.0$ Hz, C(2′) H and C(6′) H), 7.82 (12 H, m, C(4′), C(2′) H and C(6′) H), 8.56 (2 H, s, bridge H), 8.61 (4 H, s, C(4) H, β-pyrrolic H), and 8.63 and 8.68 (8 H, ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H). exo-(4′-Iodophenyl)heptakis(3″,5″-di-$tert$-butylphenyl)bis-porphyrin nickel(II) 5 was isolated as a brown solid (188 mg, 81%), mp >300 °C [Found: C, 77.49; H, 7.19; N, 7.03; m/z (FAB) 2323.9 (100%). C$_{150}$H$_{167}$N$_{12}$INi requires C, 77.54; H, 7.24; N, 7.23%; M, 2323.6]; v_{max}(CHCl$_3$)/cm^{-1} 3357 (N-H); λ_{max}(CHCl$_3$)/nm (log ε) 428 (5.50), 450sh (5.39), 501 (4.91), 612sh (4.28), 641 (4.38), and 686sh (4.09); δ_H(500 MHz; CDCl$_3$) −2.38 (1 H, s, NH), −2.36 (1 H, s, NH), 1.47–1.57 (126 H, t-butyl H), 7.71 (2 H, dd, $J_{2',4'} = J_{6',4'} = 2.0$ Hz, C(4″) H), 7.77 (4 H, br s, C(2″) H and C(6″) H), 7.83 (1 H, dd, $J_{2',4'} = J_{6',4'} = 2.0$ Hz, C(4″) H), 7.84 (4 H, d, $J_{4',2'} = J_{4',6'} = 2.0$ Hz, C(2″) H and C(6″) H), 7.87 (2 H, br m, C(4″) H), 7.96–7.97 (2 H, m, C(4″) H), 8.00 and 8.13 (4 H, AA′BB′, C(2′) H, C(3′) H, C(5′) H, and C(6′) H), 8.07 (2 H, d, $J_{4',2'} = J_{4',6'} = 2.0$ Hz, C(2″) H and C(6″) H), 8.08 (2 H, d, $J_{4',2'} = J_{4',6'} = 2.0$ Hz, C(2″) H and C(6″) H), 8.10 (2 H, d, $J_{4',2'} = J_{4',6'} = 2.0$ Hz, C(2″) H and C(6″) H), 8.57 (1 H, bridge H), 8.62 (2 H, s, β-pyrrolic H), 8.65 (1 H, bridge H), 8.67–8.71 (5 H, 5 × ½ABq, β-pyrrolic H), 8.77 (1 H, ½ABq, $J_{AB} = 4.5$ Hz, β-pyrrolic H), 8.88 (3 H, br ½ABq and br s, β-pyrrolic H), and 8.97 (1 H, ½ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H). $trans,exo$-Bis(4′-iodophenyl)hexakis(3″,5″-di-$tert$-butylphenyl)-bis-porphyrin 6 was isolated as a brown solid (8 mg, 7%), v_{max}(KBr disc)/cm^{-1} 3360 (N-H); λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 426 (5.49), 457 (5.43), 500sh (4.87), 603sh (4.22), 615sh (4.26), 628 (4.29), and 676 (3.83); δ_H(500 MHz; CDCl$_3$) −2.39 (2 H, s, NH), −2.38 (2 H, s, NH), 1.55–1.60 (108 H, 3 × s, t-butyl H), 7.83 (2 H, dd, $J_{2',4'} = J_{6',4'} = 1.5$ Hz, C(4″) H), 8.00 and 8.13 (8 H, AA′BB′, C(2′) H, C(3′) H, C(5′) H, and C(6′) H), 8.01 (4 H, m, C(4″) H), 8.09–8.10 (12 H, m, C(2″) H and C(6″) H), 8.58 (2 H, s, bridge H), 8.69 and 8.77 (4 H, ABq, $J_{AB} = 4.5$ Hz, β-pyrrolic H), 8.89 (4 H, br s, β-pyrrolic H), and 8.91 and 8.98 (4 H, br ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H) [Found: m/z (FAB) 2281.7 (100%). C$_{142}$H$_{152}$N$_{12}$I$_2$ requires M, 2280.7]. Dione 3 was isolated as a green solid (69 mg, 35%), which co-chromatographed with and had an identical ^{1}H NMR spectrum to an authentic sample.

$endo$-(4′-Iodophenyl)heptakis(3″,5″-di-$tert$-butylphenyl)bis-porphyrin nickel(II) 9

A solution of $endo$-(4′-iodophenyl)porphyrin-α-dione 8 (50 mg, 0.045 mmol) and benzene-1,2,4,5-tetraamine tetrahydrochloride (16 mg, 0.056 mmol) in dry, deoxygenated pyridine (1.2 cm^3) was heated at reflux under argon for 1 h. The solution was then transferred under argon to a flask containing 3 (89 mg, 0.077 mmol). The original flask was rinsed with pyridine (1.5 cm^3) which was then transferred to the reaction mixture under argon. The reaction mixture was then heated at reflux under argon for a further 9.5 h and allowed to cool. Dichloromethane (25 cm^3) was added, and the organic solution was washed with dilute hydrochloric acid (3 M, 2 × 25 cm^3), water (50 cm^3), sodium bicarbonate solution (5%, 50 cm^3), and water (50 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (1:4 to 2:3) as eluent and four bands were collected. Octakis(3′,5′-di-$tert$-butylphenyl)bis-porphyrin dinickel(II) 4 was isolated as a brown solid (9 mg, 10%), which co-chromatographed with and had an identical ^{1}H NMR spectrum to an authentic sample. $endo$-(4′-Iodophenyl)heptakis-(3″,5″-di-$tert$-butylphenyl)bis-porphyrin nickel(II) 9 was isolated as a brown solid (47 mg, 43%), mp >300 °C [Found: C, 77.67;

H, 7.62; N, 6.70; m/z (FAB) 2324.0 (100%). $C_{150}H_{167}N_{12}INi$ requires C, 77.54; H, 7.24; N, 7.23%; M, 2323.6]; ν_{max}(CHCl$_3$)/cm^{-1} 3356 (N-H); λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 426 (5.43), 451 (5.33), 509 (4.83), 606sh (4.18), 642 (4.28), and 692sh (4.03); δ_H(500 MHz; CDCl$_3$) −2.33 (2 H, br s, NH), 1.47–1.61 (126 H, 7 × s, t-butyl H), 7.70–7.71 (2 H, m, C(4″)), 7.76 (2 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 7.77 (2 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 7.81 (1 H, dd, $J_{2″,4″} = J_{6″,4″} = 2.0$ Hz, C(4″) H), 7.83 (1 H, dd, $J_{2″,4″} = J_{6″,4″} = 2.0$ Hz, C(4″) H), 7.83 (2 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 7.85 (2 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 7.86 (1 H, dd, $J_{2″,4″} = J_{6″,4″} = 2.0$ Hz, C(4″) H), 7.95 (1 H, dd, $J_{2″,4″} = J_{6″,4″} = 1.5$ Hz, C(4″) H), 8.01 and 8.22 (4 H, AA′BB′, C(2′) H, C(3′) H, C(5′) H, and C(6′) H), 8.07 (2 H, d, $J_{4″,2″} = J_{4″,6″} = 1.5$ Hz, C(2″) H and C(6″) H), 8.08 (2 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 8.09 (2 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 8.27 (1 H, dd, $J_{2″,4″} = J_{6″,4″} = 1.5$ Hz, C(4″) H), 8.55 (1 H, s, bridge H), 8.65 (1 H, s, bridge H), 8.63 and 8.64 (2 H, ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), 8.68 and 8.71 (2 H, ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), 8.74 and 8.88 (2 H, ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), 8.76 (3 H, br s and br ½ABq, β-pyrrolic H), 8.93 (1 H, br ½ABq, $J_{AB} = 5$ Hz, β-pyrrolic H), and 8.96 and 8.97 (2 H, br m, β-pyrrolic H).

$cis/trans,endo$-Bis(4′-iodophenyl)octakis(3″,5″-di-$tert$-butylphenyl)bis-porphyrin nickel(II) **10** was isolated as a brown solid (21 mg, 41%), mp >300 °C [Found: C, 74.62; H, 6.71; N, 7.19; m/z (FAB) 2279.7 (100%). $C_{142}H_{152}N_{12}I_2$ requires C, 74.78; H, 6.72; N, 7.37%; M, 2280.7]; λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 426 (5.45), 457 (5.39), 495sh (4.88), 608sh (4.24), 629 (4.26), and 677 (3.85); δ_H(500 MHz; CDCl$_3$) −2.34 to −2.29 (NH), 1.55–1.68 (t-butyl H), 7.82–7.84 (m, C(4″)), 8.00 (dd, $J_{2″,4″} = J_{6″,4″} = 2.0$ Hz, C(4″) H), 8.02–8.05 (m, C(2″) H, C(6″) H, and iodophenyl H), 8.10–8.11 (m, C(2″) H and C(6″) H), 8.27 (½ × AA′BB′, iodophenyl H), 8.34 (½ × AA′BB′, iodophenyl H), 8.47 (dd, $J_{2″,4″} = J_{6″,4″} = 2.0$ Hz, C(4″) H), 8.58 (s, bridge H), 8.68 (s, bridge H), 8.75–8.80 (m, bridge H and β-pyrrolic H), 8.95–9.01 (m, β-pyrrolic H), 9.03 (br ½ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), and 9.22 (br ½ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H). Dione **3** was isolated as a green solid (43 mg, 48%) which co-chromatographed with and had an identical ^{1}H NMR spectrum to an authentic sample.

Porphyrin dimer 13

A solution of (4′-iodophenyl)tetrakis(3″,5″-di-$tert$-butylphenyl)-porphyrin **12** (50 mg, 0.047 mmol), triphenylphosphine (5.0 mg, 0.019 mmol), palladium acetate (1.2 mg, 0.005 mmol), and bis(tri-n-butylstannyl)acetylene (13.0 mg, 0.022 mmol) in tri-ethylamine (5.0 cm^3) was deoxygenated with argon for 13 min and then heated at reflux for 3 h. The solvent was removed and the residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (1:4 to 1.5:3.5) as eluent and the main band was collected and the solvent completely removed. Porphyrin dimer **13** was isolated as a red solid (35 mg, 84%). A sample for analysis, recrystallised from a dichloromethane–methanol mixture, had mp >300 °C [Found: C, 85.92; H, 8.14; N, 5.75; m/z (FAB) 1924.8 (100%). $C_{138}H_{154}N_8$ requires C, 86.11; H, 8.06; N, 5.82%; M, 1924.8]; ν_{max}(KBr disc)/cm^{-1} 3316 (N-H); λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 425 (6.00), 490 (3.98), 518 (4.65), 555 (4.46), 593 (4.11), and 649 (4.16); δ_H(500 MHz; CDCl$_3$) −2.65 (4 H, s, NH), 1.55 (108 H, s, t-butyl H), 7.81 (2 H, dd, $J_{2″,4″} = J_{6″,4″} = 2.0$ Hz, C(4″) H), 7.83 (4 H, dd, $J_{2″,4″} = J_{6″,4″} = 2.0$ Hz, C(4″) H), 8.10 and 8.34 (8 H, AA′BB′, phenylacetylene H), 8.11 (4 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 8.13 (8 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 8.94–8.97 (16 H, m, β-pyrrolic H).

4,4′-Bis[exo-heptakis(3″,5″-di-$tert$-butylphenyl)bis-porphyrin-nickel(II)]diphenylacetylene 7

A solution of **5** (53 mg, 0.023 mmol), triphenylphosphine (5.0 mg, 0.019 mmol), palladium acetate (0.7 mg, 0.003 mmol), and bis(tri-n-butylstannyl)acetylene (6.4 mg, 0.011 mmol) in tri-ethylamine (5.0 cm^3) was deoxygenated with argon for 15 min and then heated at reflux for 3 h. The solvent was removed and the residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (1:4 to 1.5:3.5) as eluent. The main band was collected and the solvent completely removed to give **7** as a brown solid (36 mg, 76%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture, decomp. <300 °C [Found: C, 81.51; H, 7.37; N, 7.58; m/z (MALDI) 4418.1 (100%). $C_{302}H_{334}N_{24}Ni_2$ requires C, 82.11; H, 7.62; N, 7.61%; M, 4417.5]; ν_{max}(CHCl$_3$)/cm^{-1} 3351 (N-H); λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 429 (5.79), 454 (5.71), 507 (5.25), 614sh (4.62), 643 (4.71), and 686sh (4.41); δ_H(500 MHz; CDCl$_3$) −2.30 (4 H, s, NH), 1.48–1.60 (252 H, t-butyl H), 7.71 (4 H, dd, $J_{2″,4″} = J_{6″,4″} = 1.5$ Hz, C(4″) H), 7.78 (8 H, d, $J_{4″,2″} = J_{4″,6″} = 1.5$ Hz, C(2″) H and C(6″) H), 7.85 (8 H, d, $J_{4″,2″} = J_{4″,6″} = 1.5$ Hz, C(2″) H and C(6″) H), 7.86 (2 H, dd, $J_{2″,4″} = J_{6″,4″} = 1.5$ Hz, C(4″) H), 7.88 (4 H, m, C(4″) H), 7.98 (2 H, dd, $J_{2″,4″} = J_{6″,4″} = 1.5$ Hz, C(4″) H), 8.00 (2 H, dd, $J_{2″,4″} = J_{6″,4″} = 1.5$ Hz, C(4″) H), 8.10 (4 H, d, $J_{4″,2″} = J_{4″,6″} = 1.5$ Hz, C(2″) H and C(6″) H), 8.12–8.14 (12 H, m, C(2″)H, C(6″)H, and phenylacetylene H), 8.36 (4 H, ½AA′BB′, phenylacetylene H), 8.59 (4 H, s, bridge H), 8.63 (4 H, s, β-pyrrolic H), 8.69 and 8.72 (4 H, ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), 8.70–8.72 (4 H, ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), 8.82 and 8.83 (4 H, ABq, $J_{AB} = 4.5$ Hz, β-pyrrolic H), 8.92 and 9.01 (4 H, br ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), and 8.95 and 9.01 (4 H, br ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H).

4,4′-Bis[$endo$-heptakis(3″,5″-di-$tert$-butylphenyl)bis-porphyrin-nickel(II)]diphenylacetylene 11

A solution of **9** (47 mg, 0.020 mmol), triphenylphosphine (2.4 mg, 0.009 mmol), palladium acetate (0.5 mg, 0.002 mmol), and bis(tri-n-butylstannyl)acetylene (5.9 mg, 0.010 mmol) in tri-ethylamine (4.5 cm^3), was deoxygenated with argon for 10 min and then heated at reflux for 5.5 h. The solvent was removed and the residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (1:4) as eluent and two bands were collected and the solvent completely removed. Bis-porphyrin **9** was recovered as a brown solid (5 mg, 11%), which co-chromatographed with and had an identical ^{1}H NMR spectrum to an authentic sample. Diphenylacetylene **11** was isolated as a brown solid (4 mg, 10%); λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 430 (5.75), 450sh (5.60), 510 (5.09), 608sh (4.45), 641 (4.54), and 688sh (4.30); δ_H(500 MHz; CDCl$_3$) −2.28 (2 H, s, NH), −2.25 (2 H, s, NH), 1.50–1.59 and 1.80 (252 H, t-butyl H), 7.73 (2 H, dd, $J_{2″,4″} = J_{6″,4″} = 1.5$ Hz, C(4″) H), 7.76 (4 H, m, C(4″) H), 7.82 (4 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 7.83 (2 H, d, $J_{4″,2″} = J_{4″,6″} = 2.0$ Hz, C(2″) H and C(6″) H), 7.85 (4 H, d, $J_{4″,2″} = J_{4″,6″} = 1.5$ Hz, C(2″) H and C(6″) H), 7.86 (4 H, d, $J_{4″,2″} = J_{4″,6″} = 1.5$ Hz, C(2″) H and C(6″) H), 7.90 (6 H, m, C(2″) H, C(4″) H, and C(6″) H), 7.98 (2 H, dd, $J_{2″,4″} = J_{6″,4″} = 1.5$ Hz, C(4″) H), 8.11 (4 H, d, $J_{4″,2″} = J_{4″,6″} = 1.5$ Hz, C(2″) H and C(6″) H), 8.12 (4 H, d, $J_{4″,2″} = J_{4″,6″} = 1.5$ Hz, C(2″) H and C(6″) H), 8.13 (4 H, d, $J_{4″,2″} = J_{4″,6″} = 1.5$ Hz, C(2″) H and C(6″) H), 8.44 and 8.50 (8 H, AA′BB′, phenylacetylene H), 8.52 (2 H, br dd, C(4″) H), 8.61 (2 H, s, bridge H), 8.67 and 8.69 (4 H, ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), 8.74 and 8.75 (4 H, ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), 8.78–8.80 (8 H, m, bridge H and β-pyrrolic H), 8.91 (2 H, br ½ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H), 8.97–9.02 (6 H, br m, β-pyrrolic H), and 9.14 (2 H, ½ABq, $J_{AB} = 5.0$ Hz, β-pyrrolic H) [Found: m/z (MALDI) 4418.6 (100%). $C_{302}H_{334}N_{24}Ni_2$ requires M, 4417.5].

[5(4′-Iodophenyl)-10,15,20-tris(3″,5″-di-$tert$-butylphenyl)-porphinato]nickel(II) 16

A solution of (4′-iodophenyl)tetrakis(3″,5″-di-$tert$-butylphenyl)-porphyrin **12** (100 mg, 0.093 mmol) and nickel(II) acetate tetra-hydrate (83 mg, 0.33 mmol) in dimethylformamide (50 cm^3) was

heated at reflux for 40 min and then allowed to cool. Ether (100 cm³) was added and the solution washed with water (5 × 50 cm³), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed. The residue was passed through a plug of silica using a dichloromethane–light petroleum mixture (1 : 4) as eluent and the main band was collected and the solvent was completely removed to give **16** as a red solid (105 mg, 100%). A sample for analysis was recrystallised from a dichloromethane–methanol mixture, mp >300 °C [Found: C, 71.80; H, 6.68; N, 4.81; m/z (FAB) 1133.3 (100%). $C_{68}H_{75}N_4INi$ requires C, 72.03; H, 6.67; N, 4.94%; M, 1134.0]; $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 418 (5.40), and 529 (4.24); δ_H(500 MHz; CDCl₃) 1.47 (18 H, s, t-butyl H), 1.48 (54 H, t-butyl H), 7.71–7.73 (3 H, m, C(4″) H), 7.77 and 8.02 (4 H, AA′BB′, C(3′) H, C(4′) H, C(5′) H, and C(6′) H), 7.87 (6 H, m, C(2″) H and C(6″) H), 8.72 and 8.79 (4 H, ABq, J_{AB} = 5.0 Hz, β-pyrrolic H), and 8.82 (4 H, s, β-pyrrolic H).

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