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Butadiyne-linked bis(chlorin) and chlorin–porphyrin dyads and an improved synthesis of bis[octaethylporphyrinatonickel-(II)-5-yl]butadiyne using the Takai iodoalkenation

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Abstract—*meso*-EthynylNiOEC (OEC=dianion of octaethylchlorin) was obtained by dehydrohalogenation of the novel *meso*-(2′-bromovinyl)NiOEC, prepared from NiOEC—CHO by low-temperature Wittig bromoalkenation. An improved synthesis of the known conjugated bis(porphyrin) NiOEP—C_4—NiOEP (OEP=dianion of octaethylporphyrin) was achieved via the previously unreported *meso*-(2′-iodovinyl)NiOEP, which was prepared by Takai iodoalkenation (CHI_3, $CrCl_2$) of *meso*-formylNiOEP. The Takai chemistry was also applied to the NiOEC aldehyde, but the yield was much lower than for the Wittig bromoalkenation. The reaction was unsuccessful for H_2OEP—CHO, ZnOEP—CHO and CuOEP—CHO. The ethynyl chlorin was homocoupled to give the first example of a conjugated alkyne-linked bis(chlorin), and heterocoupled with 5-ethynylNiDPP (DPP=dianion of 5,15-diphenylporphyrin) to give the first chlorin-alkyne–porphyrin dyad. The first *meso*,*meso*-butadiyne-linked heteroporphyrin dyad NiOEP—C_4—NiDPP was also prepared. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The synthesis and spectroscopic characterisation of alkyne-linked oligo(porphyrins) has revealed some remarkable new porphyrinoid chromophores.[1–4] The extended conjugation possible through alkyne-containing bridges linked at the *meso* positions leads to split Soret bands and intensified bands in the far red and into the near-IR regions. Moreover, these systems display unique electrochemical behaviour and their electrogenerated π-anions and dianions exhibit remarkably intense near-IR bands.[1f–h] The literature in this field has been recently reviewed by Anderson,[5] and the work of the QUT group and our collaborators was summarised in an account.[6] Combination of porphyrin building blocks into trimeric and oligomeric arrays by Therien[3] and Anderson,[2b,d,f,j] respectively, has extended the early work on dimers. These authors have studied various aspects of the excited states of their systems, and the results have underlined the potential of these compounds as the basis of optoelectronic and nanotechnological materials.[2,3] We have also found that our dimeric systems in the form of Langmuir–Blodgett films can serve as conductometric gas sensors.[1i]

The *meso*-alkyne moiety has been incorporated into porphyrins in three ways: (i) in the porphyrin cyclisation step, using mono- or dipyrroles and alkynyl aldehydes;[2a,7] (ii) by coupling *meso*-haloporphyrins with alkynes or alkynyl organometallics;[3a,8] and (iii) by conversion of formyl- to alkynylporphyrins.[1a,b] We used the last of these in our syntheses of the prototype NiOEP dimer **1** and other systems with more complex alkynyl bridges (OEP=dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin).[1a–d] In the interests of generating additional dyads with novel alkynyl-porphyrinoid electronic spectral signatures, we decided to broaden the field to include the dihydroporphyrin (chlorin) nucleus. We report here the synthesis and electronic absorption spectra of the first examples of bis(chlorin)butadiynes, together with new chlorin–porphyrin and unsymmetrical porphyrin–porphyrin dyads, using NiOEC (OEC=dianion of *trans* isomer of 2,3,7,8,12,13,17,18-octaethylchlorin) as the substrate. As a starting point, we carried out model studies on the known NiOEP systems, and incidentally improved our previous synthesis of **1** and its ethynyl precursor, the latter being the essential starting material for our preparations of a range of bridged NiOEP dimers.[1d]

2. Results and discussion

2.1. Re-investigation of the Wittig bromoalkenation of *meso*-formylNiOEP

The first reported synthesis of **1** involved the sequence *meso*-formylNiOEP **3** to vinyl **4** (Wittig) to *E*/*Z*-β-bromovinyl **5** (substitutive bromination) to ethynyl **6** (dehydrohalogenation),

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Keywords: chlorin; porphyrin; dyads; butadiyne; Wittig; Takai; electronic spectra.

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then oxidative coupling to yield **1**.[1a] This route was improved by one step to form **5a** directly from **3**.[1b] However, both these routes were somewhat problematic when scaled-up and when we tried to increase yields of **5a** by the use of excess Wittig reagent, such as the combination bromomethyltriphenylphosphonium bromide and butyllithium. Under these conditions, the vinyl compound **4** became a significant by-product in **5a**, and it could not be efficiently separated by chromatography from either **5a** or **6**. Our detour around this problem was to tolerate the presence of **4** until after the oxidative coupling, when **4** could be removed from the dimer **1** by one or two recrystallisations from dichloromethane/methanol. This procedure was unsatisfying, and also was a problem if we wanted to use **5a** or **6** for other chemistry.

The limitation on the use of bromomethyltriphenylphosphonium bromide and alkyllithium bases is the metal–halogen exchange reaction which leads to formation of lithiated methylene ylide, and subsequently formation of **4** upon reaction with aldehyde **3**. This reaction occurs even at reduced temperatures. It is known that this reaction can be completely avoided by the use of weaker bases, especially potassium *t*-butoxide in THF.[9] At room temperature, the ylide is formed in low yield, but reacting at −78°C improves the situation dramatically. Conversion of aldehyde **3** to pure **5a** occurred in 53% yield, with no detectable contamination from **4**. Attempts to increase the yield by the use of excess reagents were unproductive. This yield is comparable to our previous results, but the lack of **4** in the product was an improvement. However, we still sought to raise the yield of this step, as those of the other steps from NiOEP **2** to dimer **1** are all >80%. At this stage we turned to other methods of haloalkenation, and immediately found that the Takai reaction was applicable.

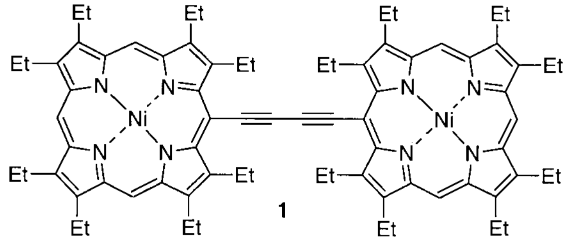
2.2. The Takai iodoalkenation of porphyrin aldehydes and the optimised preparation of 1

The Takai haloalkenation is a simple and stereoselective method for the conversion of aldehydes to the corresponding *E*-alkenyl halides using the combination haloform/chromium(II) chloride.[10] Although the halide can be Cl, Br or I, we tried first with iodoform with a view to forming the more reactive vinylic iodide for subsequent transformations. A literature version of the Takai reaction was attempted on aldehyde **3** using an aldehyde: iodoform: chromous chloride ratio of 1:2:6, and rigorously dry conditions and solvent. Examination by TLC indicated rapid consumption of about 25% of the starting material, with the formation of a less-polar red product, later confirmed to be the desired iodovinyl compound **7**. However, the reaction proceeded no further. The excess of reagents was successively increased until at a ratio of 1:10:30, there was full conversion of the starting material in 3 h. After removal of the excess iodoform by treatment with tetrabutylammonium fluoride (TBAF)[11] and column chromatography, the major product in a reaction starting with 100 mg of **3** was the desired iodovinylNiOEP **7** in 75% isolated yield. As expected from the hindered nature of the aldehyde, the product was exclusively the *E* isomer.

Careful examination of the more polar products of the reaction resulted in the isolation of two minor by-products, the methyl ketone **8** (12%) and the acetaldehyde **9** (1%). A search of the literature failed to locate any previous reports of the former, a rather simple OEP derivative. It was fully characterised by spectroscopy and elemental analysis, and a crystal structure carried out on rather poor-quality crystals revealed the presence of the *meso*-acetyl group, but we have so far failed to produce more suitable crystals. The acetaldehyde **9** was previously reported by us as the product of the nucleophilic addition of pyrrolidine to alkyne **6**, followed by hydrolysis of the enamine.[1d] The formation of **8** and **9** can be explained as an example of the Hodgson reaction, in which one pathway for the organochromium intermediates in the Takai reaction involves chromium enolates which are protonated during work-up to form the isomeric carbonyl products.[12]

Clearly, the Takai reaction results in a marked improvement in formation of halovinyl compounds from aldehyde **3**, when compared with the previous and present versions of the Wittig reaction. We already knew that dehydrobromination of **5a** with potassium *t*-butoxide was rapid and quantitative, and that the subsequent oxidative coupling of **6** to **1** gave an excellent yield.[1a,b,d,13] Therefore we attempted to telescope the last two steps so that both are performed in the one flask. The iodovinyl porphyrin **7** was dissolved in dry pyridine, potassium *t*-butoxide (2 equivalents in THF) was added, and the mixture was stirred at room temperature for 1 h. After confirmation by TLC that **7** had been consumed, excess copper(II) acetate was added, the mixture was heated to 60°C, and left for 2 h. This one-pot method generated **1** from **7**, free of **4**, in 84% yield on a 0.03 mmol scale. On a larger scale (800 mg of **3**), the Takai reaction yield dropped to 60% (with some starting aldehyde recoverable), and the one-pot method resulted in isolation of pure **1** in 50% yield for the two steps.

In one attempt at the large-scale procedure from **3** to **1**, we were able to isolate two additional polar green products. One of these was identified as *meso*-formylvinylNiOEP **10** by comparison with the literature NMR spectral data.[14] Its presence at this stage is unexplained, as even if it were formed during the Takai reaction as a novel homologation of **7** or **9**, its very polar nature should have allowed its removal in the column chromatography of **7**. Moreover, we have never detected the presence of **10** in samples of **7**. The other polar compound clearly appeared to be an OEP dimer, since its visible spectrum showed a strong broad shoulder on the low-energy edge of the Soret band, and the NMR spectrum showed two complete sets of OEP protons. The visible spectrum was reminiscent of our dimers in which the bridge contained both alkyne and alkene components.[1d,g] Also visible in the ^{1}H NMR spectrum was a *trans*-alkenyl unit, and a pair of porphyrin ethyl groups was shifted downfield from the others, a characteristic of *meso*-ethynylNiOEP fragments. By comparison with its known spectrum,[1d] the *trans*-butenyne-linked dimer was eliminated. In the new compound, the alkene protons appeared at 5.94 and 10.14 ppm, respectively, 0.6 and 0.7 ppm downfield from their positions in the butenyne. The mass spectrum showed the presence of an extra 28 mass units, and the IR spectrum showed bands at 2161 and 1637 cm^{-1}. Including an elemental analysis, all the



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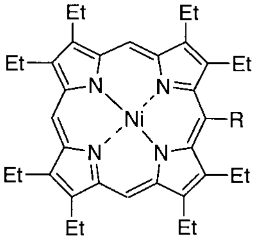
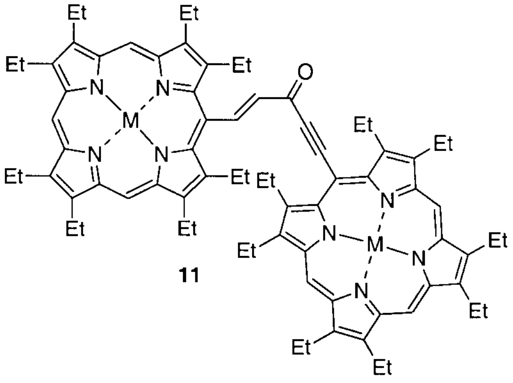
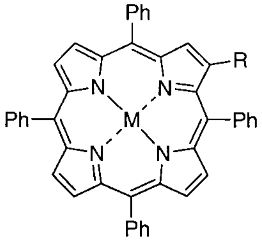


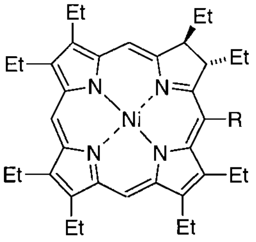
R = H **2**
CHO **3**
$CH=CH_2$ **4**
CH=CH-Br **5a** (*E*), **5b** (*Z*)
C≡C-H **6**
CH=CH-I **7**
$COCH_3$ **8**
CH_2CHO **9**
CH=CH-CHO **10**



11



R = CHO **12**
CH=CH-Br **13**
CH=CH-I **14**



R = H **15**
CHO **16**
CH=CH-I **17**
CH=CH-Br **18**
$CH=CH_2$ **19**
C≡C-H **20**

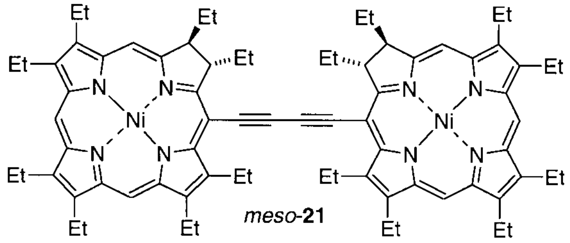
evidence indicates that the only possible structure is **11**, the NiOEP dimer linked by a conjugated *trans*-ene-one-yne bridge. This is presently the only known example of such a system. At the moment we are at a loss to explain its presence in this reaction. One possibility is a copper-mediated addition of **6** to the formylvinyl **10**, followed by oxidation. An attempt to reproduce such a reaction failed to yield any of the new dimer **11**, and the aldehyde **10** was recovered, together with the expected homocoupling product **1**. Numerous unsuccessful attempts were made to produce X-ray-quality single crystals.

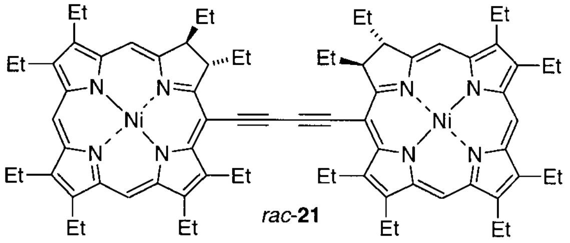
Having succeeded with the Takai reaction on aldehyde **3**, a few other porphyrin aldehydes were canvassed. With 2-formylNiTPP **12** (TPP=dianion of 5,10,15,20-tetraphenylporphyrin), we had previously obtained a mixture of *E*- and *Z*-bromovinyl species **13** using the Wittig bromoalkenation.[1b] Use of our Takai conditions produced an 87% yield of the mixed *E*- and *Z*-β-iodovinylNiTPP **14**. However, the reaction failed completely to produce iodovinyl derivatives from other OEP aldehydes, namely the free base, zinc(II) and copper(II) analogues of **3**. We had previously found a similar result for the Wittig bromoalkenation of these aldehydes. With CuOEP—CHO, whose reactivity is expected to be the closest to that of **3**, Takai reaction with a large excess of reagents, or heating in refluxing THF made no difference, and only starting aldehyde was recovered. This clearly indicates that either the electrophilicity of the aldehyde carbon of **3** is higher than that of the other analogues, or else the expected non-planar distortion of the porphyrin ring produces a favourable geometry for the approach of the bulky organochromium reagent.

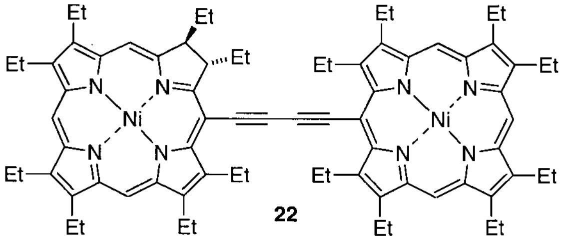
2.3. Haloalkenation of *meso*-formylNiOEC

With the porphyrin results in hand, we now turn to the application of this chemistry to our more challenging target systems derived from NiOEC **15**. The chlorin aldehyde **16** was obtained using the Vilsmeier formylation of **15**, according to the method recently reported by Senge and co-workers.[15] NiOEC was itself prepared by the known route in which the *trans*-chlorin results from dissolving metal reduction of Fe(OEP)Cl.[16] As a result of autoxidation during the formylation step, our samples of **16** were contaminated with about 5% (by NMR) of the porphyrin aldehyde **3**. Efficient separation was only feasible on a very small scale, so we proceeded with this slightly impure material, since the porphyrin NMR signals are always readily distinguished from those of the chlorins.

Based on the results of the Takai reaction with **3**, the first reaction attempted was that of **16** with $CrCl_2/CHI_3$ using the conditions applied for **3**. However, the reaction was much less satisfactory, and only 10% of the iodovinylNiOEC **17** was isolated. Increasing the excess of reagents and increasing the temperature were not helpful, and in the latter case, increasing amounts of **15** were formed, showing that deformylation was favoured by heating. Deformylation of porphyrin aldehydes under basic conditions has been observed before by us and others.[1b,17] The inapplicability of the Takai reaction led us back to the Wittig bromoalkenation. Using bromomethyltriphenylphosphonium bromide as ylide precursor, three sets of conditions of base and temperature were investigated, namely BuLi/room temperature, BuLi/−78°C, and *t*BuOK/−78°C. Under the first two conditions, the required bromovinylNiOEC **18**


meso-**21**


rac-**21**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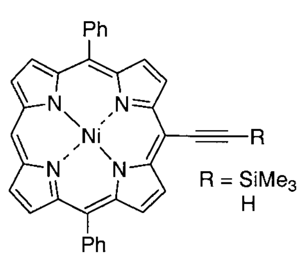
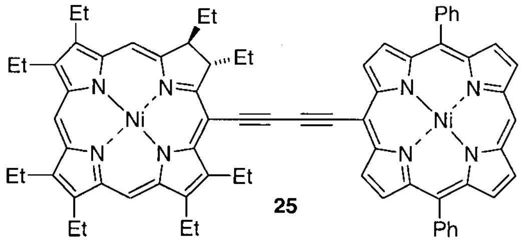

R = $SiMe_3$ **23**
H **24**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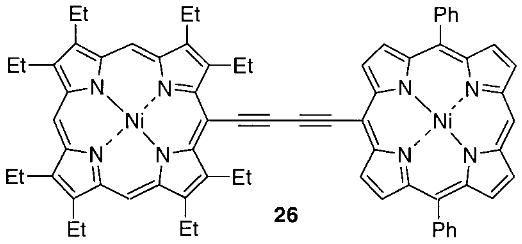
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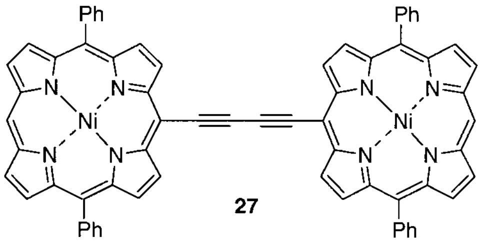
27

was heavily contaminated with the *meso*-vinylNiOEC **19**. At room temperature, **19** was actually the major product (60:40). This is the same problem as observed with the porphyrin analogues, namely metal–halogen exchange on the bromo-ylide, but it is worse with the chlorins. Alkene **19** is a new compound, so we also prepared an authentic sample of it in 72% yield by the reaction of methylenetriphenylphosphorane with **16**. As for the porphyrin analogue, changing the base to potassium *t*-butoxide, and using low-temperature gave a product free of contamination from **19**, but the best yield we obtained of **18** was 47% (contaminated with some **5a**). As for the porphyrin analogue, some unreacted aldehyde is recoverable as a more polar component by column chromatography.

2.4. Preparation of bis(chlorin) and chlorin–porphyrin dyads

Treatment of the above bromovinyl compound **18** with potassium *t*-butoxide gave a virtually quantitative yield of the new alkyne monomer **20**, with some formation of a slower-eluting green compound, later shown to be the desired bis(NiOEC)butadiyne **21**. This is in accord with the known behaviour of the analogous porphyrin systems **6** and **1**.[1a,b,18] The ^{1}H NMR spectrum of **20** shows a singlet at 3.74 ppm assigned to the unique alkyne proton. This position is some 0.8 ppm upfield of the corresponding proton signal in **6**, an indication of the diminished ring current of the chlorin system. The anisotropic effect of the alkyne substituent is visible in the chemical shift of the neighbouring chlorin proton on C3, which appears 0.4 ppm downfield from its position in **18**. This alkyne was subjected to Eglinton coupling conditions using copper(II) acetate in pyridine, and reaction appeared to be complete in 3 h at 60°C. After chromatography and crystallisation, the new bis(chlorin)butadiyne was obtained in 55% yield. We were pleased to see that the chlorin oxidation level was largely maintained under these oxidising conditions, and the slight differences in properties between bis(porphyrin) **1** and bis(chlorin) **21** enabled us to obtain a sample for detailed NMR studies with only about 5% contamination from **1**. The heteronuclear compound NiOEC—C_4—NiOEP **22** could not be separately detected, so it was either present in very small amounts, or the reson-ances of its components overlapped completely with the corresponding resonances of the two homodimers.

Another desirable target dyad was a mixed porphyrin–chlorin, but it appeared that a random coupling of **6** with **20** would lead to a mixture from which it was unlikely that a pure sample of **22** would be obtained. We therefore tried a porphyrin whose solubility and chromatographic behaviour would be very different from those of NiOEC. Thus we chose nickel(II) 5,15-diphenylporphyrin (NiDPP). Mixed coupling of **20** with *meso*-ethynylNiDPP **24** would generate a mixture of **21**, the desired **25**, and the bis(NiDPP) dimer **27**. We knew from previous work that the last of these is very insoluble in our typical chromatography solvents. Alkyne monomer **24** was prepared by TBAF deprotection of the trimethylsilyl-protected monomer **23**.[8a] It was then treated with half an equivalent of ethynylchlorin **20**, in order to disfavour the homocoupling of **20**. After the usual treatment with $Cu(OAc)_2$ in pyridine, the crude product showed three spots on TLC. The least polar proved to be the bis(chlorin) **21**, and the stationary, very insoluble material exhibited a broad Soret absorption typical of butadiynyl bis(porphyrins) and was presumed to be the bis(NiDPP) dimer **27**. The intermediate band was separated and shown by NMR to consist of the target dyad **25**, contaminated with about 30% of the corresponding NiOEP—C_4—NiDPP dyad **26**. In the case of this coupling reaction, it appears that undesirable oxidation of the chlorin did interfere, unlike in the case of the homocoupling of **20** above.

On the small scales of our experiments, it was not thought to be worthwhile to try to separate these very similar compounds. However, in order to be confident of our NMR assignments, we also prepared this new bis(porphyrin) heterodimer by coupling of **6** with **24** in the usual manner. The different chromatographic behaviour allowed relatively easy isolation of **26** in 43% yield. A spectrum measured at 750 MHz then enabled the assignment of all the signals for **25** by comparison.

It is worth noting some aspects of the NMR spectra of these dimers, especially of **21**. Before considering the points which arise peculiarly from dimer formation, one should first absorb the effects of the presence of the *meso*-triple bond, i.e. in monomers **6** and **20**. For **6**, the magnetic anisotropy of the alkyne results in a downfield shift of the CH_2 protons of the ethyl groups in positions 3 and 7 (compared to the rest of the Et groups) of 0.38 ppm.[1a,b] For the chlorin **20**, the effect is less, ca. 0.2 ppm. The signals for the methyl groups of the substituents on the reduced ring are only 0.06 ppm apart. In the dimer **21**, there is an additional downfield shift for all the protons in the neighbourhood of the bridge, namely those of the methyl groups on the 3- and 7-Et substituents, the chlorin proton on C3, and the non-equivalent CH_2 protons on the 7-Et groups. These shifts are no doubt due to the additional deshielding influence of the second chlorin ring. The comparative deshielding influences of the ring currents of the nearby NiOEC and NiDPP moieties can be estimated from the shifts of the most-affected CH_3 groups, namely those on carbons 3 and 7, in dyads **21** and **26**. From the 750 MHz spectra, in which all eight triplets are resolved for both compounds, these are 1.19 and 1.75 ppm, respectively, for **21**, and 1.28 and 1.86 ppm for **26**.

There are potentially two diastereomers of structure **21**, which are shown in the "*syn*" coplanar disposition in the structural diagrams, i.e. the reduced rings are shown proximal to each other across the bridge. The *anti* rotamer would result if one ring were rotated 180° around the bridge axis. The conformational preferences and barriers to rotation in alkyne-linked bis(porphyrins) have been considered by the Anderson and Therien groups as well as ourselves, using spectroscopy, molecular modelling, and theoretical calculations.[1e,h,2a,c,d,f,3b,5] The most that can be said at present is that there is expected to be a preference for coplanar geometry, which retains the maximum resonance interaction across the bridge, but the actual height of the energy barrier is unknown. The only crystal structure of a butadiyne-linked bis(porphyrin) shows it to be completely planar in the solid state.[2d] The ^{1}H NMR spectrum of **21** measured at 300 MHz in $CDCl_3$ shows evidence for the presence of isomers, namely a doubling of the triplet due to the chlorin methyl group on C3 (next to the bridge). The difference in chemical shift is only ca. 0.01 ppm. It is this region of the molecule which is expected to be most sensitive to the geometry and crowding by substituents. At 750 MHz, doubling of several other resonances is apparent, namely the C7 methyl triplet near 1.75 ppm, the chlorin proton on C2 at 4.00 ppm, and the multiplets for the diastereotopic methylene protons on C7 in the region 3.8–4.1 ppm. The one unusual feature is the fact that the chlorin proton on C3, nearest the alkyne bridge, is still observed as just a doublet of doublets, as for all the monomeric chlorins. One might have expected it to be at least as sensitive as the C2 proton to the exact environment in its region. In the absence of substantive evidence to the contrary, we attribute the doubling of the signals to the presence of a 50/50 mixture of the *meso* and *rac* isomers of **21**.

In order to help us to understand the spectrum of the bis(chlorin), we also recorded a 1D and COSY spectrum in C_6D_6 solution. Aromatic solvents often yield a different perspective on porphyrin NMR spectra, and in this case, there are significant shifts of the signals for protons in the bridge region. Most notably, the C3 chlorin and the 7-CH_2 protons shift >0.2 ppm downfield, while the C2 proton shifts nearly 0.2 ppm upfield. It is conceivable that these shifts may represent different populations of the *syn*/*anti* rotamers, and/or greater predominance of near-planar conformations of the diastereomers of **21**.

2.5. Visible spectra of the new dyads

Our major reason for preparing these new dinuclear systems was to examine their visible absorption spectra and compare these with known alkyne-linked bis(porphyrins). In the longer term, we will be pursuing voltammetric and spectroelectrochemical studies to probe the frontier orbitals in more detail.[1f–h] The spectra of alkyne-linked bis(porphyrins) and their monomeric components have been discussed in numerous quarters before,[1–5] so the point will not be laboured here. The diagnostic absorption features of strong ground-state inter-porphyrin electronic coupling are strongly broadened or split Soret bands with total width at half-height of ca. 3000–5000 cm^{-1}, and relatively intense Q bands. The spectra of the new dyads are shown in Fig. 1. The bis(chlorin) **21** features a split Soret band (normal trace in Fig. 1) with separation between the two major components of 2100 cm^{-1} (compare 3100 cm^{-1} for **1**[1h]). This comparison indicates less frontier orbital interaction in the bis(chlorin), and may indicate that non-coplanar conformations are more populated for **21**. There have been several other reports of bis(chlorins) and chlorin–porphyrins. Many examples are now known with a variety of linkage types, including direct single bonds,[19] direct double bonds,[20] ethane bridges,[21] ethylene bridges,[14b,15,22] as well as spiro-chlorin–chlorin dyads.[23] Most recently, bis(chlorins) joined by fused quinoxaline or benzimidazole attached to isocyclic rings have been reported.[24] Extended conjugation in the ground state is expected for the direct double bond and planar-fused systems, and their spectra indeed feature intensified Q-bands and split or strongly red-shifted Soret bands. Finally, we show the visible absorption spectrum of the novel NiOEP—C_4—NiDPP dyad **26** in Fig. 1 (bold trace); it displays a spectrum typical of a *meso*,*meso*-butadiyne-linked dinickel diporphyrin, with a Soret band split into at least three major components and spanning a range of ca. 4000 cm^{-1}.

3. Conclusion

The preparation of new covalently linked bis(chlorins) has previously been driven by attempts to understand and mimic the features responsible for efficient light-harvesting and energy- and electron-transfer by the natural chlorin chromophores. The characterisation of triply bonded systems is therefore timely. In comparison with the more tractable porphyrin dimers, very little detailed investigation of frontier orbital interactions has been carried out on bis(chlorin) or chlorin–porphyrin dimers. Previously, heterodinuclearity was conferred only by the coordination of unlike metal ions, e.g. NiOEP—C_4—ZnOEP.[1h] The differing redox potentials of porphyrin versus chlorin (in **25**) and NiOEP versus NiDPP (in **26**) promise the availability of new spectral forms due to electrogenerated mixed-valence radical anions and cations.

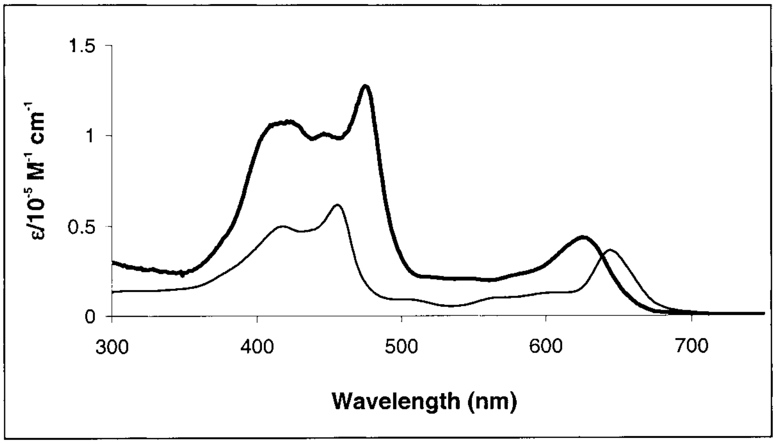

Figure 1. Electronic absorption spectra of NiOEC—C_4—NiOEC **21** (normal trace) and NiOEP—C_4—NiDPP **26** (bold trace) in chloroform solution.

4. Experimental

4.1. General

Solvents and chemicals were AR grade, and were used as received except for the following, which were distilled under Ar just before use: dichloroethane from K_2CO_3, pyridine from KOH, THF from potassium/benzophenone, and phosphorus oxychloride. Potassium *t*-butoxide was vacuum sublimed and stored under Ar. Analytical TLC was performed using Merck silica gel 60 F_{254} TLC plates and column chromatography was performed using Merck silica gel (230–400 mesh). NMR spectra were recorded in $CDCl_3$ solutions (unless otherwise noted) on a Varian Unity 300 MHz instrument using the residual protio solvent signal as internal reference. The spectra of dyads **21** and **25** were also recorded in $CDCl_3$ at 750 MHz using the Bruker DMX750 instrument at The Centre for Magnetic Resonance, The University of Queensland. UV/visible spectra were recorded on a Varian Cary 3 UV/visible spectrometer. FAB mass spectra were recorded on a Kratos Concept instrument at the University of Tasmania, Hobart, the samples being dissolved in dichloromethane and dispersed in 3-nitrobenzyl alcohol matrix. Microanalyses were performed by the Microanalytical Service, Department of Chemistry, The University of Queensland. The porphyrin aldehydes were available from our previous studies[1b] and the chlorin starting materials were prepared according to the literature methods: *trans*-H_2OEC,[16a] NiOEC **15**,[16b] and *meso*-formylNiOEC **16**.[15] In all of the chlorins prepared there was minor contamination from the corresponding porphyrin, and therefore the quoted ε values are approximate only. Calculated elemental analyses are quoted for the pure chlorins.

4.1.1. Improved preparation of 5-*trans*-(2′-bromoethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) 5a. To a stirred suspension of bromomethyltriphenylphosphonium bromide (200 mg, 0.46 mmol) in dry THF (4.0 mL) at −78°C, *t*BuOK (170 μL of 1.5 M solution in THF, 0.46 mmol) was added dropwise under argon. An aliquot (1.0 mL) of the resultant solution was added to a stirred solution of **3** (20 mg, 0.032 mmol) in dry THF (3 mL) under argon. The reaction was monitored by TLC (25/75 $CHCl_3$/hexane) and after 2 h the reaction was stopped by the addition of water. The product was extracted into $CHCl_3$ and the organic phase separated, washed thoroughly with water, dried over Na_2SO_4, filtered and the solvent removed under vacuum. The crude product was subjected to column chromatography (25/75 $CHCl_3$/hexane) and the major red band collected and recrystallised from $CHCl_3$/methanol to yield red needles (11.8 mg, 53%). From ^1H NMR analysis there was no detectable contamination by **4**. Spectral data (^1H NMR, UV/visible) were as previously reported.[1a]

4.1.2. 5-*trans*-(2′-Iodoethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) 7. $CrCl_2$ (500 mg, 4.06 mmol) was added to a dry 50 mL round-bottom flask and gently flame-dried under high vacuum. Upon cooling, the vacuum was released under argon and the flask was charged with THF (5 mL). The slurry was stirred for 15 min to prevent aggregation of the $CrCl_2$. To another flask containing aldehyde **3** (100 mg, 0.161 mmol), THF (10 mL) was added, followed by CHI_3 (400 mg, 1.02 mmol). The resulting mixture was then added dropwise by syringe to the $CrCl_2$ slurry. The reaction was stirred for 3 h at room temperature, during which the reaction mixture turned from dark green to dark red. $CHCl_3$ was added and the organic layer removed, repeatedly washed with water, dried over Na_2SO_4 and the solvent removed under vacuum. The residue was dissolved in ether, and treated with tetrabutylammonium fluoride (TBAF) (2 mL, 1 M in THF) with stirring, to remove excess CHI_3. The solution was stirred for 10 min then filtered through a plug of silica gel using ether to elute the porphyrin. The solvent was removed under vacuum then the crude residue was chromatographed (50/50 $CHCl_3$/hexane). The least polar deep-red band was collected and the residue recrystallised from $CHCl_3$/methanol to yield red needles of **7** (90 mg, 75%). ^1H NMR: δ 1.61–1.79 (overlapping t, 24H, CH_3), 3.70–3.90 (overlapping q, 16H, CH_2), 5.52 (d, J=14.4 Hz, 1H, CH=C*H*I), 9.45 (s, 1H, 15-*meso*H), 9.46 (s, 2H, 10-,20-*meso*H), 9.71 (d, J=14.4 Hz, 1H, C*H*=CHI); UV/vis: λ_{max} (ε, L mol^{-1} cm^{-1}) 349 (13 100), 406 (154 200), 530 (9400), 566 (14 200) nm; FAB MS: *m*/*z* 742 (M^+), 743 $(M+H)^+$; Anal. Calcd. for $C_{38}H_{45}IN_4Ni$: C, 61.39; H, 6.10; N, 7.54. Found: C, 61.32; H, 6.09; N, 7.33%.

Two slower-eluting red bands were also collected, the solvent was removed under vacuum, and the residues were recrystallised from $CHCl_3$/methanol to give red prisms (12.3 mg, 12%) and a purple powder (2.0 mg, 2%), respectively. In order of elution these were shown by ^1H NMR to be the following compounds.

4.1.3. 5-Acetyl-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) 8. ^1H NMR: δ 1.62 (t, J=7.5 Hz, 6H, CH_3 of 3,7 ethyl groups), 1.61–1.79 (overlapping t, 18H, CH_3), 2.74 (s, 3H, CO—CH_3) 3.57 (q, J=7.5 Hz, 4H, CH_2 of 3,7-ethyl groups), 3.84–3.90 (overlapping q, 12H, CH_2), 9.54 (s, 1H, 15-*meso*H), 9.60 (s, 2H, 10-,20-*meso*H); UV/vis: λ_{max} (ε, L mol^{-1} cm^{-1}) 350 (12 700), 401(161 500), 524 (9800), 560 (15 600); FAB MS: *m*/*z* 632 (M^+); Anal. Calcd. for $C_{38}H_{46}N_4NiO$: C, 72.04; H, 7.32; N, 8.84. Found: C, 71.84; H, 7.34; N, 8.56%.

[2′,3′,7′,8′,12′,13′,17′,18′-Octaethylporphyrinatonickel-(II)-5′-yl]ethanal **9** by comparison of its ^1H NMR spectrum with the literature.[1d]

4.1.4. 5-Ethynyl-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) 6. The iodovinyl monomer **7** (20 mg, 0.034 mmol) was dissolved in dry THF (5 mL) under argon. Excess *t*BuOK (110 μL of 1.5 M in THF, 0.165 mmol) was added via syringe and the solution immediately turned purple/green. The solution was stirred for a further 10 min then the reaction was quenched by the addition of water. $CHCl_3$ was added and the organic layer was removed and washed thoroughly with water, dried over Na_2SO_4, filtered and the solvent was removed under vacuum to yield a purple residue of **6** (16.1 mg, 97%). Further purification was not attempted as oxidation to **1** proceeded spontaneously. Spectral data (^1H NMR, UV/visible) were as previously described.[1a]

4.1.5. 1,4-Bis[2′,3′,7′,8′,12′,13′,17′,18′-octaethylporphyrinatonickel(II)-5′-yl]-1,3-butadiyne 1. (i) Iodovinyl monomer **7** (20 mg, 0.027 mmol) was dissolved in dry pyridine (5 mL) under argon. *t*BuOK (40 μL of 1.5 M in THF, 0.060 mmol) was added via syringe and the mixture allowed to stir for 1 h at room temperature. $Cu(OAc)_2{\cdot}H_2O$ (20 mg, 0.11 mmol) was added and the mixture heated to 60°C for 3 h with a drying tube in place to allow exposure to air. The pyridine was removed under high vacuum, and the residue was dissolved in $CHCl_3$ and the organic layer was washed with 2 M HCl, then thoroughly washed with water, dried with Na_2SO_4, filtered and the solvent removed under vacuum. The crude product was chromatographed (50/50 $CHCl_3$/hexane). Fractions containing **1** were recrystallised from $CHCl_3$/methanol to yield a dark green powder (14.0 mg, 84%). Spectral data (^{1}H NMR, UV/visible) were as previously described.[1a,1h] (ii) In one case, a large-scale procedure was attempted, without isolation of the ethynyl monomer **6**, and the $Cu(OAc)_2{\cdot}H_2O$ was inadvertently added before the dehydroiodination of **7** was complete. Apart from **1** and **7**, two slower-eluting green bands were collected from chromatography on the crude product and these were recrystallised from $CHCl_3$/methanol to give dark green needles (9%) and dark green microcrystals (4%), respectively. The latter compound was identified as 3-[2′,3′,7′,8′,12′,13′,17′,18′-octaethylporphyrinatonickel(II)-5′-yl]-propenal **10** by comparison of its NMR spectrum with the literature.14 The former species was shown to be 1-[2′,3′,7′,8′,12′,13′,17′,18′-octaethylporphyrinatonickel(II)-5′-yl]-5-[2″,3″,7″,8″,12″,13″,17″,18″-octaethylporphyrinatonickel(II)-5″-yl]-pent-1-en-4-yn-3-one **11**. ^{1}H NMR: δ 1.48 (t, *J*=7.5 Hz, 6H, CH_3), 1.60 (t, *J*=7.5 Hz, 6H, CH_3), 1.65–1.83 (overlapping t, 36H, CH_3), 3.60–3.90 (overlapping q, 32H, CH_2), 4.13 (q, *J*=7.5 Hz, 4H, 3″,7″-CH_2), 5.94 (d, *J*=15.0 Hz, 1H, CH=C*H*—CO), 9.34 (s, 2H, 10′-,20′-*meso*H), 9.37 (s, 1H, 15′-*meso*H), 9.42 (s, 2H, 10″-, 20″-*meso*H), 9.44 (s, 1H, 15″-*meso*H), 10.14 (d, *J*=15.0 Hz, 1H, C*H*=CH—CO); UV/vis: λmax (ε, L mol^{-1} cm^{-1}) 406 (130 000), 457 (sh) (73 500), 564 (sh) (16 000), 618 (21 400); IR (KBr) 2161 s, 1637 m cm^{-1}; FAB MS: *m*/*z* 1256 (M$^+$), 1257 (M+H)$^+$; Anal. Calcd. for $C_{77}H_{88}N_8Ni_2O$: C, 73.46; H, 7.05; N, 8.90. Found: C, 73.16; H, 7.10; N, 8.83%.

The preparation of this compound was also attempted as follows. To a stirred solution of **6** (10 mg, 0.016 mmol) and **10**[14b] (12 mg, 0.019) in dry pyridine (10 mL), $Cu(OAc)_2{\cdot}H_2O$ (10 mg, 0.055 mmol) was added and the reaction mixture was heated at 60°C for 3 h. ^{1}H NMR analysis of the crude product showed that **1** was the only new product with most of the starting material **10** being recovered, and the desired product **11** was not detected. (iii) Starting with 832 mg of **3**, 612 mg of **7** (62%) was isolated, and subsequently converted to **1** (252 mg, 49%).

4.1.6. 2-(2′-Iodoethenyl)-5,10,15,20-tetraphenylporphyrinatonickel(II) 14 (*E*/*Z* mixture). This preparation was carried out by a similar procedure to that used for **7**. A mixture of aldehyde **12** (17 mg, 0.024 mmol), CHI_3 (93 mg, 0.24 mmol) in dry THF (10 mL) was added to flame-dried $CrCl_2$ (87 mg, 0.72 mmol) under argon. After the work-up and column chromatography (50/50 $CHCl_3$/hexane) the major red band was collected and fractions containing **14** were combined and recrystallised from $CHCl_3$/methanol to yield a red powder (17 mg, 87%). ^{1}H NMR: δ 6.21 (d, *J*=8.4 Hz, 1H, CH=C*H*I of *Z* isomer), 6.75 (d, *J*=14.4 Hz, 1H, CH=C*H*I of *E* isomer), 6.87 (dd, *J*=14.4, 1.2 Hz, 1H, C*H*=CHI of *E* isomer), 6.88 (dd, *J*=8.4, 1.2 Hz, 1H, C*H*=CHI of *Z* isomer), ca. 7.6–8.1 (m, phenyl groups), 8.67 (d, *J*=1.2 Hz, 3-*β*-H of *E* isomer), 8.65–8.75 (m, *β*-H), 9.01 (d, *J*=1.2 Hz, 3-*β*-H of *Z* isomer); UV/vis: λ_{max} (ε, L mol^{-1} cm^{-1}) 422 (190 600), 535 (16 100), 567 sh (3900); FAB MS: *m*/*z* 822 (M$^+$), 823 (M+H)$^+$; Anal. Calcd. for $C_{46}H_{29}IN_4Ni$: C, 67.10; H, 3.55; N, 6.80. Found: C, 67.22; H, 3.73; N, 6.45%.

4.1.7. 5-*trans*-(2′-Iodoethenyl)-2,3,7,8,12,13,17,18-octaethylchlorinatonickel(II) 17. $CrCl_2$ (100 mg, 0.81 mmol) was added to a dry 25 mL round-bottom flask and gently flame-dried under high vacuum. Upon cooling, the vacuum was released under argon and the flask was charged with THF (3 mL). The slurry was stirred for 15 min to prevent aggregation of the $CrCl_2$. To another flask containing aldehyde **16** (20 mg, 0.032 mmol), THF (5 mL) was added followed by CHI_3 (80 mg, 0.20 mmol). These were then added dropwise by syringe to the $CrCl_2$ slurry. The reaction was stirred for 3 h at room temperature, during which the reaction was monitored by TLC (25/75 $CHCl_3$/hexane) and the appearance of a more mobile green spot was observed. Prolonged reaction had no apparent effect on the composition of the reaction mixture. $CHCl_3$ was added to the reaction mixture and the organic layer removed, repeatedly washed with water, dried over Na_2SO_4 and the solvent removed under vacuum. The residue was dissolved in ether, and treated with TBAF (0.5 mL, 1 M in THF) with stirring to remove excess CHI_3. This solution was allowed to stir for 10 min and then filtered through a plug of silica gel using ether for elution. The solvent was removed under vacuum and the crude product was chromatographed (25/75 $CHCl_3$/hexane). The fastest moving band was collected and fractions containing **17** were recrystallised from $CHCl_3$/5% aqueous methanol to yield a green powder (2.4 mg, 10%). Residual starting material was also recovered. Attempts to increase the yield of **17** by increasing the excess of $CrCl_2$ and CHI_3 and the use of elevated temperatures resulted in partial deformylation of **16**. ^{1}H NMR: δ 0.90 (t, *J*=7.5 Hz, 3H, CH_3), 1.00 (t, *J*=7.5 Hz, 3H, CH_3), 1.30, 1.42 (each m, 2H, CH_2), 1.40–1.69 (overlapping t, 18H, CH_3), 1.73, 1.76 (each m, 2H, CH_2), 3.30–3.68 (overlapping q, 12H, CH_2), 3.92 (t, *J*=7.2 Hz, 1H, 2-H), 4.02 (dd, *J*=9.6, 3.6 Hz, 1H, 3-H), 5.80 (d, *J*=14.7 Hz, 1H, CH=C*H*I), 7.92 (s, 1H, 20-*meso*H), 8.64 (d, *J*=14.7 Hz, 1H, C*H*=CHI), 8.90, 8.94 (each s, 2H, 10-,15-*meso*H); UV/vis: λ_{max} (rel. int.) 408 (11.2), 580 sh (1.0), 626 (3.3); HRFAB MS: *m*/*z* 744.2179 (*m*/*z* calc. for $C_{38}H_{47}IN_4Ni$ 744.2158).

4.1.8. 5-*trans*-(2′-Bromoethenyl)-2,3,7,8,12,13,17,18-octaethylchlorinatonickel(II) 18. (i) To a stirred suspension of bromomethyltriphenylphosphonium bromide (200 mg, 0.46 mmol) in dry THF (4.0 mL), BuLi (290 μL of 1.6 M in hexane, 0.46 mmol) was added dropwise under argon. An aliquot (1.0 mL) of the resulting solution was added to a stirred solution of **16** (18 mg, 0.028 mmol) in dry THF (3 mL) under argon. The reaction was followed by TLC (25/75 $CHCl_3$/hexane) and after 30 min the reaction was quenched by the addition of water. The product was extracted into $CHCl_3$ and the organic phase separated, washed thoroughly with water, dried over Na_2SO_4, filtered and the solvent removed under vacuum. The crude product was subjected to column chromatography (25/75 $CHCl_3$/hexane) and the major green band collected. From ^{1}H NMR analysis the major products were **18** and *meso*-vinyl-NiOEC **19** (ca. 40:60). (ii) To a stirred suspension of bromomethyltriphenylphosphonium bromide (100 mg, 0.23 mmol) in dry THF (3.0 mL) at −78°C under argon, BuLi (145 μL of 1.6 M in hexane, 0.23 mmol) was added dropwise and the solution was allowed to stir for a further 10 min. To this solution **16** (20 mg, 0.032 mmol) dissolved in dry THF (3 mL) was added dropwise. The reaction was monitored by TLC (25/75 $CHCl_3$/hexane) and the reaction quenched after 1 h by the removal of the cooling bath and the addition of water. Work-up as above and ^{1}H NMR analysis showed the major products to be **18** and **19** (ca. 50:50). (iii) To a stirred suspension of bromomethyltriphenylphosphonium bromide (200 mg, 0.46 mmol) in dry THF (4.0 mL) at −78°C, *t*BuOK (170 μL of 1.5 M in THF, 0.46 mmol) was added dropwise under argon. A portion of the resulting solution (1.0 mL) was added to a stirred solution of **16** (20 mg, 0.032 mmol) in dry THF (3 mL) at −78°C under argon. The reaction was followed by TLC (25/75 $CHCl_3$/hexane) and after 2 h the reaction was quenched by the addition of water. Work-up as above yielded a major green band, which was collected and recrystallised from $CHCl_3$/5% aqueous methanol to yield a green powder (10.5 mg, 47%). From ^{1}H NMR analysis the major product was **18** with no detectable **19** contamination, although there was a minor (<10%) impurity of **5a**. ^{1}H NMR: δ 0.91 (t, J=7.5 Hz, 3H, CH_3), 1.05 (t, J=7.5 Hz, 3H, CH_3), 1.28, 1.45 (each m, 2H, CH_2), 1.42–1.70 (overlapping t, 18H, CH_2), 1.77, 1.79 (each m, 2H, CH_2), 3.40–3.67 (overlapping q, CH_2), 3.94 (t, J=6.9 Hz, 1H, 2H), 4.03 (dd, J=9.3, 3.3 Hz, 1H, 3H), 5.79 (d, J=13.8 Hz, 1H, CH=C*H*Br) 7.93 (s, 1H, 20-*meso*H), 8.33 (d, J=13.8 Hz, 1H, C*H*=CHBr), 8.91, 8.96 (each s, 2H, 10-,15-*meso*H). UV/vis: λ_{max} (ε, L mol^{-1} cm^{-1}) 408 (82 500), 501 (4200), 528 sh (3200), 577 sh (6400), 627 (27 100); HRFAB MS: *m*/*z* 696.2305 (*m*/*z* calc. for $C_{38}H_{47}BrN_4Ni$ 696.2337).

4.1.9. 5-Ethenyl-2,3,7,8,12,13,17,18-octaethylchlorinatonickel(II) 19. Butyllithium (95 μL of 1.6 M in hexane, 0.15 mmol) was added dropwise to a stirred suspension of methyltriphenylphosphonium bromide (50 mg, 0.14 mmol) in dry THF (4.0 mL) under argon. The resulting bright yellow solution was stirred for 10 min then an aliquot (1.0 mL) was added via syringe to a stirred solution of aldehyde **16** (20 mg, 0.032 mmol) in dry THF (5 mL). After 30 min, TLC (25/75 $CHCl_3$/hexane) showed the disappearance of starting material so the reaction was quenched by the addition of water. The product was extracted into $CHCl_3$ and the organic layer washed thoroughly with water, dried over Na_2SO_4, filtered and the solvent removed under vacuum. The crude product was chromatographed (25/75 $CHCl_3$/hexane) to remove a trace of the more polar **16**. Fractions containing **19** were recrystallised from $CHCl_3$/5% aqueous methanol to yield a green powder (14.3 mg, 72%). ^{1}H NMR: δ 0.94 (t, J=7.5 Hz, 3H, CH_3), 1.08 (t, J=7.5 Hz, 3H, CH_3), ca. 1.35 (m, 2H, CH_2), 1.42–1.72 (overlapping t, 18H, CH_3), 1.81, 1.83 (each m, 2H, CH_2), 3.47–3.70 (overlapping q, 12H, CH_2), 3.94 (t, J=7.2 Hz, 1H, 2-H), 4.10 (dd, J=10.2, 3.3 Hz, 1H, 3-H), 4.85 (dd, J=17.4, 2.2 Hz, 1H, CH=C*H cis* to chlorin), 5.75 (dd, J=10.8, 2.2 Hz, 1H, CH=C*H trans* to chlorin), 7.93 (s, 1H, 20-*meso*H), 7.98 (dd, J=17.4, 10.8 Hz, 1H, C*H*=CH_2), 8.91, 8.93 (each s, 2H, 10-,15-*meso*H); UV/vis: λ_{max} (ε, L mol^{-1} cm^{-1}) 409 (64 600), 501 (3600), 581 sh (5300), 627 (23 900); HRFAB MS: *m*/*z* 618.3229 (*m*/*z* calc. for $C_{38}H_{48}N_4Ni$ 618.3232).

4.1.10. 5-Ethynyl-2,3,7,8,12,13,17,18-octaethylchlorinatonickel(II) 20. The bromovinyl monomer **18** (16 mg, 0.023 mmol) was dissolved in dry THF (5 mL) under argon and an excess of *t*BuOK (200 μL of 1.5 M in THF, 0.3 mmol) was added dropwise. The reaction was stirred for 1 h at room temperature. The reaction mixture was evaporated to dryness and extracted with $CHCl_3$. The organic layers were combined and washed thoroughly with water, dried over Na_2SO_4, filtered and the solvent removed under vacuum to yield a blue-green powder (14 mg, 99%) of crude **20**. From the ^{1}H NMR spectrum the product was contaminated with small amounts of **21** and **6**. Further purification was not attempted as the monomer spontaneously oxidises to the dimer. ^{1}H NMR: δ 0.99 (t, J=7.5 Hz, 3H, CH_3), 1.05 (t, J=7.5 Hz, 3H, CH_3), 1.24, 1.54 (each m, 2H, CH_2), 1.49–1.68 (overlapping t, 18H, CH_3), 1.76, 1.91 (each m, 2H, CH_2), 3.46–3.63 (overlapping q, 12H, CH_2), 3.74 (s, 1H, C≡CH), 3.75 (m, 2H, CH_2 on C7), 3.93 (t, J=6.9 Hz, 1H, 2-H), 4.43 (dd, J=10.2, 3.3 Hz, 1H, 3-H), 7.97 (s, 1H, 20-*meso*H), 8.91, 8.95 (each s, 2H, 10-,15-*meso*H). UV/vis: λ_{max} (rel. int.) 396 sh (12.8), 412 (16.3), 502 (1.0), 588 sh (1.5), 630 (6.4).

4.1.11. 1,4-Bis[2′,3′,7′,8′,12′,13′,17′,18′-octaethylchlorinatonickel(II)-5′-yl]-1,3-butadiyne 21. To the crude alkyne **20** (11 mg, 0.018 mmol) dissolved in dry pyridine, $Cu(OAc)_2\cdot H_2O$ (10 mg, 0.050 mmol) was added and the reaction mixture was stirred at 60°C for 3 h. The solvent was removed under high vacuum, the dark green residue was dissolved in $CHCl_3$ and washed with 2 M HCl. The organic layer was separated, washed thoroughly with water, dried over Na_2SO_4, filtered and the solvent removed under vacuum. The crude product was chromatographed (15/85 dichloromethane/hexane) and fractions containing **21** were combined and recrystallised from $CHCl_3$/methanol to yield dark green crystals (6 mg, 55%). NMR showed the presence of only ca. 5% **1**. ^{1}H NMR: (750 MHz, $CDCl_3$): δ 1.05 (t, J=7.2 Hz, 6H, 2′-CH_3), 1.19 (doubled t, J=7.5 Hz, 6H, 3′-CH_3), 1.56, 1.61, 1.63, 1.66, 1.68 (all t, J=7.6 Hz, 30H, CH_3), 1.75 (doubled t, J=7.6 Hz,6H, 7′-CH_3), 1.79, 1.85 (each m, 4H, 2′-CH_2), 1.72, 2.10 (each br m, 2H, 3′-CH_2), 3.39 (sextet, J=7.7 Hz, 2H, half of CH_2 pair), 3.5–3.65 (overlapping q, 18H, CH_2), 3.84 (septet, J=7.7 Hz, 2H, half of 7′-CH_2 pair), 4.00 (doubled t, J=7.0 Hz, 2H, 2′-H), 4.08 (septet, J=7.3 Hz, 2H, half of 7′-CH_2 pair), 4.57 (dd, J=9.0, 3.3 Hz, 2H, 3′-H), 8.01 (s, 2H, 20′-*meso*H), 8.91, 8.97 (each s, 4H, 10′-,15′-*meso*H); (300 MHz, C_6D_6): δ 0.82 (t, J=7.2 Hz, 6H, 2′-CH_3), 1.15 (doubled t, J=7.2 Hz, 6H, 3′-CH_3), ca. 1.5 [obscured m (COSY), 2H, 3′-CH_2], 1.46–1.6 (overlapping t, 30H, CH_3), 1.66, 2.16 (each m, 4H, 2′-CH_2), 2.03 (t, J=7.2 Hz, 6H, 7′-CH_3), 3.25 (m, 2H, half of CH_2 pair), 3.3–3.5 (overlapping t, 18H, CH_2), 3.82 (t, J=6.9 Hz, 2H, 2′-H), 4.05, 4.30 (each m, 4H, 7′-CH_2), 4.77 (dd, *J*=9.0, 3.3 Hz, 2H, 3′-H), 8.02 (s, 2H, 20′-*meso*H), 9.01, 9.06 (each s, 4H, 10′-,15′-*meso*H). UV/vis: λ_{max} (ε, L mol^{-1} cm^{-1}) 413 (48800), 453 (59 200), 504 sh (9100), 558 (9100), 595 (12 300), 641 (35 900); FAB MS: *m*/*z* 1230 (M^+); Anal. Calcd. for $C_{76}H_{90}N_8Ni_2$: C, 74.03; H, 7.36; N, 9.09. Found: C, 74.64; H, 7.21; N, 9.11%.

4.1.12. 5-Ethynyl-10,20-diphenylporphyrinatonickel(II) 24. The TMS-protected alkyne **23**^{8a} (20 mg, 0.032 mmol) was dissolved in dichloromethane (10 mL). TBAF (16 mg, 0.06 mmol) was added and the reaction stirred at room temperature for 1 h. Methanol (5 mL) was added and the solvent removed under vacuum. The residue was extracted with $CHCl_3$, washed thoroughly with water, dried over Na_2SO_4, filtered and the solvent removed under vacuum. This yielded **24** (16.6 mg, 96%) as a red powder. The ^{1}H NMR spectrum of the product showed complete deprotection, and further purification was not attempted because of spontaneous coupling to the dimer. ^{1}H NMR: δ 4.16 (s, 1H, C≡CH), 7.72 (m, 6H, *m*-, *p*-H phenyl), 8.02 (m, 4H, *o*-H phenyl), 8.82 (d, *J*=5.1 Hz, 2H, β-H on C2, C8), 8.85 (d, *J*=5.1 Hz, 2H, β-H on C12, C18), 9.08 (d, *J*=5.1 Hz, 2H, β-H on C13, C17), 9.58 (d, *J*=5.1 Hz, 2H, β-H on C3, C7), 9.79 (s, 1H, *meso*H); UV/vis: λ_{max} (rel. int.) 412 (24.5), 527 (2.5), 558 sh (1.0).

4.1.13. 1-[10′,20′-Diphenylporphyrinatonickel(II)-5′-yl]-4-[2″,3″,7″,8″,12″,13″,17″,18″-octaethylchlorinatonickel-(II)-5″-yl]-1,3-butadiyne 25. The alkynyl chlorin **20** (10 mg, 0.016 mmol) was added to **24** (16 mg, 0.030 mmol) dissolved in dry pyridine (10 mL) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20 mg, 0.10 mmol). The reaction mixture was stirred for 3 h at 60°C under a drying tube to allow for the infusion of air. The solvent was removed under high vacuum and the residue extracted with $CHCl_3$. This solution was washed with 2 M HCl, then thoroughly with water, dried over Na_2SO_4, filtered and the solvent was removed under vacuum. The crude product was chromatographed (15/85 dichloromethane/hexane) to separate **25** from unreacted starting materials and homocoupled dimers. Fractions containing **25** were combined and recrystallised from $CHCl_3$/methanol to yield **25** as green crystals (6.6 mg, 35%). The ^{1}H NMR spectrum of the product revealed the presence of ca. 30% NiOEP—C_4—NiDPP **26** (see below) as an inseparable impurity. ^{1}H NMR (750 MHz): δ 1.06 (t, *J*=7.5 Hz, 3H, 2″-CH_3), 1.28 (t, *J*=7.5 Hz, 3H, 3″-CH_3), 1.56, 1.62, 1.64, 1.67, 1.70, 1.86 (t, *J*=7.6 Hz, 18H, CH_3), 1.8–1.9 (obscured m, 2H, C2″-, C3″—CH_2), 2.19 (m, 1 of 3″-CH_2), 3.39 (sextet, *J*=7.7 Hz, 1H, 1 of CH_2), 3.5–3.7 (overlapping q, 11H, CH_2), 4.04 (br t, *J*=7.2 Hz, 1H, 2″-H), 4.17 (sextet, *J*=7.7 Hz, 1H, 1 of 7″-CH_2), 4.65 (br dd, *J*=9.6, 3.3, 1H, 3″-H), ca. 7.74 (m, 6H, *m*-, *p*-H phenyl), 8.02 (s, 1H, 20′-*meso*H), 8.05 (m, 4H, *o*-H phenyl), 8.82 (d, *J*=4.8 Hz, 2H, β-H on C2′, C8′), 8.89 (d, *J*=4.8 Hz, 2H, β-H on C12′, C18′), 8.90, 8.97 (each s, 2H, 10″-,15″-*meso*H), 9.08 (d, *J*=4.8 Hz, 2H, β-H on C13′, C17′), 9.66 (d, *J*=4.8 Hz, 2H, β-H on C3′, C7′), 9.78 (s, 1H, 15′-*meso*H); UV/vis: λ_{max} (rel. int.) 435 (4.6), 467 (4.4), 547 (1.0), 620 sh (1.63), 636 (1.7); HRFAB MS: *m*/*z* 1156.3958 (*m*/*z* calc. for $C_{72}H_{64}N_8Ni_2$ 1156.3960).

4.1.14. 1-[10′,20′-Diphenylporphyrinatonickel(II)-5′-yl]-4-[2″,3″,7″,8″,12″,13″,17″,18″-octaethylporphyrinato)-nickel(II)-5″-yl]-1,3-butadiyne 26. The alkynyl porphyrins **6** (15 mg, 0.024 mmol) and **24** (15 mg, 0.028 mmol) were coupled as above, using $Cu(OAc)_2{\cdot}H_2O$ (20 mg, 0.01 mmol). After work-up and chromatography as above, fractions containing **26** were combined and recrystallised from $CHCl_3$/methanol to yield **26** as green crystals (12 mg, 43%). ^{1}H NMR: δ 1.71–1.83 (overlapping t, 18H, CH_3), 2.05 (t, *J*=7.5 Hz, 6H, CH_3 flanking triple bond), 3.75–3.93 (overlapping q, 12H, CH_2), 4.37 (q, *J*=7.5 Hz, 4H, CH_2 flanking triple bond), 7.73 (m, 6H, *m*-, *p*-H phenyl), 8.05 (m, 4H, *o*-H phenyl), 8.81 (d, *J*=4.8 Hz, 2H, β-H on C2′, C8′), 8.90 (d, *J*=4.8 Hz, 2H, β-H on C12′, C18′), 9.08 (d, *J*=4.8 Hz, 2H, β-H on C13′, C17′), 9.41 (s, 1H, 15″-*meso*H), 9.46 (s, 2H, 10″,20″-*meso*H), 9.64 (d, *J*=4.8 Hz, 2H, β-H on C3′, C7′), 9.78 (s, 1H, 15′-*meso*H); UV/vis: λ_{max} (rel. int.) 419 (4.2), 448 (4.0), 475 (5.0), 584 sh (1.0), 625 (1.8); HRFAB MS: *m*/*z* 1154.3823 (*m*/*z* calc. for $C_{72}H_{62}N_8Ni_2$ 1154.3804).

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