DOI: 10.1002/ejoc.201000388

A Cyclic Porphyrin Tetramer Linked by Azo and Butadiyne Bridges

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Keywords: Porphyrinoids / Porphyrins / Azo compounds

A soluble cyclic porphyrin oligomer (CPO) consisting of four 5,10-diarylporphyrins linked by alternating azo and butadiyne bridges has been synthesised via an aminated dinickel(II) butadiyne dimer. This is the first cyclic tetramer that combines both azo and butadiyne bridges and extends the azoporphyrin family, which comprises only a very few examples. The electronic absorption spectrum of the tetramer is more similar to spectra of azoporphyrins than to those of butadiyne-linked dimers or tetramer, exhibiting a two-component Soret band with a splitting of 4190 cm^{-1} and a strongly red-shifted Q band maximum at 735 nm.

Introduction

Porphyrins play an important role in several biological systems including oxygen transport, photosynthesis, and enzymes. Their capacity to absorb visible light, facilitate oxidation and reduction, and act as energy- and electron-transfer agents, in particular when several are held closely together, is of particular interest to chemists who seek to mimic Nature and to make and use these compounds in order to synthesise novel advanced materials.

Elucidation of the crystal structure of the light-harvesting antenna complex LH2 of *Rhodopseudomonas acidophila*[1–3] has brought about efforts to synthesise a range of cyclic porphyrin oligomers (CPOs) with the aim of studying excitation energy transfer (EET) and creating analogues of natural light-harvesting antennae. Since the pioneering work of Sanders and Anderson,[4] several CPOs in which the individual porphyrin rings are connected by covalent bonds have been reported.[5–10] CPOs have also been investigated in other fields such as host-guest chemistry and single molecule photochemistry.[7] We are interested in covalently linked arrays in which the bridging units are fully conjugated with the porphyrin π-system, including CPOs. Since the first conjugated diporphyrin system, a butadiyne-linked dimer,[11] was synthesised, many other porphyrin systems that offer strong electronic communication through their conjugated linkers have been investigated. The butadiyne and other linkers have been studied extensively, with numerous papers reporting interesting results with potential in various fields,[7,10,12–36] including recently two-photon absorption[31,34,37–44] and two-photon photodynamic therapy.[14,15,41,45] Anderson suggested that an azo linkage would provide the optimum degree of interporphyrin conjugation and be a good bridge for facilitating electronic communication between the porphyrins in the ground state.[29] The azo bridge provides a short distance between the porphyrin rings and a conjugated linker with little steric hindrance.

We reported the copper-promoted synthesis of the first azoporphyrin dimers from 5,10,15-triphenyl- and 5,15-diarylporphyrinylamines.[46] More recently a 5,10-diaryl-substituted porphyrin ("corner porphyrin") has also been linked to give an azo dimer.[47] Chen and co-workers reported the synthesis using iron(III) mediated coupling, of the dizinc azoporphyrin derived from 5,10,15-triphenylporphyrin.[48] Inspired by previous work in the field[5–7,49] our research aims towards the synthesis of new cyclic azo-linked tetramers, for example **1**, that utilises alternating azo and butadiyne bridges (Figure 1).

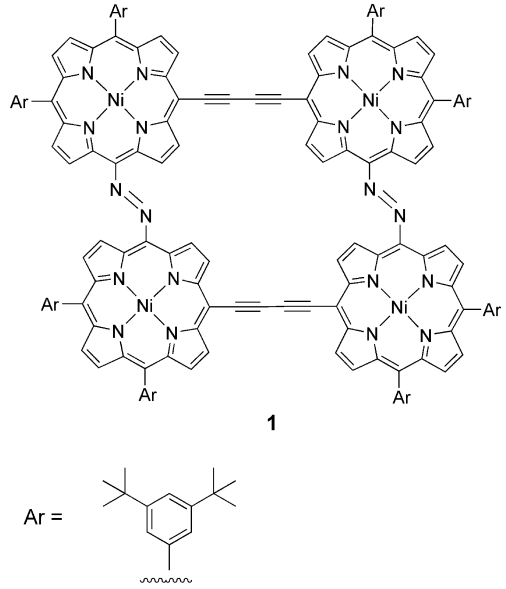

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Figure 1. Azo/butadiyne-linked Ni-cyclic porphyrin tetramer **1**.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000388.

Previously we sought to synthesise compound **2**, a cyclic porphyrin tetramer that is linked by azo bridges alone (Figure 2). The intended synthetic route was supposed to use an aminated dinickel(II) azo dimer **3** that would have been obtained from a nitrated precursor (**4**). Though the unsubstituted dinickel(II) azo-linked dimer **5** was synthesised, compound **4** could not be made reliably.[47] Attempts to make compound **2** from compound **4** failed, resulting in the loss of the dimer.[47] The unsubstituted azo-linked dimer **5** was also considered as a starting material for compound **1** provided that it could be brominated and then furnished with (trimethylsilyl)acetylene groups (Figure 3). We found that the bromination of the dimer proved unreliable so that compound **7** could not be obtained from compound **8**.[47] Here we present an alternative methodology that led to the successful synthesis of tetramer **1** (Scheme 1).

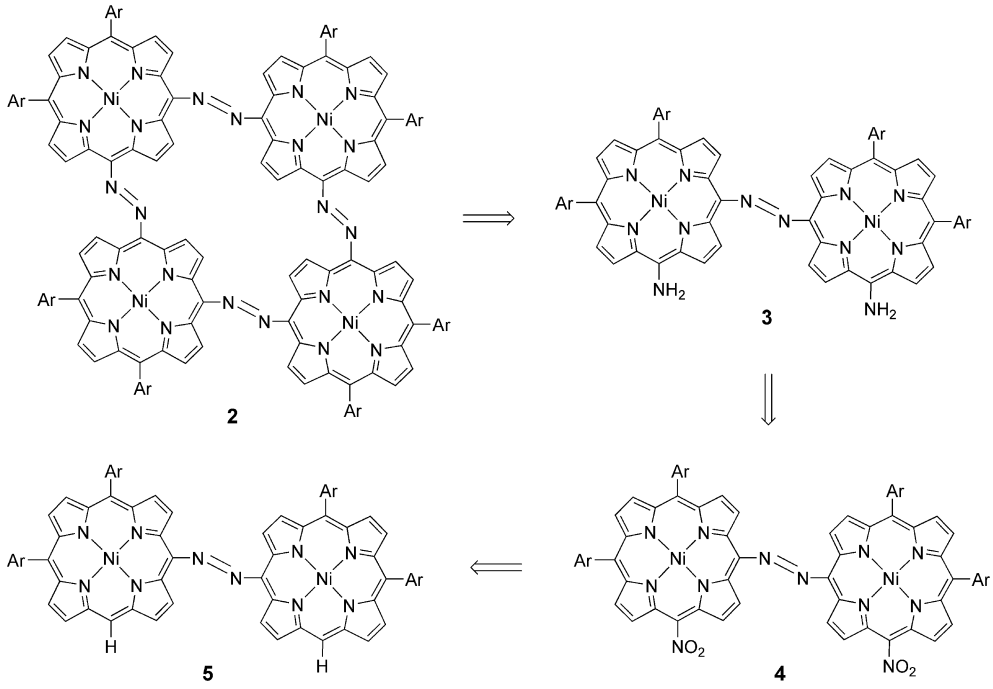


Figure 2. Proposed retrosynthesis of compound **2**.

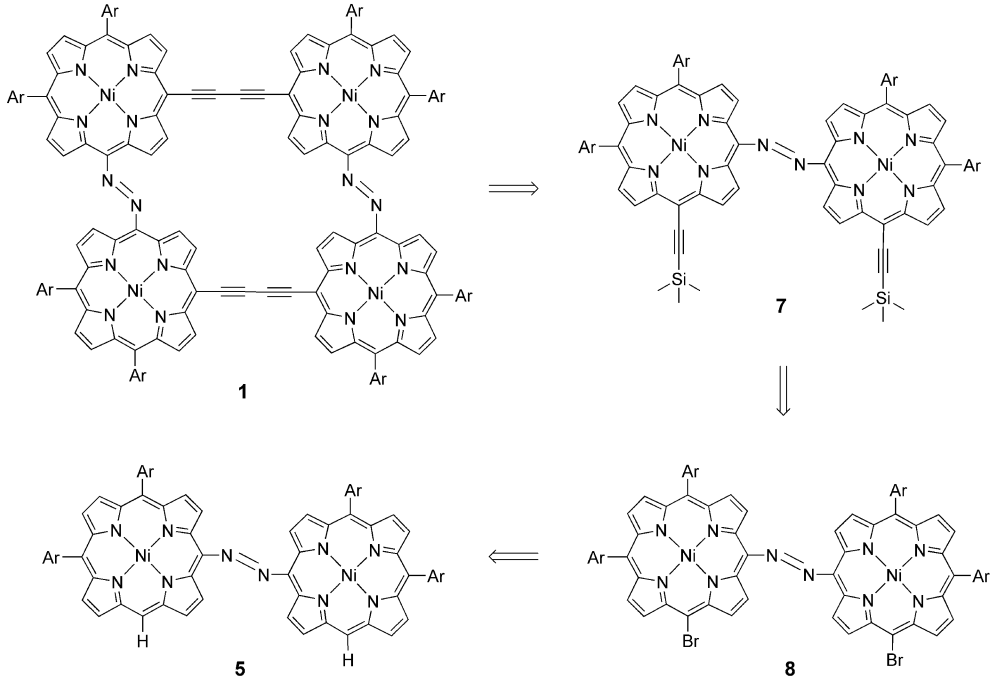
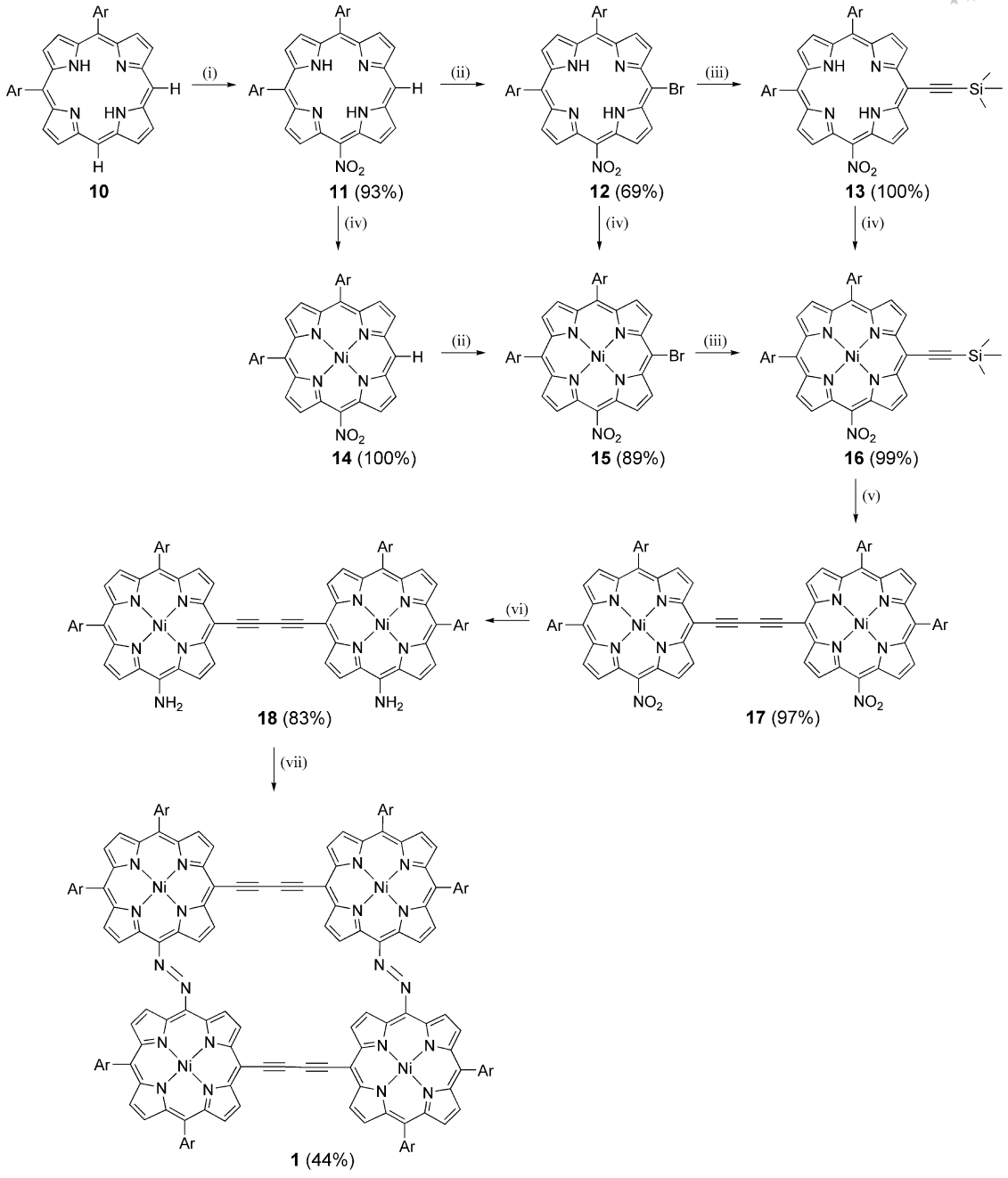


Figure 3. Proposed retrosynthesis of compound **1**.



Scheme 1. Synthesis of the azo/butadiyne-linked cyclic porphyrin tetramer **1**: (i) 0.75 equiv. I_2, 1.5 equiv. $AgNO_2$, DCM/MeCN; (ii) 1.5 equiv. NBS, $CHCl_3$/pyridine; (iii) 20 equiv. $HCCSiMe_3$, 80 mol-% $AsPh_3$, 20 mol-% $Pd_2(dba)_3$, TEA 45 °C; (iv) $Ni(acac)_2$, toluene 120 °C; (v) 6 equiv. $Cu(OAc)_2{\cdot}H_2O$, pyridine 80 °C; (vi) 10% Pd on C, 8 equiv. $NaBH_4$, DCM/MeOH; (vii) 0.5 equiv. $Cu(OAc)_2{\cdot}H_2O$, 2 equiv. pyridine, toluene 80 °C. Ar = 3,5-di-*tert*-butylphenyl.

Results and Discussion

The general instability of the azo bridge suggested to us that compound **1** would have to be synthesised by establishing a butadiyne-linked dimer first. In order to avoid the possible pitfalls of nitrating the unsubstituted *meso* positions of the dinickel(II) butadiyne-linked corner porphyrin dimer **9** (Figure 4), we decided that the monomer from which a dimer is to be synthesised should already be nitrated (**16** in Scheme 1).

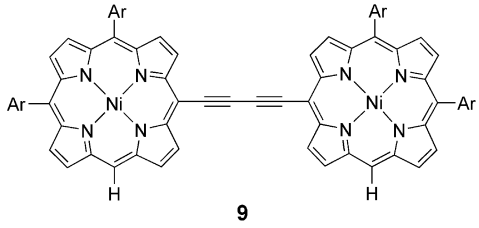
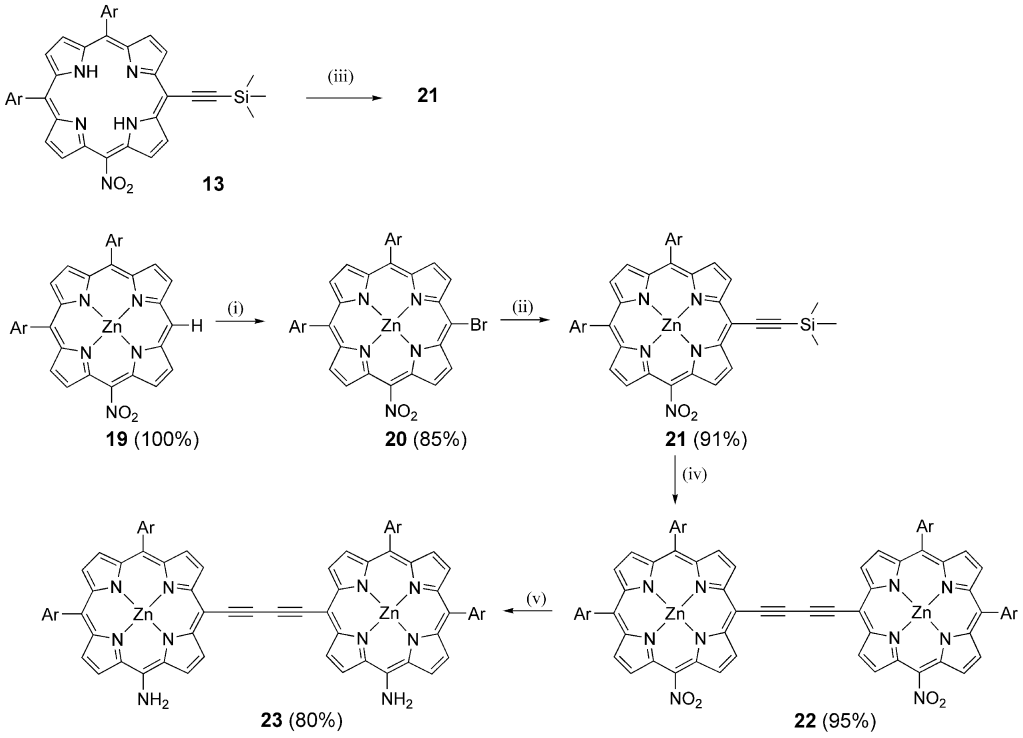


Figure 4. Structure of compound **9**.

The unsubstituted corner porphyrin monomer (**10**) was nitrated using the $AgNO_2/I_2$ method[47,50,51] yielding compound **11** in a 93% recrystallised yield. From here several synthetic routes were explored (Scheme 1). The first route involved brominating the nitrated free-base corner porphyrin (**11**) to yield compound **12** which was converted into the free-base porphyrin **13** via a copperless method.[52] Metallation of **13** gave compound **16** that was then self-coupled using the $Cu(OAc)_2$ method[46] to give the nitrated dinickel(II) butadiyne-linked dimer **17** in a 97% yield and 50% recrystallised yield. The non-recrystallised material was used to obtain the aminated dinickel(II) butadiyne-linked dimer **18**. Although there were some concerns that the butadiyne link might be lost, the $NaBH_4$ method used for the reduction of the nitro group did not affect the butadiyne bridge. Dimer **18** was synthesised in an 83% yield. However, due to its high solubility in common organic solvents, only a 10% recrystallised yield was obtained. Here, too, the non-recrystallised product proved to be substantially pure by NMR spectroscopy and was used in the subsequent copper(II) catalysed self-coupling step that yielded the azo/butadiyne-linked tetramer **1**. It is remarkable that the tetramer was obtained reproducibly in 44% recrystallised yield in this double coupling reaction. No other products, including linear oligomers, were identified. Dark intractable matter was left at the top of the chromatography column. The other synthetic routes in Scheme 1 differ in the order in which metallation, bromination and alkynylation take place. The yields and the reaction times do not differ much, however, we found that the route involving the bromination of **14** and the subsequent introduction of the acetylene group to give **16** took slightly less time with a slightly greater overall yield.

It is interesting to note that the synthesis of dimer **17** involved a one-pot desilylation/dimerisation reaction using copper(II) acetate in pyridine in which there was no need to isolate the intermediate compound with a deprotected acetylene group prior to coupling. This was observed in earlier work done by the Arnold group involving porphyrins with acetylene linkers,[53] and by others working in different fields.[54–59] We find it to be a very convenient and high-yielding method.

Our attempts to create a zinc analogue of tetramer **1** have so far been unsuccessful, however, Zn analogues of compounds **17** and **18** have been made (Scheme 2). Initially, porphyrin **21** was made from compound **20**, which in turn was obtained by brominating compound **19**. However, the yields were low and so porphyrin **13** was used as the precursor to synthesise porphyrin **21** in a 91% yield. The compound was very soluble in common organic solvents and the first crop recovered after recrystallization amounted to only a 9% yield. Therefore the non-recrystallised product was self-coupled to give dimer **22**. The nitro groups were reduced giving the aminated dizinc(II) butadiyne-linked dimer **23**. While the syntheses of **22** and **23** were achieved in 95% and 80% yield, respectively, the self-coupling step of the aminated dimer **23** resulted in the loss of the starting material in favour of non-porphyrinic material. The inability to synthesise the Zn_4 azo/butadiyne-linked cyclic porphyrin tetramer also meant that a free base analogue was



Scheme 2. Synthesis of butadiyne-linked Zn corner porphyrin dimers: (i) 1.5 equiv. NBS, $CHCl_3$/pyridine; (ii) 20 equiv. $HCCSiMe_3$, 80 mol-% $AsPh_3$, 20 mol-% $Pd_2(dba)_3$, TEA 45 °C; (iii) $Zn(OAc)_2$, chloroform 60 °C; (iv) 6 equiv. $Cu(OAc)_2 \cdot H_2O$, pyridine 80 °C; (v) 10% Pd on C, 6 equiv. $NaBH_4$, DCM/MeOH. Ar = 3,5-di-*tert*-butylphenyl.

out of reach. Currently, it stands that the synthesis of the zinc tetramer will have to follow a different path from that established for the nickel tetramer **1**.

Although nitrated monomers were selected as the precursors for the tetramer (**1**), the unsubstituted butadiyne-linked Ni corner porphyrin dimer **9** could have been used as well. As stated above we chose to synthesise dimer **17** from a monomer rather than risk losing the butadiyne bridge during nitration. However, 10,10′-unsubstituted butadiyne dimer **9** was synthesised in order to compare the effect of the substituent groups on the spectra of butadiyne-linked dimers (Scheme 3). The synthesis itself was challenging as it required the monobrominated corner porphyrin **24**. Monobromination of the porphyrin *meso* positions can be frustrating for two main reasons. Firstly, it is difficult to ensure that only one *meso* position will be brominated. Secondly, the monobromoporphyrin and dibromoporphyrin are hard, though not impossible, to separate.

After chromatographic purification, compound **24** was metallated with nickel giving **25** in a quantitative yield that was converted into **26** by substituting the bromine with the protected alkynyl group. Previous reactions of this type proceeded well using the copperless method. In this instance the reaction did not proceed. It was necessary to use copper(I) iodide as coupling reagent for the target compound to be achieved. Compound **26** was then self-coupled to give dimer **9** in a 76% recrystallised yield. Further modification of this compound was not pursued at this time. The compound should be seen as a potential substrate for the investigation of reactions involving the unsubstituted *meso* positions.

The tetramer **1** was characterised by ^{1}H NMR, UV/Vis, MALDI-TOF mass and Raman spectroscopy. The mass spectrum of the molecular ion region corresponded with the theoretical isotopic pattern for $[M + H]^+$ as shown in Figure 5. The mass spectrogram gave $[M + H]^+$ at *m*/*z* 3114.16. This supported the notion that compound **1** was indeed prepared as *m*/*z* calculated for $[M + H]^+$ of the cyclic tetramer, $C_{200}H_{201}N_{20}Ni_4$, requires 3114.38.

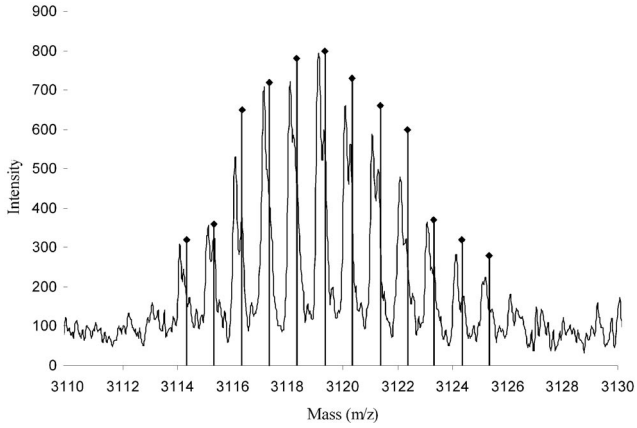
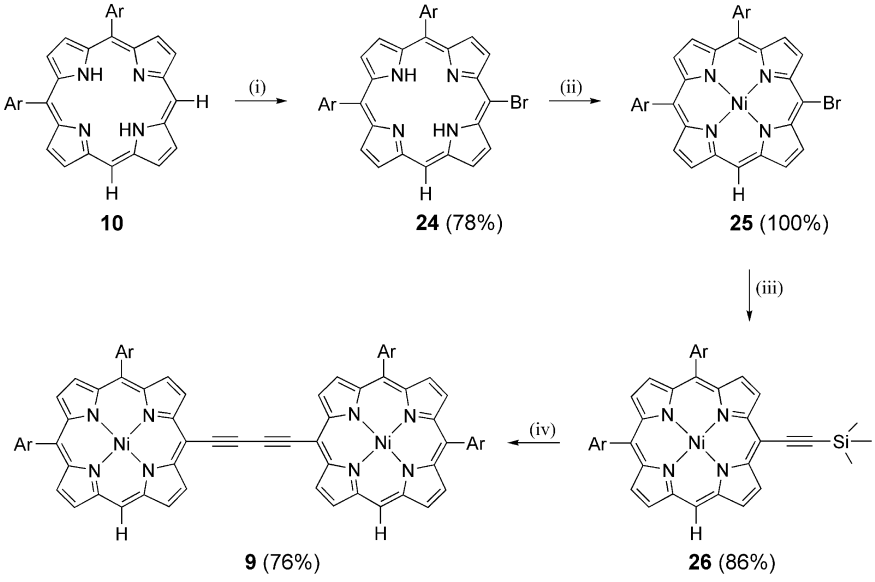


Figure 5. Obtained (line) and predicted (bar) MS data for the azo/butadiyne-linked Ni cyclic porphyrin tetramer (**1**).

The ^{1}H NMR spectrum of tetramer **1** shows eight β-proton peaks (Table 1, Figure S1). This is due to the lack of symmetry within the individual porphyrin units. Though

Table 1. Chemical shifts of the porphyrin hydrogen atoms (Figure 6) for the butadiyne-linked dimers and the cyclic porphyrin tetramer.

Compound	2-H	3-H	7-H	8-H	12-H	13-H	17-H	18-H
1	8.97	10.14	10.59	10.29	9.55	8.84	8.64	8.66
17	8.95	9.70	9.80	9.36	9.17	8.88	8.76	8.74
18	8.62	9.43	9.41	9.02	8.86	8.50	8.49	8.41
22	9.06	9.92	10.05	9.48	9.26	8.97	8.85	8.82
23	8.66	9.61	9.62	9.20	8.99	8.55	8.54	8.46



Scheme 3. Synthesis of the unsubstituted butadiyne-linked dimer **9**: (i) 1 equiv. NBS, $CHCl_3$/pyridine 0 °C; (ii) $Ni(acac)_2$, toluene 120 °C; (iii) 20 equiv. $HCCSiMe_3$, 80 mol-% CuI, 10 mol-% $Pd_2(PPh_3)_2Cl_2$, TEA 45 °C; (iv) 6 equiv. $Cu(OAc)_2{\cdot}H_2O$, pyridine 80 °C. Ar = 3,5-di-*tert*-butylphenyl.

the four monomers are chemically equivalent their own symmetry resembles that of a monomer with two different substituent groups. Thus, the eight peripheral protons are all chemically different. The peaks of the protons flanking the azo and butadiyne linkers are shifted significantly downfield due to the electron-withdrawing effect of those groups. The signal of the 7-H is further downfield than for any other nickel(II) porphyrin in our experience.

The ^{1}H NMR spectra of the butadiyne-linked compounds **17**, **18**, **22** and **23** also show eight β peaks that are a result of asymmetry of the porphyrin macrocycles (Table 1). Figure 6 shows the numbering of the β-protons. The peaks of dimers **17** and **22** are shifted further downfield than the peaks of dimers **18** and **23** due to the electron-withdrawing properties of the nitro groups and the electron-donating properties of the amino groups.

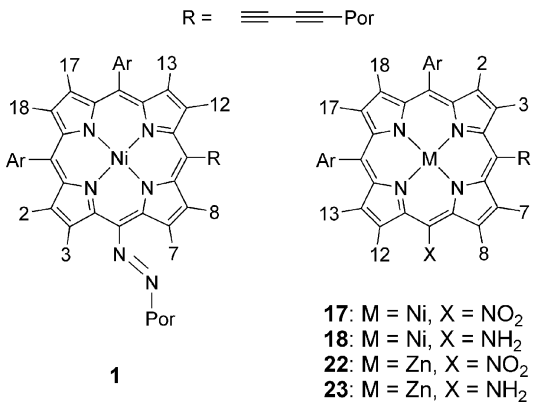


Figure 6. Proton position assignments for butadiyne dimers and the tetramer.

The electronic absorption spectra of the synthesised butadiyne-linked dimers (Figure 7) exhibit the general features of similar dimers. The Q-bands are broad and red-shifted and more intense relative to the Soret bands when compared with monomers. It should be noted that the Soret band splittings are much smaller than the splittings observed for the azo-linked nickel corner porphyrin dimer (Table 2). Compound **9** is a butadiyne-linked analogue of azoporphyrin **5**. Its Q-band is found at 619 nm while the Soret band shows two splittings of approximately 1000 cm^{-1} each. The nitrated butadiyne-linked Ni dimer **17** has an even smaller splitting of 810 cm^{-1} while the Q-band has red-shifted by 10 nm. The aminated Ni dimer **18** does not show a clear splitting of the Soret band, however, the Q-band has shifted significantly to 705 nm.

Table 2. Summary of absorption spectroscopy data for the butadiyne-linked dimers.

Compound	M	Substituents	λ_{max} Q /nm	Splitting /cm^{-1}
5[47]	Ni	H, H	738	4340
9	Ni	H, H	619	1000
17	Ni	NO_2, NO_2	629	810
18	Ni	NH_2, NH_2	705	n/a
22	Zn	NO_2, NO_2	660	1190
23	Zn	NH_2, NH_2	755	n/a

The nitrated butadiyne-linked Zn dimer **22** displays a Soret band splitting of 1190 cm^{-1} and the Q-band at 660 nm. The aminated zinc dimer **23** does not have a clear splitting of the Soret band, which is similar to its nickel analogue. However, the Q-band is red-shifted to 755 nm, which is 50 nm more than compound **18**. Taking the splitting in the Soret band as an indication of good ground state electronic communication, the spectroscopic data suggest that the azo bridge caters for a better electronic communication than the butadiyne linker.

The absorption spectrum of the azo/butadiyne-linked cyclic tetramer (**1**) shows features that are more characteristic of the azo-linked systems than butadiyne-linked systems (Figure 8). There is a significant splitting of the Soret band amounting to 4190 cm^{-1} and the very broad Q-band is at 735 nm. Although the Soret splitting is not as large as for the azo-linked nickel corner porphyrin dimer **5**, it is much bigger than the splittings of the butadiyne-linked dimers.

Furthermore, when compared to the absorption spectra of the butadiyne-linked tetramer (**27**)[6] and diphenylethyne-linked tetramer **28**,[5] the spectrum of compound **1** indicates a much better electronic communication throughout the system (Figure 9, Table 3). Neither the spectrum of compound **27** nor that of **28** shows a splitting of the Soret band. The electronic communication for compound **28** is decreased because the porphyrin rings are not in the same plane with respect to the diphenylethyne linkers and this hinders the π-overlap. Compound **27** does not show Soret

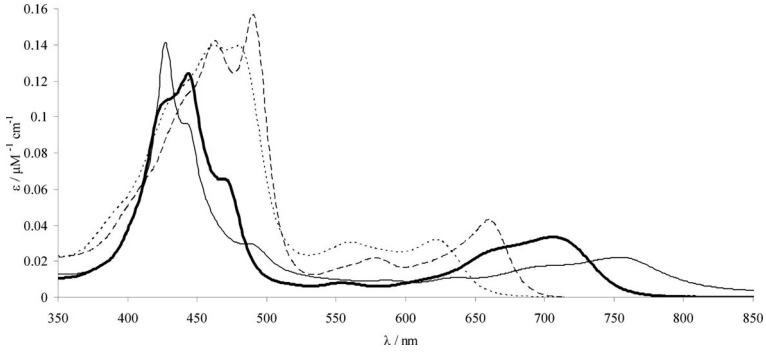


Figure 7. Comparison of the absorption spectra of butadiyne-linked dimers **17** (dotted), **18** (bold), **22** (dashed), and **23** (solid) in CH_2Cl_2.

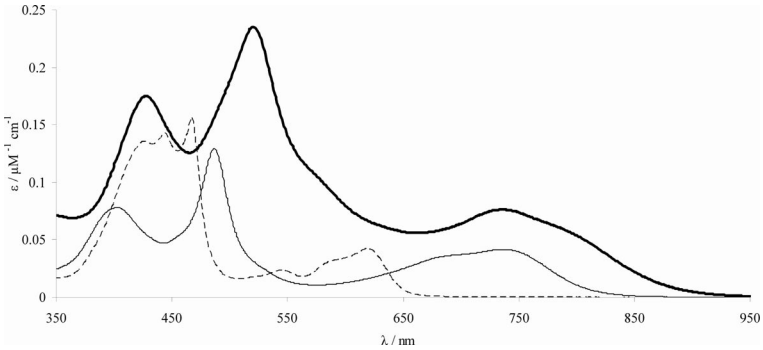


Figure 8. Comparison of the absorption spectra of tetramer **1** (bold), azo-linked dimer **5** (solid),[47] and butadiyne-linked dimer **9** (dashed) in CH_2Cl_2.

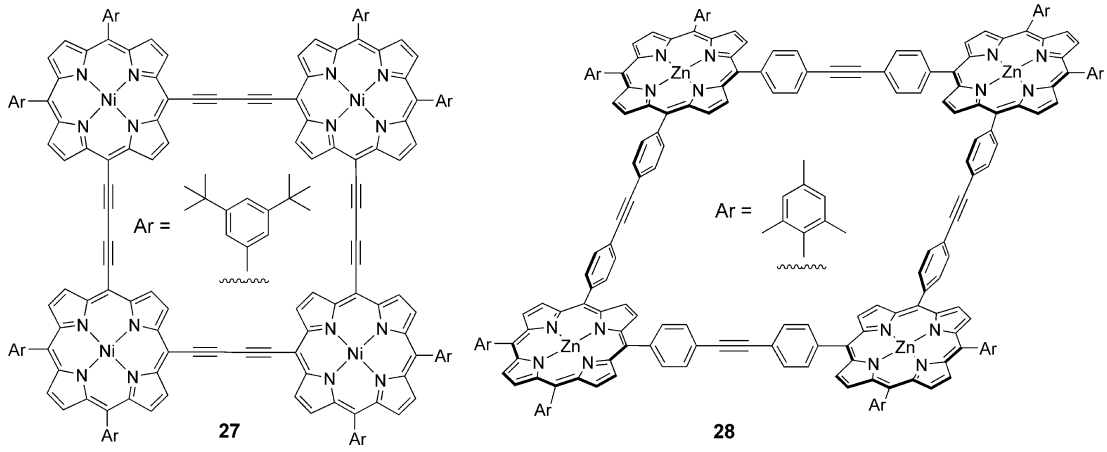


Figure 9. Butadiyne-linked tetramer **27**[6] and diphenylethyne-linked tetramer **28**.[5]

band splitting, however, the intensity of its Q-band normalized per chromophore was increased compared with that of the parent monomer.[6] Conversely, the intensity of the Soret band was decreased. This phenomenon confirms that the degeneracy of the a_{1u} and a_{2u} orbitals of the porphyrins is significantly lifted and that a new π-electronic system in the tetramer is formed..[18]

Table 3. Absorption spectroscopy data for the cyclic porphyrin tetramers.

Compound	M	λ_{max} Soret /nm	λ_{max} Q /nm	Splitting /cm^{-1}
1[a]	Ni	427 and 520	735	4190
1[b]	Ni	428 and 521	737	4170
1[c]	Ni	429 and 523	737	4190
27[b][6]	Ni	503	659	n/a
28[c][5]	Zn	430	591	n/a

[a] In DCM. [b] In chloroform. [c] In toluene.

The Q-band of compound **28** is at 591 nm in toluene and at 659 nm for compound **27** in chloroform. The absorption spectra of compound **1** in both chloroform and toluene have the Q-band located at 737 nm. The spectrum of tetramer **1** also shows a large red-shift when the UV/Vis spectrum is recorded in pyridine solution (Figure 10). The Q-band has a shift of more than 100 nm as it moves from 735 to 852 nm. The difference in the spectra could be explained as a result of the nickel core atoms changing from low spin four-coordinate to a high spin six-coordinate state. This is significant as the Ni–N bond length of the four-coordinate nickel porphyrin is shorter than that of the six-coordinate nickel compounds.[60–63] The shorter bond length between the nickel and the nitrogen atoms translates into puckering of the macrocycle.[64] It is not as flat as a free base porphyrin for example. Because the six-coordinate nickel compounds have longer Ni–N bond lengths the macrocycle is not as puckered. This allows for a much better π-overlap and an increase in the overall conjugation of the system. Further evidence of the six-coordinate state of nickel when in pyridine comes from ^{1}H NMR analysis. The proton spectrum of the compound could not be obtained in deuterated pyridine as the six-coordinate nickel(II) is paramagnetic. Similar results were obtained for the first azoporphyrin.[65]

It is worth noting that the relatively broad range of absorption displayed by the tetramer might be applicable to organic photonics and electronics. The large π-conjugation and photochemical and thermal stability, makes porphyrin derivatives attractive as possible materials for photonic and electronic applications. The fact that porphyrin derivatives are part of light harvesting and photo-induced electron transfer systems in the photosynthetic apparatus of plants suggests that porphyrins could be used as photosensitisers in dye-sensitized solar cells.[13,66–69] However, individual porphyrin units exhibit relatively narrow absorption bands

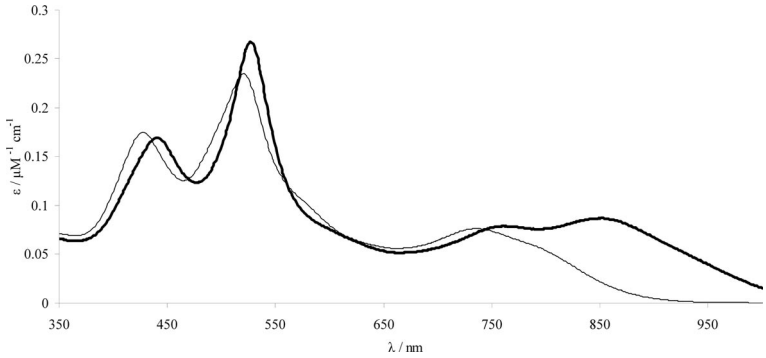


Figure 10. Absorption spectra of **1** in DCM (solid) and pyridine (bold).

which results in low power conversion efficiencies when porphyrin-containing polymers are used as active layers in organic solar cells.[68,70] Thus, a polymer incorporating larger porphyrinic arrays such as that found in compound **1** might exhibit a greater efficiency.

Conclusions

In summary, by synthesising the azo/butadiyne-linked Ni cyclic porphyrin tetramer we have extended both the families of azo- and butadiyne-linked porphyrin compounds. We have demonstrated that the butadiyne linker is much more robust than the azo linker. Previously we have found that the unsubstituted *meso* positions of the azo-linked porphyrin dimer are not amenable to further modification without incurring the loss of the bridge. Here we have demonstrated that the remaining *meso* positions of the porphyrin dimers linked by a butadiyne bridge can be further modified to facilitate the synthesis of a new CPO that has both the butadiyne and azo bridges. The three-dimensional geometry of the tetramer is presently unknown, although we have determined the X-ray crystal structures of three nickel(II) dimers containing azo linkers.[46,47] The presence of the Ni^{II} ion causes out-of-plane deformation of the macrocycles, leading to a ruffled geometry for the rings,[64] and an overall shallow sigmoidal shape for the dimers. The tetramer, therefore, is expected to assume the shape of a gently undulating sheet.

Finally, we have concluded that the coordinated metal plays an important role when it comes to linking porphyrin moieties by azo bridges. Further investigation is required to explain the fact that nickel corner porphyrins with an amino group can be linked using copper catalysis, while the analogous zinc compounds cannot.

Experimental Section

General Procedures: All chemicals used were of Analytical Reagent grade and were purchased from Sigma–Aldrich. 5,10-Diarylporphyrin **10**, nitro derivative **11** and its nickel(II) complex **14** and zinc(II) complex **19** were prepared as described.[47,71,72] 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 ^{1}H NMR spectra were measured on a Bruker Avance instrument operating at 400 MHz. All samples were prepared in deuterated chloroform. The chemical shifts are reported in ppm and referenced against the residual $CHCl_3$ peak at δ = 7.26 ppm. The coupling constants are given in Hz. ^{13}C NMR spectra were not recorded, as these spectra for porphyrins do not add materially to structure confirmation when ^{1}H spectra can be fully assigned by the use of two-dimensional techniques. The UV/Vis 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 10 kV cesium ions as the primary beam, and *m*-nitrobenzyl alcohol as the liquid matrix. ESI 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 μL/min. A voltage of 4500 V was applied at the tip. Matrix-assisted laser desorption/ionisation (MALDI) spectra were obtained at The University of Queensland, Brisbane. Analysis was performed with an Applied Biosystems Voyager-DE STR BioSpectrometry workstation. The instrument was operated in positive polarity in reflectron mode for analysis. The samples were spotted on a stainless steel sample plate using sinapinic acid as the matrix and allowed to air-dry. Data from 100 laser shots (337 nm laser) were collected, signal-averaged, and processed with the instrument manufacturer's Data Explorer software. Isotopic modelling was calculated by MassLynx V3.5 software by Micromass Limited and online using Isotopident on the Expert Protein Analysis System (ExPASY) server. 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. The Raman spectra were collected on a Renishaw Spectroscope 1000 coupled to an Olympus microscope using a helium/neon 633 nm laser with power of 0.2 mW at the sample.

5-Bromo-15,20-bis(3,5-di-*tert*-butylphenyl)-10-nitroporphyrin (12): Porphyrin **11** (56 mg, 7.65×10^{-5} mol) was dissolved in 10 cm^3 of chloroform. To this *N*-bromosuccinimide (NBS) (27 mg, 2 equiv., 1.53×10^{-4} mol) and pyridine (123 μL, 20 equiv., 1.53×10^{-3} mol) were added. The solution was heated at reflux for 5 h. The reaction did not go to completion. The solvent was removed and the residue purified by column chromatography using DCM/hexane/triethylamine (TEA) (100:100:1) as eluent. Two red fractions were isolated. The first was the target compound; yield 69% (43 mg). The second

was the starting material. The product was recrystallised from DCM/methanol; yield 61% (38 mg). The product was contaminated with an unidentified porphyrin impurity. ^{1}H NMR: δ = 9.74 (d, J = 5.0 Hz, 1 H, 7-H), 9.62 (d, J = 5.0 Hz, 1 H, 3-H), 9.34 (d, J = 5.0 Hz, 1 H, 8-H), 9.26 (d, J = 5.0 Hz, 1 H, 12-H), 8.98 (d, J = 5.0 Hz, 1 H, 13-H), 8.92 (d, J = 5.0 Hz, 1 H, 2-H), 8.85 (d, J = 5.0 Hz, 1 H, 18-H), 8.82 (d, J = 5.0 Hz, 1 H, 17-H), 8.03 (d, J = 1.8 Hz, 2 H, o-H_{aryl}), 8.02 (d, J = 1.8 Hz, 2 H, o-H_{aryl}), 7.86 (m, J = 1.8 Hz, 2 H, p-H_{aryl}), 1.56 (s, 18 H, tBu-H), 1.55 (s, 18 H, tBu-H), –2.56 (br. s, 2 H, inner NH) ppm. IR: $\upsilon(NO_{2\,asym})$ 1515 s, $\upsilon(NO_{2\,sym})$ 1364 s cm^{-1}. UV/Vis λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}): 425 (183), 523 (11.9), 563 (7.39), 594 (5.75), 653 (3.43). MS (LSI): m/z: (LSI) 810.3399 ($C_{48}H_{53}BrN_5O_2$ [M + H]$^+$ requires 810.3383). The reaction was repeated successfully on a 160 mg scale giving the same percentage yield.

15,20-Bis(3,5-di-*tert*-butylphenyl)-5-[2-(trimethylsilyl)ethynyl]-10-nitroporphyrin (13): Compound **12** (20 mg, 2.46×10^{-5} mol) was dissolved in TEA (15 cm^3) in a Schlenk flask under argon. To this (trimethylsilyl)acetylene (70 μL, 20 equiv., 4.92×10^{-4} mol), $Pd_2(dba)_3$ (5 mg, 20 mol-%, 4.92×10^{-6} mol), and $AsPh_3$ (6 mg, 80 mol-%, 1.96×10^{-5} mol) were added. The solution was stirred at 45 °C for 4 h. The solvent was removed and the residue purified by column chromatography using DCM/hexane/TEA (100:200:1) as eluent. A single red compound was isolated; yield 100% (20 mg). It was recrystallised from DCM/methanol; yield 24% (5 mg). The product was contaminated with an unidentified porphyrin impurity. ^{1}H NMR: δ = 9.77 (d, J = 4.8 Hz, 1 H, 7-H), 9.63 (d, J = 4.9 Hz, 1 H, 3-H), 9.36 (d, J = 4.8 Hz, 1 H, 8-H), 9.24 (d, J = 4.9 Hz, 1 H, 12-H), 8.95 (d, J = 4.9 Hz, 1 H, 13-H), 8.92 (d, J = 4.9 Hz, 1 H, 2-H), 8.83 (d, J = 4.7 Hz, 1 H, 18-H), 8.80 (d, J = 4.7 Hz, 1 H, 17-H), 8.03 (d, J = 2.0 Hz, 2 H, o-H_{aryl}), 8.01 (d, J = 2.0 Hz, 2 H, o-H_{aryl}), 7.85 (m, J = 2.0 Hz, 2 H, p-H_{aryl}), 1.55 (s, 18 H, tBu-H), 1.54 (s, 18 H, tBu-H), 0.65 (s, 9 H, $CH_{3\,silyl}$-H), –2.25 (br. s, 2 H, inner NH) ppm. IR: υ(CC) 2166 m cm^{-1}, $\upsilon(NO_{2\,asym})$ 1516 m cm^{-1}, $\upsilon(NO_{2\,sym})$ 1364 s cm^{-1}. UV/Vis: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}) 434 (191), 535 (12.3), 570 (9.89), 605 (5.78), 664 (2.31). MS (ESI): m/z: 827.4586 ($C_{53}H_{61}N_5O_2Si$, [M]$^+$ requires 827.4595). The reaction was repeated successfully on a 180 mg scale giving the same percentage yield.

5-Bromo-15,20-bis(3,5-di-*tert*-butylphenyl)-10-nitroporphyrinatonickel(II) (15): Compound **14** (54 mg, 6.84×10^{-5} mol) was dissolved in 5 cm^3 of chloroform. To this NBS (18 mg, 1.5 equiv., 1.03×10^{-14} mol) and pyridine (8 μL, 1.5 equiv., 1.03×10^{-4} mol) were added. The solution was heated at reflux for 1 h. The solvent was removed and the residue purified by column chromatography using DCM/hexane (1:1) as eluent. A single red compound was isolated; yield 97% (58 mg). It was recrystallised from DCM/methanol; yield 66% (39 mg). The product was a dark red powder. Alternatively, compound **12** (44 mg, 5.42×10^{-5} mol) was dissolved in minimum amount of toluene. To this Ni(acac)$_2$ (44 mg, 1.71×10^{-4} mol) was added. The solution was heated at reflux for 3 h. The solvent was removed and the residue purified by column chromatography using DCM/hexane (1:2) as eluent. A single red compound was isolated; yield 89% (42 mg). It was recrystallised from DCM/methanol; yield 60% (28 mg). The product was a dark red powder. ^{1}H NMR: δ = 9.57 (d, J = 5.1 Hz, 1 H, 7-H), 9.46 (d, J = 5.0 Hz, 1 H, 3-H), 9.26 (d, J = 5.1 Hz, 1 H, 8-H), 9.18 (d, J = 5.2 Hz, 1 H, 12-H), 8.86 (d, J = 5.2 Hz, 1 H, 13-H), 8.81 (d, J = 5.0 Hz, 1 H, 2-H), 8.75 (d, J = 5.0 Hz, 1 H, 18-H), 8.72 (d, J = 5.0 Hz, 1 H, 17-H), 7.81 (br. s, 4 H, o-H_{aryl}), 7.77 (br. s, 2 H, p-H_{aryl}), 1.50 (s, 36 H, tBu-H) ppm. IR: $\upsilon(NO_{2\,asym})$ 1513 s cm^{-1}, $\upsilon(NO_{2\,sym})$ 1336 s cm^{-1}. UV/Vis: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}) 423 (121), 538 (14.7). MS (LSI): m/z: 865.2507 ($C_{48}H_{50}BrN_5NiO_2$ [M]$^+$ requires 865.2501). The reaction was repeated successfully on a 160 mg scale and the alternative route was repeated successfully on an 80 mg scale giving the same percentage yields.

15,20-Bis(3,5-di-*tert*-butylphenyl)-5-[2-(trimethylsilyl)ethynyl]-10-nitroporphyrinatonickel(II) (16): Porphyrin **15** (30 mg, 3.45×10^{-5} mol) was dissolved in TEA (15 cm^3) in a Schlenk flask under argon. To this (trimethylsilyl)acetylene (97 μL, 20 equiv., 6.90×10^{-4} mol), $Pd_2(dba)_3$ (6 mg, 20 mol-%, 6.90×10^{-6} mol), and $AsPh_3$ (8.5 mg, 80 mol-%, 2.76×10^{-5} mol) were added. The solution was stirred at 45 °C for 2 h. The solvent was removed and the residue purified by column chromatography using DCM/hexane (1:2) as eluent. A single red compound was isolated; yield 98% (30 mg). It was recrystallised from DCM/methanol; yield 42% (13 mg). The product was a dark red powder. Alternatively, compound **13** (8.5 mg, 1.02×10^{-5} mol) was dissolved in 2 cm^3 of toluene. To this Ni(acac)$_2$ (8.5 mg, 3.30×10^{-5} mol) was added. The solution was heated at reflux for 2 h. The solvent was removed and the residue purified by column chromatography using DCM/hexane (1:2) as eluent. A single red compound was isolated; yield 99% (9 mg). It was recrystallised from DCM/methanol; yield 65% (6 mg). The product was a dark red powder. ^{1}H NMR: δ = 9.60 (d, J = 5.0 Hz, 1 H, 7-H), 9.48 (d, J = 5.0 Hz, 1 H, 3-H), 9.27 (d, J = 5.0 Hz, 1 H, 8-H), 9.15 (d, J = 5.0 Hz, 1 H, 12-H), 8.86 (d, J = 5.0 Hz, 1 H, 13-H), 8.83 (d, J = 5.0 Hz, 1 H, 2-H), 8.73 (d, J = 5.0 Hz, 1 H, 18-H), 8.71 (d, J = 5.0 Hz, 1 H, 17-H), 7.83 (d, J = 1.8 Hz, 2 H, o-H_{aryl}), 7.82 (d, J = 1.8 Hz, 2 H, o-H_{aryl}), 7.78 (m, J = 1.8 Hz, 2 H, p-H_{aryl}), 1.50 (s, 18 H, tBu-H), 1.49 (s, 18 H, tBu-H), 0.58 (s, 9 H, $SiCH_3$-H) ppm. IR: υ(CC) 2151 w cm^{-1}, $\upsilon(NO_{2\,asym})$ 1509 s cm^{-1}, $\upsilon(NO_{2\,sym})$ 1349 s cm^{-1}. UV/Vis: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}) 431 (144), 545 (12.2). MS (ESI): m/z: 884.3870 ($C_{43}H_{60}N_5NiO_2Si$ [M + H]$^+$ requires 884.3870). The reaction was repeated successfully on a 170 mg scale giving the same percentage yield.

1,4-Bis[15,20-bis(3,5-di-*tert*-butylphenyl)-10-nitroporphyrinatonickel(II)-5-yl]butadiyne (17): Compound **16** (30 mg, 3.39×10^{-5} mol) was dissolved in pyridine (18 cm^3). To this copper(II) acetate (40 mg, 6 equiv., 2.03×10^{-4} mol) was added and the solution was stirred at 80 °C. The starting material was consumed after 19 h. The reaction mixture was poured into 2 M HCl (50 cm^3) and extracted with DCM. The organic layer was washed with 2 M HCl (50 cm^3) and water (50 cm^3) before being dried with anhydrous potassium carbonate. The organic layer was decanted and the solvent evaporated; yield 97% (26 mg). It was recrystallised from DCM/methanol; yield 50% (14 mg). The product was a dark red/brown powder. ^{1}H NMR: δ = 9.80 (d, J = 5.0 Hz, 2 H, 7,7′-H), 9.70 (d, J = 4.8 Hz, 2 H, 3,3′-H), 9.36 (d, J = 5.0 Hz, 2 H, 8,8′-H), 9.17 (d, J = 4.8 Hz, 2 H, 12,12′-H), 8.95 (d, J = 4.8 Hz, 2 H, 2,2′-H), 8.88 (d, J = 4.8 Hz, 2 H, 13,13′-H), 8.76 (d, J = 5.0 Hz, 2 H, 17,17′-H), 8.74 (d, J = 5.0 Hz, 2 H, 18,18′-H), 7.88 (br. s, 4 H, o-H_{aryl}), 7.84 (br. s, 4 H, o-H_{aryl}), 7.80 (br. s, 2 H, p-H_{aryl}), 7.78 (br. s, 2 H, p-H_{aryl}), 1.52 (s, 36 H, tBu-H), 1.50 (s, 36 H, tBu-H) ppm. IR: υ(CC) 2171 w cm^{-1}, $\upsilon(NO_{2\,asym})$ 1508 m cm^{-1}, $\upsilon(NO_{2\,sym})$ 1342 s cm^{-1}. Raman: υ(CC) 2190 s cm^{-1}, υ(CC) 1369 m cm^{-1}. UV/Vis: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}) 461 (140), 479 (140), 559 (29.4), 629 (31.1). MS (ESI): m/z: 1621.6781, ($C_{100}H_{101}N_{10}NiO_4$ [M + H]$^+$ requires 1621.6714). The reaction was repeated successfully on a 100 mg scale giving the same percentage yield.

1,4-Bis[10-amino-15,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II)-5-yl]butadiyne (18): Dimer **17** (10 mg, 6.10×10^{-6} mol) was dissolved in DCM/methanol (4 cm^3/4 cm^3) that was bubbled with argon for 10 min. Argon atmosphere was maintained and then 10% palladium on carbon (3 mg) was added followed by addition

of sodium borohydride (2 mg, 8 equiv., 4.88×10^{-5} mol). The starting material was consumed after 45 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; yield 83% (8 mg). It was recrystallised from DCM/methanol; yield 10% (1 mg). The product was a dark green/purple sticky powder. ^{1}H NMR: δ = 9.43 (d, J = 4.8 Hz, 2 H, 3,3′-H), 9.41 (d, J = 4.8 Hz, 2 H, 7,7′-H), 9.02 (d, J = 4.8 Hz, 2 H, 8,8′-H), 8.86 (d, J = 4.6 Hz, 2 H, 12,12′-H), 8.62 (d, J = 4.8 Hz, 2 H, 2,2′-H), 8.50 (d, J = 4.6 Hz, 2 H, 13,13′-H), 8.49 (d, J = 4.6 Hz, 2 H, 17,17′-H), 8.41 (d, J = 4.6 Hz, 2 H, 18,18′-H), 7.81 (d, J = 1.8 Hz, 4 H, o-H_{aryl}), 7.79 (d, J = 1.8 Hz, 4 H, o-H_{aryl}), 7.70 (m, J = 1.8 Hz, 4 H, p-H_{aryl}), 5.77 (br. s, 4 H, NH_2), 1.49 (s, 36 H, tBu-H), 1.48 (s, 36 H, tBu-H) ppm. IR: υ(NH_2) 3378 m, υ(CC) 2128 w cm^{-1}, υ(NH_2) 1228 m cm^{-1}. Raman: υ(CC) 2182 s cm^{-1}, υ(CC) 1370 m cm^{-1}. UV/Vis: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}) 424 sh (106), 444 (124), 469 sh (65.5), 554 (8.02), 705 (33.5). MS (ESI): m/z: 1561.7233 ($C_{100}H_{105}N_{10}Ni_2$ [M + H]$^+$ requires 1561.7231). The reaction was repeated successfully on a 30 mg scale giving the same percentage yield.

Azo/Butadiyne Ni Tetramer (1): Compound **18** (29 mg, 1.84×10^{-5} mol) was dissolved in toluene (18.4 cm^3) creating a 0.001 M solution. To this copper(II) acetate (1.8 mg, 0.5 equiv., 9.20×10^{-6} mol) was added followed by pyridine (3 μL, 2 equiv., 3.68×10^{-5} mol). The solution was stirred at 80 °C for 20 h. The solvent was removed and the residue washed with water and extracted with DCM. The solvent was removed and the residue purified by column chromatography using DCM/hexane (1:1) as eluent. A single wine-red compound was isolated; yield 55% (16 mg). The compound was recrystallised from DCM/methanol as dark purple crystals; yield 44% (13 mg). ^{1}H NMR: δ = 10.59 (d, J = 4.8 Hz, 4 H, 7,7′,7″,7‴-H), 10.29 (d, J = 4.8 Hz, 4 H, 8,8′,8″,8‴-H), 10.14 (d, J = 5.0 Hz, 4 H, 3,3′,3″,3‴-H), 9.55 (d, J = 4.8 Hz, 4 H, 12,12′,12″,12‴-H), 8.97 (d, J = 4.8 Hz, 4 H, 2,2′,2″,2‴-H), 8.84 (d, J = 4.8 Hz, 4 H, 13,13′,13″,13‴-H), 8.66 (d, J = 4.9 Hz, 4 H, 18,18′,18″,18‴-H), 8.64 (d, J = 4.9 Hz, 4 H, 17,17′,17″,17‴-H), 7.91 (d, J = 1.7 Hz, 8 H o-H_{aryl}), 7.90 (d, J = 1.7 Hz, 8 H, o-H_{aryl}), 7.77 (d, J = 1.7 Hz, 8 H, o-H_{aryl}), 1.53 (s, 72 H, tBu-H), 1.52 (s, 72 H, tBu-H) ppm. UV/Vis: λ_{max}/nm, (ε/10^3 M^{-1} cm^{-1}) 427 (174), 520 (235), 735 (76.7). Raman: υ(CC) 2178 s cm^{-1}, υ(CC) 1350 s cm^{-1}. UV/Vis in toluene: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}) 441 (169), 527 (268), 761 (79.0), 852 (87.2). MS (MALDI-TOF): m/z: 3114.16 ($C_{200}H_{201}N_{20}Ni_4$ [M + H]$^+$ requires 3114.38).

5-Bromo-15,20-bis(3,5-di-*tert*-butylphenyl)-10-nitroporphyrinatozinc(II) (20): Compound **19** (195 mg, 2.23×10^{-4} mol) was dissolved in 10 cm^3 of chloroform. To this NBS (60 mg, 1.5 equiv., 3.35×10^{-14} mol) and pyridine (27 μL, 1.5 equiv., 3.35×10^{-4} mol) were added. The solution was heated at reflux for 30 min. The solvent was removed and the residue purified by column chromatography using DCM/hexane/pyridine (100:100:1) as eluent. A single green/purple compound was isolated; yield 85% (166 mg). It was recrystallised from DCM/methanol; yield 74% (145 mg). The product was a dark purple powder that was contaminated with an unidentified porphyrin impurity. ^{1}H NMR ($CDCl_3$ with [D_5]pyridine): δ = 9.79 (d, J = 4.7 Hz, 1 H, 7-H), 9.67 (d, J = 4.8 Hz, 1 H, 3-H), 9.37 (d, J = 4.7 Hz, 1 H, 8-H), 9.28 (d, J = 4.9 Hz, 1 H, 12-H), 8.97 (d, J = 4.9 Hz, 1 H, 13-H), 8.93 (d, J = 4.8 Hz, 1 H, 2-H), 8.85 (d, J = 4.5 Hz, 1 H, 18-H), 8.81 (d, J = 4.5 Hz, 1 H, 17-H), 7.99 (br. s, 2 H, o-H_{aryl}), 7.97 (br. s, 2 H, o-H_{aryl}), 7.81 (br. s, 2 H, p-H_{aryl}), 1.54 (br. s, 36 H, tBu-H) ppm. IR: υ($NO_{2\ asym}$) 1515 s cm^{-1}, υ($NO_{2\ sym}$) 1329 m cm^{-1}. UV/Vis: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}) 427 (235), 556 (17.1), 601 (7.10). MS (MALDI-TOF): m/z: 870.88 ($C_{48}H_{50}BrN_5O_2Zn$ [M]$^+$ requires 871.24).

15,20-Bis(3,5-di-*tert*-butylphenyl)-5-[2-(trimethylsilyl)ethynyl]-10-nitroporphyrinatozinc(II) (21): Porphyrin **20** (107 mg, 1.29×10^{-5} mol) was dissolved in 10 cm^3 of chloroform and stirred. To this Zn(OAc)$_2$ (107 mg, 4.87×10^{-4} mol) in 2 cm^3 of methanol was added. The mixture was refluxed at 60 °C. After 30 min the starting material was consumed. The solution was washed with water and the product was extracted with DCM. The solvent was evaporated and the product was dark purple/green; yield 91% (105 mg). It was recrystallised from DCM/methanol yielding a few shiny purple crystals; yield 9% (10 mg). The product was contaminated with an unidentified porphyrin impurity. ^{1}H NMR ($CDCl_3$ with [D_5]-pyridine): δ = 9.77 (d, J = 4.7 Hz, 1 H, 7-H), 9.64 (d, J = 4.8 Hz, 1 H, 3-H), 9.36 (d, J = 4.7 Hz, 1 H, 8-H), 9.24 (d, J = 4.8 Hz, 1 H, 12-H), 8.94 (d, J = 4.8 Hz, 1 H, 13-H), 8.92 (d, J = 4.8 Hz, 1 H, 2-H), 8.82 (d, J = 4.8 Hz, 1 H, 18-H), 8.79 (d, J = 4.8 Hz, 1 H, 17-H), 7.98 (d, J = 1.8 Hz, 2 H, o-H_{aryl}), 7.96 (d, J = 1.8 Hz, 2 H, o-H_{aryl}), 7.80 (m, J = 1.8 Hz, 2 H, p-H_{aryl}), 1.53 (s, 18 H, tBu-H), 1.52 (s, 18 H, tBu-H), 0.63 (s, 9 H, $CH_{3\ silyl}$-H) ppm. IR: υ(CC) 2145 w cm^{-1}, υ($NO_{2\ asym}$) 1500 s cm^{-1}, υ($NO_{2\ sym}$) 1330 s cm^{-1}. UV/Vis: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}) 435 (195), 565 (13.0). MS (LSI): m/z: 890.3783 ($C_{53}H_{60}N_5NiZnO_2$ [M + H]$^+$ requires 890.3808).

1,4-Bis[15,20-bis(3,5-di-*tert*-butylphenyl)-10-nitroporphyrinatozinc(II)-5-yl]butadiyne (22): Compound **21** (30 mg, 3.36×10^{-5} mol) was dissolved in pyridine (20 cm^3). To this copper(II) acetate (40 mg, 6 equiv., 2.02×10^{-4} mol) was added and the solution was stirred at 80 °C. The starting material was consumed after 24 h. The solvent was removed and the residue extracted with DCM after being washed with water (2 × 15 cm^3). The solvent was evaporated and the residue purified by column chromatography using DCM/hexane/pyridine (200:200:1); yield 95% (26 mg). It was recrystallised from DCM/methanol; yield 58% (16 mg). The product was a dark purple/green powder. ^{1}H NMR: δ = 10.05 (d, J = 4.7 Hz, 2 H, 7,7′-H), 9.92 (d, J = 4.5 Hz, 2 H, 3,3′-H), 9.48 (d, J = 4.7 Hz, 2 H, 8,8′-H), 9.26 (d, J = 4.8 Hz, 2 H, 12,12′-H), 9.06 (d, J = 4.5 Hz, 2 H, 2,2′-H), 8.97 (d, J = 4.8 Hz, 2 H, 13,13′-H), 8.85 (d, J = 4.6 Hz, 2 H, 17,17′-H), 8.82 (d, J = 4.6 Hz, 2 H, 18,18′-H), 8.05 (d, J = 2.0 Hz, 4 H, o-H_{aryl}), 8.00 (d, J = 2.0 Hz, 4 H, o-H_{aryl}), 7.84 (t, J = 2.0 Hz, 2 H, p-H_{aryl}), 7.82 (t, J = 2.0 Hz, 2 H, p-H_{aryl}), 1.57 (s, 36 H, tBu-H), 1.57 (s, 36 H, tBu-H) ppm. IR: υ(CC) 2187 w cm^{-1}, υ($NO_{2\ asym}$) 1500 m cm^{-1}, υ($NO_{2\ sym}$) 1333 s cm^{-1}. Raman: υ(CC) 2187 s cm^{-1}, υ(CC) 1352 m cm^{-1}. UV/Vis: λ_{max}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1}) 463 (141), 490 (156), 578 (19.1), 660 (40.1). MS (MALDI-TOF): m/z: 1632.58 ($C_{100}H_{101}N_{10}ZnO_4$ [M + H]$^+$ requires 1632.65). The reaction was repeated successfully on a 60 mg scale giving the same percentage yield.

1,4-Bis[10-amino-15,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II)-5-yl]butadiyne (23): Dimer **22** (66 mg, 4.03×10^{-5} mol) was dissolved in DCM/methanol (25 cm^3/25 cm^3) that was bubbled with argon for 10 min. Argon atmosphere was maintained and then 10% palladium on carbon (21 mg) was added followed by addition of sodium borohydride (9.1 mg, 6 equiv., 2.42×10^{-5} mol). The starting material was consumed after 40 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 yielding small purple crystals; yield 80% (51 mg). ^{1}H NMR: δ = 9.62 (d, J = 4.6 Hz, 2 H, 7,7′-H), 9.61 (d, J = 4.6 Hz, 2 H, 3,3′-H), 9.20 (d, J = 4.6 Hz, 2 H, 8,8′-H), 8.99 (d, J = 4.6 Hz, 2 H, 12,12′-H), 8.66 (d, J = 4.6 Hz, 2 H, 2,2′-H), 8.55 (d, J = 4.6 Hz, 2 H, 13,13′-H), 8.54 (d, J = 5.0 Hz, 2 H, 17,17′-H), 8.46 (d, J = 5.0 Hz, 2 H, 18,18′-H), 7.95 (t, J = 1.6 Hz, 8 H, o-H_{aryl}), 7.74 (t, J = 1.6 Hz, 2 H, p-H_{aryl}), 7.72 (t, J = 1.6 Hz, 2 H, p-H_{aryl}), 6.38 (br. s, 4 H, NH_2), 1.53 (s, 36

H, *t*Bu-H), 1.52 (s, 36 H, *t*Bu-H) ppm. IR: υ(NH_2) 3395b, υ(CC) 2125 w cm^{-1}, υ(NH_2) 1217 s cm^{-1}. Raman: υ(CC) 2174 m cm^{-1}, υ(CC) 1350 m cm^{-1}. UV/Vis: λ_{max}/nm ($\varepsilon/10^3$ $mol^{-1}dm^3cm^{-1}$) 427 (142), 442 (96.2), 687 (16.2), 755 (22.2). MS (MALDI-TOF): *m*/*z*: 1572.59 ($C_{100}H_{105}N_{10}Ni_2$ $[M + H]^+$ requires 1572.70).

Attempted Synthesis of Azo/Butadiyne Zn Tetramer: Compound **23** (27 mg, 1.72×10^{-5} mol) was dissolved in toluene (17.2 cm^3) creating a 0.001 M solution. To this copper(II) acetate (1.7 mg, 0.5 equiv., 8.51×10^{-6} mol) was added followed by pyridine (5.6 μL, 4 equiv., 6.88×10^{-5} mol). The solution was stirred at 80 °C. The starting material was consumed within 1 h. The solvent was removed and the residue washed with water and extracted with DCM. The tetramer was not formed. The main products were non-porphyrinic compounds as shown by ^{1}H NMR spectroscopy.

5-Bromo-10,15-bis(3,5-di-*tert*-butylphenyl)porphyrin (24): Porphyrin **10** (58 mg, 8.44×10^{-5} mol) was dissolved in 10 cm^3 of chloroform and stirred in an ice bath. To this pyridine (68 μL, 8.44×10^{-4} mol) was added followed by NBS (15 mg, 1 equiv., 8.44×10^{-5} mol). After 30 min the reaction was stopped and solvent removed. Product was purified by column chromatography using DCM/hexane/TEA (200:200:1) as eluent. Three red fractions were collected. The first was the dibrominated porphyrin; yield 15%. The second was the target compound; yield 80%. The third was starting material; yield 5%. The target compound was recrystallised from DCM/methanol. The product was a red/purple powder; yield 78% (51 mg). ^{1}H NMR: δ = 10.12 (s, 1 H, 20-H), 9.77 (d, *J* = 4.9 Hz, 1 H, 3-H), 9.70 (d, *J* = 4.9 Hz, 1 H, 7-H), 9.37 (d, *J* = 4.9 Hz, 1 H, 2-H), 9.31 (d, *J* = 4.5 Hz, 1 H, 18-H), 9.05 (d, *J* = 4.5 Hz, 1 H, 17-H), 8.99 (d, *J* = 4.9 Hz, 1 H, 8-H), 8.94 (d, *J* = 4.8 Hz, 1 H, 13-H), 8.91 (d, *J* = 4.8 Hz, 1 H, 12-H), 8.09 (d, *J* = 2.0 Hz, 2 H, *o*-H_{aryl}), 8.08 (d, *J* = 2.0 Hz, 2 H, *o*-H_{aryl}), 7.85 (m, *J* = 2.0 Hz, 2 H, *p*-H_{aryl}), 1.57 (s, 18 H, *t*Bu-H), 1.56 (s, 18 H, *t*Bu-H), –2.91 (br. s, 2 H, inner NH) ppm. UV/Vis: λ_{max}/nm ($\varepsilon/10^3$ $mol^{-1}dm^3cm^{-1}$) 416 (406), 513 (17.1), 547 (8.03), 587 (5.26), 643 (3.80). MS (LSI): *m*/*z*: 764.3487 ($C_{48}H_{53}BrN_4$ $[M]^+$ requires 764.3454).

5-Bromo-10,15-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (25): Porphyrin **24** (50 mg, 6.52×10^{-5} mol) was dissolved in 10 cm^3 of toluene and stirred. To this $Ni(acac)_2$ (50 mg, 1.95×10^{-4} 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 recrystallised from DCM/methanol to give red/purple crystals; yield 100% (53 mg). ^{1}H NMR: δ = 9.74 (s, 1 H, 20-H), 9.65 (d, *J* = 4.8 Hz, 1 H, 3-H), 9.58 (d, *J* = 5.0 Hz, 1 H, 7-H), 9.18 (d, *J* = 4.8 Hz, 1 H, 2-H), 9.10 (d, *J* = 4.6 Hz, 1 H, 18-H), 8.91 (d, *J* = 4.6 Hz, 1 H, 17-H), 8.88 (d, *J* = 5.0 Hz, 1 H, 8-H), 8.82 (d, *J* = 4.9 Hz, 1 H, 13-H), 8.80 (d, *J* = 4.9 Hz, 1 H, 12-H), 7.88 (d, *J* = 2.0 Hz, 2 H, *o*-H_{aryl}), 7.86 (d, *J* = 2.0 Hz, 2 H, *o*-H_{aryl}), 7.75 (t, *J* = 2.0 Hz, 2 H, *p*-H_{aryl}), 1.50 (s, 36 H, *t*Bu-H) ppm. UV/Vis: λ_{max}/nm ($\varepsilon/10^3$ $mol^{-1}dm^3cm^{-1}$) 412 (196), 526 (10.5). MS (LSI): *m*/*z*: 820.2655, ($C_{48}H_{53}BrN_4Ni$ $[M]^+$ requires 820.2651).

10,15-Bis(3,5-di-*tert*-butylphenyl)-5-[2-(trimethylsilyl)ethynyl]-porphyrinatonickel(II) (26): Porphyrin **25** (27 mg, 3.28×10^{-5} mol) was dissolved in TEA (25 cm^3) in a Schlenk flask under argon. To this (trimethylsilyl)acetylene (91 μL, 20 equiv., 6.56×10^{-4} mol), $Pd_2(PPh_3)_2Cl_2$ (2.3 mg, 10 mol-%, 3.28×10^{-6} mol), and CuI (1.2 mg, 20 mol-%, 6.56×10^{-6} mol) were added. The solution was stirred at 50 °C for 22 h. The solvent was removed and the residue purified by column chromatography using DCM/hexane (1:2) as eluent. A single red compound was isolated. It was recrystallised from DCM/methanol. The product was a dark red powder; yield 86% (24 mg). ^{1}H NMR: δ = 9.79 (s, 1 H, 20-H), 9.65 (d, *J* = 4.6 Hz, 1 H, 3-H), 9.58 (d, *J* = 5.0 Hz, 1 H, 7-H), 9.19 (d, *J* = 4.6 Hz, 1 H, 2-H), 9.09 (d, *J* = 4.8 Hz, 1 H, 18-H), 8.90 (d, *J* = 4.8 Hz, 1 H, 17-H), 8.88 (d, *J* = 5.0 Hz, 1 H, 8-H), 8.80 (d, *J* = 4.6 Hz, 1 H, 12-H), 8.78 (d, *J* = 4.6 Hz, 1 H, 13-H), 7.88 (m, *J* = 2.0 Hz, 4 H, *o*-H_{aryl}), 7.76 (t, *J* = 2.0 Hz, 2 H, *p*-H_{aryl}), 1.50 (s, 36 H, *t*Bu-H), 0.60 (s, 9 H, $CH_{3\ silyl}$-H) ppm. UV/Vis: λ_{max}/nm ($\varepsilon/10^3$ $mol^{-1}dm^3cm^{-1}$) 420 (253), 535 (16.8), 567 (9.26). MS (ESI): *m*/*z*: 839.4004, ($C_{53}H_{61}N_4NiSi$ $[M + H]^+$ requires 839.4019).

1,4-Bis[10,15-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II)-5-yl-]butadiyne (9): Compound **26** (20 mg, 2.38×10^{-5} mol) was dissolved in pyridine (12 cm^3). To this solution, copper(II) acetate (29 mg, 6 equiv., 1.43×10^{-4} mol) was added and the solution was stirred at 80 °C. The starting material was consumed after 21 h. The reaction mixture was poured into 2 M HCl (25 cm^3) and extracted with DCM. The organic layer was washed with 2 M HCl (25 cm^3) and water (25 cm^3) before being dried with anhydrous potassium carbonate. The organic layer was decanted and the solvent evaporated; yield 93% (17 mg). It was recrystallised from DCM/methanol; yield 76% (14 mg). The product was a dark green powder. ^{1}H NMR: δ = 9.89 (d, *J* = 4.8 Hz, 2 H, 3,3′-H), 9.83 (s, 2 H, 20,20′-H), 9.82 (d, *J* = 4.8 Hz, 2 H, 7,7′-H), 9.29 (d, *J* = 4.8 Hz, 2 H, 2,2′-H), 9.11 (d, *J* = 4.8 Hz, 2 H, 18,18′-H), 9.00 (d, *J* = 4.8 Hz, 2 H, 8,8′-H), 8.92 (d, *J* = 4.8 Hz, 2 H, 17,17′-H), 8.82 (d, *J* = 5.1 Hz, 2 H, 12,12′-H), 8.80 (d, *J* = 5.1 Hz, 2 H, 13,13′-H), 7.93 (d, *J* = 2.0 Hz, 4 H, *o*-H_{aryl}), 7.90 (d, *J* = 2.0 Hz, 4 H, *o*-H_{aryl}), 7.78 (t, *J* = 2.0 Hz, 2 H, *p*-H_{aryl}), 7.76 (t, *J* = 2.0 Hz, 2 H, *p*-H_{aryl}), 1.53 (s, 36 H, *t*Bu-H), 1.51 (s, 36 H, *t*Bu-H) ppm. Raman: υ(CC) 2194 s cm^{-1}, υ(CC) 1368 s cm^{-1}. UV/Vis: λ_{max}/nm ($\varepsilon/10^3$ $mol^{-1}dm^3cm^{-1}$) 425 (136), 444 (143), 467 (157), 545 (24.1), 619 (42.8). MS (ESI): *m*/*z*: 1531.7058, ($C_{100}H_{103}N_8Ni_2$ $[M + H]^+$ requires 1531.7013).

Supporting Information (see also the footnote on the first page of this article): ^{1}H NMR spectra of all new compounds (Figures S1–S15).

Acknowledgments

We thank the Australian Research Council for financial support through Discovery Grant DP0663774 and Prof. K.-i. Sugiura for collaboration on the corner porphyrin synthesis. B. B. thanks the Queensland University of Technology for post-graduate scholarships.

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Received: March 22, 2010
Published Online: May 27, 2010

