

# Dimers and Model Monomers of Nickel(II) Octaethylporphyrin Substituted by Conjugated Groups Comprising Combinations of Triple Bonds with Double Bonds and Arenes. 1. Synthesis and Electronic Spectra

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Porphyrin dimers linked in the *meso*-positions by bridges containing alkynes conjugated with the porphyrin  $\pi$ -systems display highly perturbed electronic absorption spectra. We have prepared a series of such dimers using *meso*-ethynyl nickel(II) octaethylporphyrin as the primary building block. The bridging units include diethynylbenzenes, 2,5-diethynylthiophene, hexenediyne, octatetrayne, butenyne, hexenediyne, and octadienediyne. Some *meso*-to- $\beta$  dimers were also made. The dimers are complemented by a set of monomers containing the bridging units as *meso*-substituents. The compounds were prepared by a combination of palladium-catalyzed couplings of alkynes with unsaturated halides and oxidative alkyne couplings. The separate effects of the substituents and the presence of the second porphyrin chromophore are delineated by comparisons of the visible absorption spectra for the various monomers and dimers. The dimers fit into three spectral classes: (i) those displaying strongly split Soret bands indicative of inter-porphyrin conjugation (diyne, tetrayne, enediyne, enyne, diethynylthiophene), (ii) those in which this conjugation is interrupted (diethynylbenzenes), and (iii) those with double bonds attached to the *meso*-carbons, which exhibit broad, low-energy bands, but small splittings of the Soret band. These illustrate some of the promising light-harvesting properties which can be achieved by tailoring the composition of the conjugating bridges linking the units in multi-porphyrin arrays.

## Introduction

The covalent linking of porphyrins and related macrocycles into dimers and larger arrays has been exhaustively studied in recent years. A major impetus for such work is the understanding of the multichromophore arrays involved in the photosynthetic reaction centers and light-harvesting apparatus.<sup>1</sup> This research has generated numerous structures in which porphyrins are joined side-by-side or face-to-face by an assortment of bridges, including unsaturated groups. In many cases related to photosynthetic models, the aim has been to slow down charge recombination after light excitation. For this reason, it has been thought to be desirable to avoid unsaturated bridges which are fully conjugated with the porphyrin  $\pi$ -electron systems. Because of steric constraints,  $sp^2$ -hybridized carbon atoms bonded to the *meso*- or  $\beta$ -positions of a porphyrin ring are forced out of the macrocycle plane, partially interrupting the conjugative path between the two porphyrins. This has stimulated chemists to prepare a variety of structures with porphyrins linked in linear, oblique, or parallel fashions by aromatic or heteroaromatic spacers.<sup>2</sup>

We have entered this field from a different viewpoint, namely that structures with very efficient conjugative communication between porphyrins in dimers and higher oligomers will have useful and novel properties, albeit of peripheral relevance to natural photosynthesis, except perhaps as light-harvesting arrays. The redox activity and photoactivity of porphyrins, and the ability to tailor

these properties by incorporation of various metal ions, points to the use of such arrays in "molecular electronic devices", as signal receptors, conductors, or switching elements.<sup>3</sup> In 1992, we published the results of our reinvestigation of the dimer **1**, which comprises two nickel(II) octaethylporphyrin (NiOEP) units linked in the *meso*-positions by a butadiyne bridge, which was first made by one of us and reported in 1978.<sup>4,5</sup> There has since been a flurry of activity in the field of alkyne-substituted porphyrins, including dimers and oligomers with alkyne-containing bridges.<sup>6–17</sup> Anderson has reported arrays of up to 10 porphyrins linked by butadiyne

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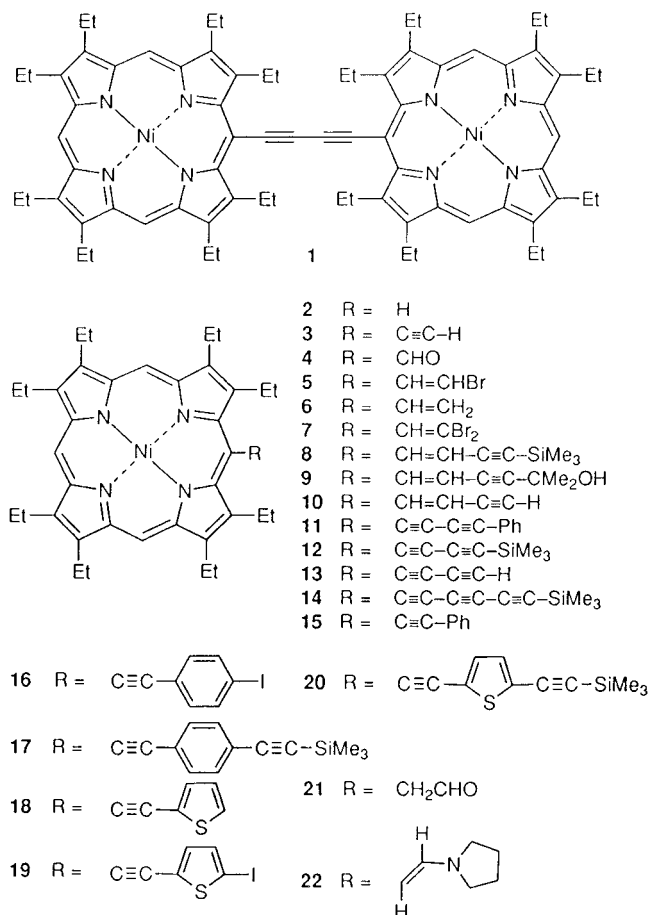
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bridges,<sup>6,7</sup> while Lin *et al.* have described ethyne-bridged dimers and trimers.<sup>9,10</sup> These syntheses involved palladium-catalyzed couplings of terminal alkynes or alkynyl organometallics with various halides, as well as standard alkyne oxidative couplings. Others, and particularly the Lindsey group, have reported oligomeric porphyrins linked by alkynes at sites remote from the porphyrin  $\pi$ -systems, e.g. at peripheral phenyl substituents.<sup>18</sup> Although these elegant systems possess interesting and novel properties, they belong in a separate spectral class to the porphyrins in which the alkyne moiety is directly attached to the *meso*-carbon. Alkynyl substituents in the *meso*-position(s) exert strong bathochromic effects on electronic spectra, and the alkynyl-bridged dimers and oligomers exhibit a unique spectral signature.<sup>5-10</sup> Thus these species are being studied in detail for their possible application in light-harvesting arrays and nonlinear optical devices.<sup>8,19-21</sup>

We have reported in preliminary form our studies of dimers of NiOEP (**2**) linked by various unsaturated bridges incorporating at least one triple bond.<sup>22,23</sup> Our aims in this work were to investigate how the nature of the unsaturated moiety affects the electronic spectra and redox behavior of the dimers. Our spectroelectrochemical studies of **1** and analogous complexes of other four-coordinate metal ions showed that the spectra of their  $\pi$ -anion reduction products have remarkably intense near-IR bands.<sup>24,25</sup> This suggests the presence of unusual interactions between the  $\pi$ -orbitals on the two macrocycles, mediated by the orbitals of the bridge, and further reinforces the potential of these molecules for optoelectronic applications. In this paper, we report in detail our synthetic studies on these NiOEP systems and comment on the effects of structural variation on the electronic spectra of the set of dimers and of model monomers possessing the same alkynyl moiety blocked by aryl or trimethylsilyl end groups. Some comparisons are also made with dimers possessing double bonds attached in

Chart 1



the *meso*-positions, whose spectra exhibit their own interesting features. Our electrochemical and spectroelectrochemical studies on these compounds will be reported elsewhere.<sup>26</sup>

## Results and Discussion

**General Synthetic Approach.** We have used exclusively the nickel(II) complexes in this work, for the following reasons. Initially we reasoned that we needed to avoid free-base porphyrins in Pd/Cu-catalyzed couplings, although this has since been shown to be incorrect.<sup>18c</sup> Moreover, we have found for the butadiyne ligand in **1** (Chart 1) that the dinickel(II) complex is considerably more soluble than the dizinc analog, that the Ni<sub>2</sub> complex displays the largest electrochemical evidence of inter-porphyrin interaction, and that it also shows no evidence of aggregation.<sup>24,25</sup> Most of the compounds in this study were derived from 5-ethynyl-NiOEP **3**. The preparation of this compound was refined by us from that in the original report<sup>4</sup> to that published in 1992.<sup>5</sup> The yield of the Wittig reaction of 5-formyl-NiOEP **4** to form 5-( $\beta$ -bromovinyl)-NiOEP **5**, has still not been raised above about 60%. However, by using potassium *tert*-butoxide instead of sodium hydride, as suggested in the communication by Gosper and Ali,<sup>11</sup> the conversion of **5** to **3** is rapid and quantitative at room temperature. The one contaminant (about 5%) is 5-vinyl-NiOEP **6**, which is formed in the Wittig reaction and not conveniently separated from **5**. This impurity can be

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tolerated in the later coupling reactions of **3** to give *dimers*, since it is readily separated from them by column chromatography. It can also usually be separated from the more elaborated monomers by recrystallization. The extent of contamination of **3** by **6** is easily estimable by NMR spectroscopy and can be accounted for in the stoichiometry of the coupling reactions. As reported by us, and since by Sakata's group, **3** is not usually purified because of losses due to its coupling to form **1**.<sup>5,14</sup> Strangely, the oxidative stability of **3** seems to vary from batch to batch, suggesting the presence of unknown catalytic impurities in minor and variable amounts. We attempted to carry out the conversion of **4** to **3** in a one-pot procedure (as achieved by Gosper and Ali for their  $\beta$ -substituted tetraphenylporphyrin (TPP) series<sup>11</sup>), but this method fails for the NiOEP compounds because of the very rapid deformylation of **4** by excess *tert*-butoxide. We have found it better to tolerate a slightly lower yield of **5**, although some **4** remains, since **4** and **5** are readily separated and **4** can then be recycled. Deformylation of **4** was reported by Callot, in his attempts to prepare 5-( $\beta,\beta$ -dibromovinyl)-NiOEP **7** by treatment of **4** with  $\text{CBr}_4/\text{PPh}_3$ .<sup>27</sup> We have confirmed this result, since **7** is a desirable, but so far elusive, starting material.

Using the general approach outlined in our preliminary communication,<sup>22</sup> we have coupled alkyne **3** with a variety of unsaturated halides, to prepare a range of porphyrin monomers and dimers of novel structure. The palladium-catalyzed coupling of terminal alkynes with unsaturated halides is a well-known process in general organic chemistry.<sup>28</sup> As expected, the ethyl groups flanking the 5-position in **3** cause significant hindrance in the Pd intermediates, so our reactions are sluggish compared with those carried out, for example, with the 5,15-diphenylporphyrin compounds by Lin *et al.*<sup>9</sup> The latter were able to invert the coupling method, i.e. by using *meso*-haloporphyrins and a terminal alkyne or 1-alkynyl organometallic reagent, because *meso*-haloporphyrins are easily prepared in the 5,15-diphenylporphyrin system. The required halides are not readily accessible in the OEP system.<sup>29,30</sup> An unavoidable consequence of the use of **3** is that its homo-coupling to yield **1** becomes a competitive reaction, even when we strenuously remove oxygen. The problem becomes worse as the difficulty of the desired coupling increases. The presence of CuI, a cocatalyst often used in Pd-catalyzed couplings, exacerbates this problem, so we avoided its use in most cases. It rapidly became clear that the Pd catalysts alone can carry out homo-couplings of alkynes (as also recently reported by Lindsey and co-workers<sup>18c</sup>), so we were sometimes faced with severe separation problems. These aspects will be noted in the Discussion below.

**Preparation of Monomers.** The compounds in this group were prepared either as precursors to dimers or as model systems on which to base comparisons of substituent effects on spectra and redox potentials. The synthesis of **8** was achieved by coupling (trimethylsilyl)acetylene (TMSA) with (bromovinyl)-NiOEP **5**. This was a high-yielding process, since a large excess of TMSA could be used with CuI as cocatalyst, there being no porphyrin homo-coupling side products. The alternative

protected enyne **9** was readily prepared by the same approach using 2-methylbut-3-yn-2-ol as sacrificial alkyne. The deprotection of **9** to yield **10** was found to be sluggish using typical conditions, so this route was abandoned in favor of the TMS-protected monomer **8**. The desilylation of **8** proceeded readily using tetrabutylammonium fluoride (TBAF) in  $\text{CH}_2\text{Cl}_2$ . The crude terminal enyne **10** was characterized by NMR and used without further purification for dimerization (see below).

The phenyl-terminated butadiyne monomer **11** was prepared in conjunction with our electrochemical studies of the butadiyne dimers and was first mentioned in that communication.<sup>24</sup> Our method was to couple **3** with (bromoethynyl)benzene, using  $\text{PdCl}_2/\text{PPh}_3$  as catalyst in  $\text{NEt}_3$ . This compound has recently been reported by Sakata and co-workers, who prepared it (and a series of phenyl-substituted analogs) by reacting **3** with an excess of phenylethyne, using oxidative cross-coupling with  $\text{Cu}(\text{OAc})_2/\text{pyridine}$ .<sup>14</sup> Using the latter alkyne as a sacrificial reagent, they were able to minimize the production of porphyrin dimer **1**. The separation of diphenylbutadiyne (and in our case, excess (bromoethynyl)benzene) was accomplished by column chromatography. The spectroscopic data reported by Sakata compare well with ours, except for an apparent error in their published extinction coefficient for the lowest energy visible band.<sup>14</sup>

The trimethylsilyl-protected butadiyne **12**, required for the synthesis of our octatetrayne (see below), was prepared by two methods. In the first, we reacted **3** with a 5-fold excess of (iodoethynyl)trimethylsilane, using conditions similar to those used for **11**. As for **11**, two flash columns were required for the thorough purification of **12**. The first column separated most of the non-porphyrin contaminants (starting iodide and its homo-coupled product) and dimer **1**. The second column was needed to eliminate traces of **3**, as well as remaining silyl impurities. It was essential to remove **3**, or else in subsequent reactions its coupling product **1** causes intractable separation problems. Some vinyl monomer **6** remained but was removed by recrystallization, giving a final yield of about 25%. The (trimethylsilyl)butadiynyl substituent has previously been introduced into the *meso*-position of an octaalkylporphyrin by Anderson, who coupled a 5,15-diethynylporphyrin (as the zinc complex) with a large excess of TMSA, using the CuI/TMEDA method, to give both mono- and bis[(trimethylsilyl)butadiynyl] derivatives.<sup>6</sup> We therefore also applied this method to prepare **12**, using a 15-fold excess of TMSA, and obtained it in 67% yield. The deprotection of **12** to **13** was readily achieved by the same method as for **8**.

The hexatriyne monomer **14** was first observed during our study of the preparation of **12**. In the presence of a 30-fold excess of TMSA, with a 30 h reaction time, apparently some C-Si bond cleavage occurs, in either **12** or in the byproduct bis(trimethylsilyl)butadiyne, and this subsequently couples with **3**. Triyne **14** was isolated by chromatography in low yield from this reaction, but it was also prepared in 68% yield by CuI/TMEDA-promoted coupling of **13** with a 16-fold excess of TMSA. Model monomers containing *meso*-phenylethynyl substituents (**15** and **16**) were readily prepared by coupling **3** with iodobenzene or excess 1,4-diiodobenzene, respectively. A second coupling of **16** with TMSA produced **17**. This sequence was repeated using the thiophene derivatives, leading uneventfully to monomers **18-20**.

In most of the reactions described here and below, we used only a limited set of possible catalysts, mainly  $\text{PdX}_2/$

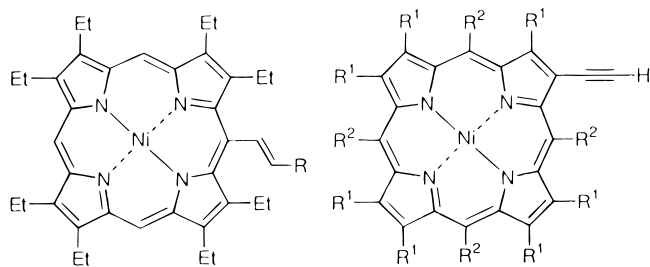
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Chart 2



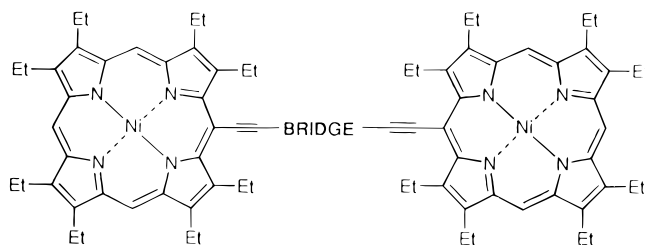
- 23 R = C≡C-OEPNi  
 24 R = C≡C-CH=CH-OEPNi  
 25 R = C≡C-C≡C-CH=CH-OEPNi  
 26 R = C≡C-HEPNi  
 28 R = C≡C-TPPNi  
 27 R<sup>1</sup> = Et; R<sup>2</sup> = H  
 29 R<sup>1</sup> = H; R<sup>2</sup> = Ph

PPh<sub>3</sub> (X = Cl or OAc), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, or Pd(PPh<sub>3</sub>)<sub>4</sub>, with or without cocatalysis by CuI. These systems all gave very similar results, whenever we compared them. It is very common in Pd-catalyzed alkyne couplings to use secondary amines, of which diethylamine and pyrrolidine are particularly active.<sup>31</sup> However, secondary amines cannot be used in reactions of **3**, as they rapidly add nucleophilically to the very electron-deficient triple bond. For example, reaction of **3** with tetraiodoethylene (see preparation of **36/37** below) in the presence of pyrrolidine using either PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst gave exclusively the acetaldehyde **21** after aqueous acid workup. The intermediacy of the enamine **22** was confirmed by modifying the workup. This reaction represents a useful preparation of the aldehyde **21**. Anderson also reported briefly the addition of diethylamine to *meso*-alkynylporphyrins.<sup>12</sup>

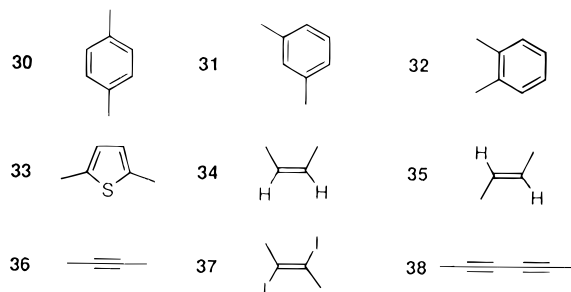
**Preparation of Dimers.** We begin with those dimers with a double bond in the 5-position of NiOEP, i.e. dimers **23–26** and **28** (Chart 2). These were prepared to survey the efficacy of coupling procedures for various structural types of alkynylporphyrins and to serve as comparison compounds with dimers containing only *meso*-alkynyl linkers. The bis(NiOEP)butenyne **23** was readily formed by coupling **3** with a 3-fold excess of **5**, using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as catalyst. The desired compound **23** was separated from **1** by column chromatography, giving a 74% yield. The hexadienyne dimer **24** was prepared in 20% yield by coupling the terminal enyne **10** with excess **5** using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and separating **24** from the homocoupled product **25** by column chromatography. A high yield of the octadienyne **25** was obtained by coupling either enyne **10** or, even better, the silyl-protected enyne **8**, using Cu(OAc)<sub>2</sub> in pyridine.

The mixed *meso*/β-butenyne dimer **26** was prepared by coupling **5** and 2-ethynyl-NiHEP (HEP = heptaethylporphyrin) **27** using Pd(OAc)<sub>2</sub>/PPh<sub>3</sub>/CuI in NEt<sub>3</sub>. The coupling reactions of the β-alkynes are much slower than those of **3**, so the CuI co-catalyst was included. We reported the preparation of **27** in 1992<sup>5</sup> and used it then to form the corresponding butadiyne. Sakata and co-workers recently used **27** to prepare a range of 2-(phenylbutadiynyl)-NiHEP derivatives, but made it by a much longer route via 2-acetyl-HEP and 2-(1-chloro-2-formylvinyl)-HEP.<sup>14</sup> We isolated a 30% yield of **26**, using preparative TLC. Dimer **32** was prepared similarly by reacting 2-ethynyl-NiTPP **29**<sup>5</sup> with **5**. This reaction was also rather sluggish (as is the homo-coupling of this

Chart 3



BRIDGE =



alkyne under the conditions we used previously<sup>5,11</sup>), and after preparative TLC we obtained the required dimer **28** in 15% yield. At 500 MHz, a complete assignment of the complex NMR spectrum of **28** was possible.

We now turn to the class of dimers with the alkyne substituent directly attached to the 5-position of NiOEP in both halves of the molecule. Their synthesis relies on the double coupling of **3** with unsaturated dihalides. The 1,4-phenylene derivative **30** (Chart 3) was described in our preliminary communication.<sup>22</sup> The 1,3-phenylene analog **31** was prepared similarly and isolated in 30% yield. The unusual behavior of the 1,2-analog **32** was mentioned previously.<sup>22</sup> The coupling reaction to produce this dimer is much slower because of crowding, and the intermediate 2-(iodophenyl)ethynyl monomer (the *ortho*-analog of **16**) was isolated in 34% yield. The dimer **32** is unstable during chromatographic separation from butadiyne **1**, and a low yield resulted. We have not yet identified any of the numerous products of this decomposition. In some of them, the protons of the ethyl groups display significant upfield shifts, suggestive of structures with *gem*-diethyl substitution and/or closely cofacial porphyrins. The solutions are an unusual golden-brown, and at least one component has an absorption band at 705 nm. The dimer **32** is a doubly ethynylous "gable" bis-porphyrin, and the disposition of the porphyrin rings in a widely spaced face-to-face orientation is apparent in the upfield shifts of the *meso*-proton signals in the NMR spectrum. The 2,5-bis(ethynyl-NiOEP)thiophene **33**, prepared in 58% yield by coupling **3** with 2,5-diiodothiophene, is an important compound in this series, since we obtained single crystals suitable for X-ray analysis. The crystal structure was reported in a communication.<sup>23</sup> In no other case have we been able to grow high-quality single crystals of alkyne-linked dimers.

The coupling of **3** with the commercially available *cis/trans*-1,2-dibromoethylene, under the usual conditions, led to a product mixture comprising butadiyne **1** and a mixture of *cis*- and *trans*-isomers **34** and **35**. Extensive column and radial chromatography separated the mixture of **34** and **35** from butadiyne **1**, but we could not completely separate the *cis*- and *trans*-isomers. Heating the mixture in benzene caused thermal isomerization of the *cis*-isomer, leading to a small amount of pure *trans*-isomer **35**. Thus the overall yield was very low, and

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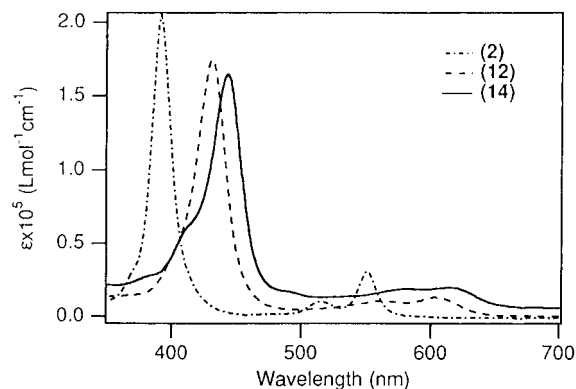
much tedious chromatography was required. However, enough was obtained to carry out the experiments needed to compare it with the rest of the series.<sup>26</sup>

Various strategies were attempted or contemplated for the synthesis of the hexatriyne **36**. The fundamental problem in obtaining **36** pure is the inevitable presence of **1**. As explained above, the Pd-catalyzed couplings of **3** are really very sluggish in comparison with those of simpler molecules, so the homo-coupling often dominates. Therefore, coupling of **3** with diiodoethyne was not attempted, since our experience of coupling alkynyl halides (e.g. in preparing **11** and **12**) suggested this would be unrewarding. Instead, we first tried the double coupling of **3** with tetraiodoethylene, in the hope that the proposed product 1,2-diiodo-1,2-bis(NiOEPethynyl)ethylene **37** would be sufficiently different in its chromatographic behavior to enable its separation from **1**. However, NMR and mass spectra showed that the only significant product other than **1** was, in fact, the final target compound **36**. Apparently, the catalyst also promoted deiodination of **37**. Repeated column or radial chromatography failed to separate the two dimers completely, and at best a 1:1 (by NMR) mixture of **1** and **36** was produced. At this stage we were resigned to the fact that this dimer would not be obtained pure, and in order to get enough for comparison of its spectroelectrochemistry with **1** and the octatetrayne **38**,<sup>26</sup> we deliberately prepared a mixture of the three dimers by reacting equimolar amounts of **3** and **13** in the presence of CuCl/TMEDA in a random coupling. The total dimer fraction was collected and examined by NMR. It is possible to distinguish the dimers **1**, **36**, and **38** by close examination of the NMR signals due to the methylene groups flanking the bridge. These quartets shift further upfield as the alkyne chain is lengthened. By repeated column chromatography, a sample estimated to be a 1:1 mixture of **1** and **36** was again obtained. A high yield of the pure octatetrayne **38** was readily obtained by Cu(OAc)<sub>2</sub>/pyridine coupling of the terminal butadiyne **13** or the silyl-protected version **12**.

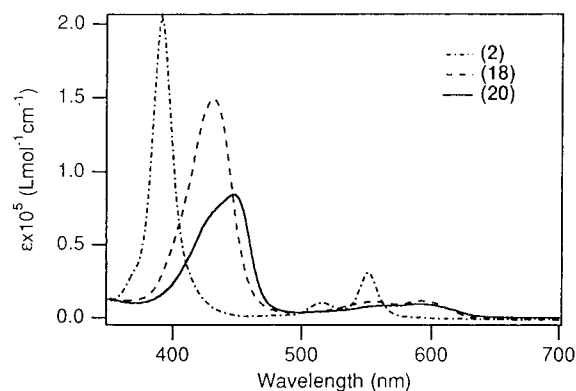
#### Comparison of Electronic Absorption Spectra.

One of the driving forces behind our interest in this suite of compounds is the novel and profound effects seen in the electronic absorption spectra of the alkyne-linked dimers.<sup>4-8,10,11,14</sup> It has also become apparent that dimers linked by a *trans* double bond have unique visible and near-IR absorption features.<sup>32,33</sup> It is our aim in this section to compare the visible spectra of the various groups of monomers and dimers in a qualitative sense. In a subsequent paper, we will discuss the theoretical implications of the spectra, together with the electrochemistry and spectroelectrochemistry.<sup>26</sup> There are two components to our comparison: the effect of the bridge as a substituent (as revealed by study of monomers) and the effect of the second porphyrin chromophore.

It is known from various reports that *meso*-alkynyl substituents cause significant red-shifts in porphyrin spectra, consistent with stabilization of the LUMO.<sup>4-16</sup> This is very evident from Figure 1, in which we compare **2**, **12**, and **14**. There is also a loss of resolution in the Q bands and a broadening of the Soret band, as the symmetry is lowered from *D*<sub>4h</sub> to *C*<sub>2v</sub>, but the spectrum



**Figure 1.** Visible absorption spectra (in CHCl<sub>3</sub>) of NiOEP (**2**) and monomers **12** and **14**.

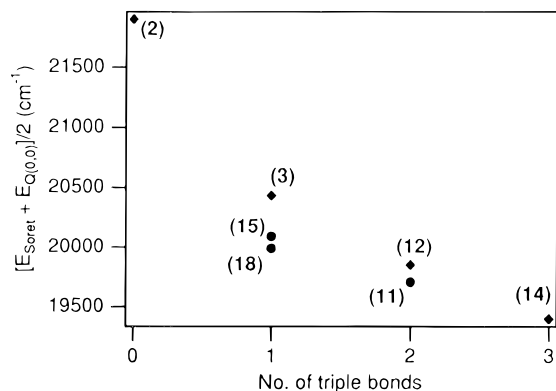


**Figure 2.** Visible absorption spectra (in CHCl<sub>3</sub>) of NiOEP (**2**) and thiophene monomers **18** and **20**.

is still essentially that of a typical Ni(II) porphyrin. As the substituent is extended, some complexity is revealed, and the spectrum of **14**, with the C<sub>6</sub>-SiMe<sub>3</sub> substituent, shows a pronounced shoulder on the blue edge of the Soret band. Next we consider the monomers with C<sub>2</sub>-aryl substituents, i.e. **15**, **17**, **18**, and **20**. The thiophene end group is apparently more electron-withdrawing than a phenyl group. The effect of an additional C<sub>2</sub>-SiMe<sub>3</sub> substituent conjugated through the aryl group is to shift the Soret band to the red, but the Q band is slightly blue-shifted. Moreover, the Soret bands of **17** and **20** are broadened relative to those of **15** and **18**, respectively. As an example, we show a comparison of NiOEP, **18**, and **20** in Figure 2. The asymmetric Soret band of **20** shows that there are at least two overlapping bands of similar intensity in this envelope. It is useful to compare our spectra with those published by the Sakata group for the series NiOEP-C<sub>4</sub>-Ph-*p*-X.<sup>14</sup> They found that for X = NO<sub>2</sub>, the Soret band is split, the Q bands appear as an unresolved envelope, and the spectral shape is strongly dependent on solvent polarity. This was seen as evidence for admixture of charge transfer character due to the NO<sub>2</sub> substituent. In our compounds, the thiophene seems to be exhibiting some of the same tendency. A sharply split Soret band for an alkynylporphyrin monomer was reported by Lin *et al.* for the compound [5,15-bis(trimethylsilyl)ethynyl]-10,20-diphenylporphyrinato]zinc(II).<sup>8</sup> Strangely, the analogous [5,15-bis(aryl)ethynyl]-10,20-diphenylporphyrinato]zinc(II) complexes do not show such splitting, and the spectrum shown in ref 8 may be in error. We have prepared the corresponding Ni(II)

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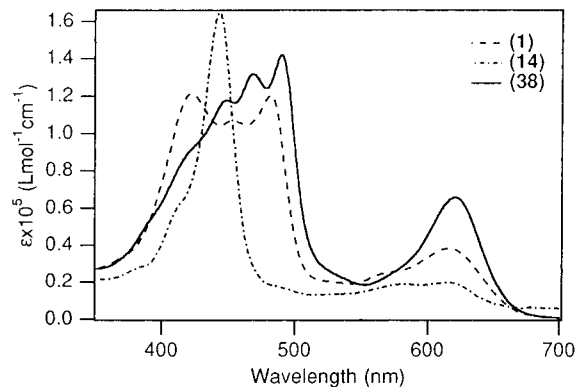


**Figure 3.** Plot of the "electronic center of gravity" vs the number of attached contiguous triple bonds for the monomers **2**, **3**, **11**, **12**, **14**, **15**, and **18**.

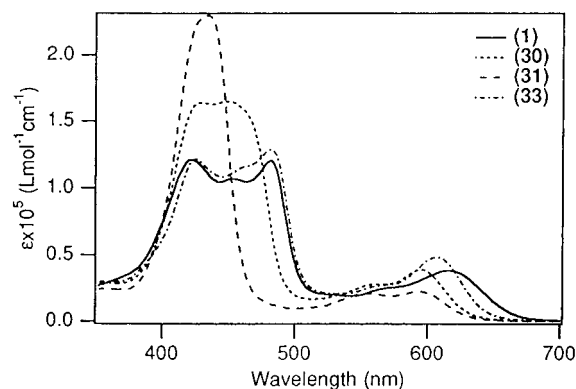
complex and have seen no splitting.<sup>34</sup> Anderson reported the spectrum of the zinc complex of a 5,15-bis(trimethylsilyl)butadiynyl]octaalkylporphyrin and this also showed a single, sharp Soret band.<sup>6</sup> Therien has recently published the results of extensive experiments and calculations on the diarylethynyl species,<sup>35</sup> and his conclusions on the bis(*p*-nitrophenyl)ethynyl derivative reinforce the Sakata postulate.<sup>14</sup> We will discuss these points further in our paper on the electrochemistry.<sup>26</sup>

An indicator of the substituent effect in porphyrin spectra is the shift of the average energy of the Soret and Q(0,0) bands. This was termed the "electronic center of gravity" by Binstead et al., and it is a useful parameter as it is independent of the extent of configuration interaction between the states which give rise to these bands.<sup>36</sup> In Figure 3, the parameter  $(E_{\text{Soret}} + E_{\text{Q}(0,0)})/2$  (in  $\text{cm}^{-1}$ ) is plotted against the number of contiguous triple bonds in the substituent, for the compounds **2**, **3**, **11**, **12**, **14**, **15**, and **18**. This plot gives a summary of the electronic effects of these substituents and also shows the attenuation of the incremental shifts of the center of gravity as the number of triple bonds increases.

With these monomer spectra in mind, we now turn to the effects of connecting a second porphyrin ring, while retaining the connection of a triple bond to each porphyrin (compounds **1**, **30**, **31**, **33**, **35**, and **38**). The first comparison (Figure 4) is between the butadiyne **1** and octatetrayne **38** linkers, with the hexatriyne monomer **14** for reference. It is clear from this comparison that there is very little red shift of the Q bands due solely to dimerization. Moreover, if the center of the Soret envelope is considered, there is also a negligible bathochromic effect due to the second porphyrin. The major effect of the second porphyrin is the large splitting of the Soret bands, as is now well-known for ethyne and butadiyne bridges.<sup>4-8,10,12</sup> The Kasha exciton theory of "weakly coupled" proximate chromophores<sup>37</sup> has been shown by Anderson to fail in explaining the magnitude of this splitting.<sup>6</sup> The multiple splitting shown by **38** has not been reported before for porphyrin dimers. One obvious conclusion from these spectra is that the band splitting certainly does not fit an  $R^{-3}$  distance dependence, which



**Figure 4.** Visible absorption spectra (in  $\text{CHCl}_3$ ) of butadiyne dimer **1**, octatetrayne dimer **38**, and the hexatriyne monomer **14**.



**Figure 5.** Visible absorption spectra (in  $\text{CHCl}_3$ ) of butadiyne dimer **1**, the diethynylarene dimers **30** and **31**, and the thiophene dimer **33**.

would be demanded by the point dipole approximation.<sup>37</sup> Another feature to note for **38** is the increased intensity of the Q(0,0) band relative to that in **1**, although there is little difference in the  $\lambda_{\text{max}}$  of the bands for the two compounds. We have recently described our density functional calculations on Ni(II) bis(porphyrinyl)butadiyne (an unsubstituted model of **1**), which qualitatively predict the features of the spectra of conjugated dimers.<sup>38</sup>

Another interesting comparison is found in the "interrupted" dimers, as shown in Figure 5 for **1**, **30**, **31**, and **33**. The very close similarity of the spectra of **1** and **33** is remarkable. Moreover, the *trans*-enediynes **35** has an almost identical spectrum to those of **1** and **33**. Thus the 2,5-thiophene and the *trans*-ethene units are effectively "transparent", as far as the appearance of the Soret band is concerned. This is in contrast to the distinct blocking effect of the 1,4-phenylene unit in **30**. The interruption of resonance communication is almost complete in the 1,3-phenylene dimer **31**, which displays a broadened, flat-topped Soret band, which suggests a maximum splitting of only *ca.* 500  $\text{cm}^{-1}$ .

While the spectral type represented by **1** is now familiar in the literature,<sup>4-8</sup> the dimers with ene/yne bridges are an entirely new class. As mentioned above, compound **35**, with the bridge  $-\text{C}\equiv\text{CCH}=\text{CHC}\equiv\text{C}-$ , fits in the former group. Compounds **26** and **28** have spectra which are basically the superposition of the two

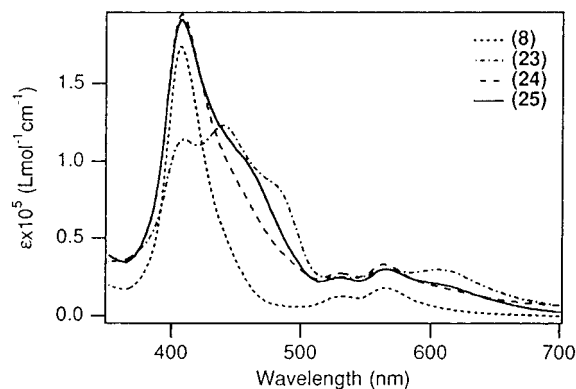
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**Figure 6.** Visible absorption spectra (in  $\text{CHCl}_3$ ) of the enyne-containing dimers **23**, **24**, and **25**, compared with the enyne monomer **8**.

component chromophores. Thus **28** has a Soret band with a higher energy shoulder due to the OEP side and a more intense band due to the TPP moiety. One novel feature is the presence of a broad "tail" on the Q(0,0) band. At the time it was first observed, we attached no importance to it, but its significance is now revealed by consideration of the other compounds in this class, namely **23**–**25**. These spectra, and that of the model enyne monomer **8** are shown in Figure 6. A strong interporphyrin interaction, not unlike that in **1**, **33**, and **35**, is evident for **23**. This diminishes with distance, as seen from **24** and **25**. However, all these compounds exhibit the gradual tailing on the low-energy end, which is clearly absent in the similar monomer. Such a feature has recently come to prominence in the spectrum of the OEP dimer linked only by a *trans*-ethenyl unit (and its mono- and dinickel(II) complexes).<sup>20,32,33</sup> It appears to be characteristic of dimers with a double bond directly linked to the *meso*-position of at least one of the porphyrin rings and may be due to a mixture of conformations, some of which have the double bond(s) and the porphyrins near coplanar.<sup>33</sup> The only other octaalkylporphyrin dimer in the literature with a structure which suggests it should show this behavior is the *all-trans*-bis(NiOEP)hexatriene reported by Vicente and Smith.<sup>39</sup> The spectrum was not shown in that paper, and the data given in their Experimental Section do not indicate whether such a tail is present, but it would be surprising if it were not, on the basis of our findings.

## Conclusions

We have prepared a set of porphyrin dimers containing a variety of unsaturated linkages, together with model monomers. These have enabled us to examine the electronic absorption spectra and deal separately with the effects of the unsaturated substituent and the presence of the second porphyrin unit. The triply bonded substituents have strong bathochromic effects, while dimerization causes only minor additional shifts, but profound modification of the shapes of the Soret band. The ability to tailor the spectral shape and the wavelength spread of the absorption is conferred by the use of various bridge lengths and compositions. The dimers with double bonds in the *meso*-positions represent a new structural class, and our results indicate that these

dimers have potential for further interesting developments. Our work on the double-bonded dimers is continuing.

## Experimental Section

Porphyrin starting materials, solvents, instruments, and procedures were generally the same as those described in previous papers.<sup>5</sup> Amines were distilled from KOH pellets and were stored in the dark over 4 Å molecular sieves. THF was distilled from sodium/benzophenone. Tetrabutylammonium fluoride hydrate (TBAF), (trimethylsilyl)acetylene, 2-methyl-3-butyn-2-ol, 2,5-diiodothiophene, *o*- and *p*-diiodobenzene, tetraiodoethylene, dibromoethylene (*cis/trans* mixture), triphenylphosphine, and palladium and copper salts were commercial samples. (Bromoethynyl)benzene,<sup>40</sup> iodo(trimethylsilyl)acetylene,<sup>40</sup> *m*-diiodobenzene,<sup>41</sup>  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ,<sup>42</sup> and  $\text{Pd}(\text{PPh}_3)_4$ <sup>43</sup> were prepared by literature methods. Silica gel for column chromatography was Merck grade 9385, 230–400 mesh, or, for less stringent separations, Merck grade 7733, 35–70 mesh, or Merck grade 7734, 70–230 mesh. FAB mass spectra were recorded by Dr J. MacLeod at the Research School of Chemistry, The Australian National University. The values quoted for MS data are the *m/z* values of the largest peak of the molecular ion cluster.

**Improved Preparation of Alkyne 3.** The bromovinyl complex **5**<sup>4,5</sup> (240 mg, 0.345 mmol) was dissolved in dry THF under  $\text{N}_2$ . Potassium *tert*-butoxide (0.35 mL of 1 M solution in THF, 0.35 mmol) was added. The solution immediately changed color from red to the characteristic green/purple of **3**. After 15 min, the solvent was evaporated, and the residue was extracted with  $\text{CHCl}_3$ . After washing with water and drying, the solvent was removed to yield 210 mg of **3**, contaminated with small quantities of **1** and **6**.

**General Procedures for Palladium-Catalyzed Couplings.** The alkyne **3** and the appropriate halide were dissolved in  $\text{NEt}_3$  at about 0.01 M, and the mixture was degassed by argon bubbling for at least 10 min. The palladium catalyst [e.g.  $\text{PdCl}_2(\text{PPh}_3)_2$ ] was added at 5–20% w/w of **3**, and the mixture was heated to reflux or held at an appropriate temperature. The reaction progress was monitored by TLC and (in some cases) by visible spectroscopy. Sometimes additional **3**, halide, and/or catalyst was added. Standard workup consisted of evaporation of the solvent, extraction with  $\text{CHCl}_3$ , washing of this extract with 2 M HCl and then water, drying, and evaporation to dryness. Purification involved flash chromatography, using appropriate mixtures of  $\text{CHCl}_3$  and hexane as eluent. Fractions from the column were compared by TLC and/or NMR spectroscopy. Further separation was sometimes necessary using another column, preparative TLC, or radial chromatography.

***trans*-1-[2,3,7,8,12,13,17,18-Octaethyl-5-[4-(trimethylsilyl)buten-3-ynyl]porphyrinato]nickel(II) (8).** A mixture of **5** (70 mg, 0.1 mmol),  $\text{Pd}(\text{OAc})_2$  (6 mg),  $\text{PPh}_3$  (14 mg),  $\text{CuI}$  (5 mg), and (trimethylsilyl)acetylene (71  $\mu\text{L}$ , 50 mg, 5-fold excess) in  $\text{NEt}_3$  (10 mL) was stirred for 3 h at room temperature. Workup gave a crude residue which was purified by column chromatography on 70–230 mesh silica gel, eluting with 25%  $\text{CHCl}_3$ /hexane. The broad major red band was collected, and the resulting solid was recrystallized from  $\text{CHCl}_3$ /MeOH to give two crops of dark red needles (55 mg, 77%): NMR  $\delta_{\text{H}}$  9.44 (s, 2H), 9.43 (s, 1H), 9.28 (d,  $J = 15.6$  Hz, 1H), 4.81 (d,  $J = 15.6$  Hz, 1H), *ca.* 3.8 (overlapping q, 16H), 1.78, 1.77, 1.73, 1.72 (overlapping t, 24H), 0.28 (s, 9H); vis  $\lambda_{\text{max}}$  406 nm ( $\epsilon$  132 400), 531 (9200), 564 (13 200); IR (KBr) 2158w, 2115w  $\text{cm}^{-1}$ ; FAB MS 712. Anal. Calcd for  $\text{C}_{43}\text{H}_{52}\text{N}_4\text{NiSi}$ : C, 72.4; H, 7.6; N, 7.9. Found: C, 72.9; H, 7.7; N, 7.8.

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**trans-[2,3,7,8,12,13,17,18-Octaethyl-5-(2-hydroxy-2-methylhex-5-en-3-ynyl)porphyrinato]nickel(II) (9).** A mixture of **5** (200 mg, 0.29 mmol), Pd(OAc)<sub>2</sub> (18 mg), PPh<sub>3</sub> (42 mg), CuI (15 mg), and 2-methyl-3-butyn-2-ol (280  $\mu$ L, 243 mg, 10-fold excess) in NEt<sub>3</sub> (40 mL) was stirred for 2 h at room temperature. The mixture was poured slowly into 2 M HCl (150 mL) and then extracted with CHCl<sub>3</sub> (3  $\times$  50 mL). The combined CHCl<sub>3</sub> layers were washed with 2 M HCl (25 mL) and then dried and evaporated. Column chromatography (eluting with 50% CHCl<sub>3</sub>/hexane) gave the product as the major red band. The product was recrystallized from CHCl<sub>3</sub>/hexane by slow evaporation, giving two crops of **9** (142 mg, 70%): NMR  $\delta_{\text{H}}$  9.44 (s, 2H), 9.43 (s, 1H), 9.22 (d,  $J$  = 15.8 Hz, 1H), 4.78 (d,  $J$  = 15.8 Hz, 1H), *ca.* 3.8 (overlapping q, 16H), 2.04 (br s, 1H), *ca.* 1.7 (overlapping t, 24H), 1.63 (s, 6H); vis  $\lambda_{\text{max}}$  406 nm ( $\epsilon$  129 000), 531 (8700), 565 (13 000); IR (KBr) 2213w cm<sup>-1</sup>; FAB MS 698. A satisfactory elemental analysis was not obtained.

**trans-[5-Buten-3-ynyl-2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II) (10).** The product **8** from above (26 mg, 0.036 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), TBAF (13 mg, 50 mmol) was added, and the mixture was stirred at room temperature for 30 min. MeOH was added, then the solvents were evaporated, and the residue was extracted with CHCl<sub>3</sub>. The CHCl<sub>3</sub> extract was washed with water, dried, and evaporated to yield **10** as a purple powder (17 mg, 75%). This material was used without further purification to prepare **28** (see below): NMR  $\delta_{\text{H}}$  9.47 (s, 2H), 9.45 (s, 1H), 9.40 (d,  $J$  = 15.9 Hz, 1H), 4.82 (dd,  $J$  = 15.9, 2.1 Hz, 1H), *ca.* 3.8 (overlapping q, 16H), 3.16 (d,  $J$  = 2.1 Hz, 1H), *ca.* 1.76 (overlapping t, 24H).

**[2,3,7,8,12,13,17,18-Octaethyl-5-(phenylbutadiynyl)porphyrinato]nickel(II) (11).**<sup>14,24</sup> Alkyne **3** (28 mg, 0.046 mmol) was reacted with (bromoethynyl)benzene (40 mg, 0.22 mmol) in NEt<sub>3</sub> (5 mL) using PdCl<sub>2</sub> (7 mg) and PPh<sub>3</sub> (14 mg). The reaction mixture was refluxed for 5 h under Ar. The usual workup, followed by column chromatography and recrystallization from CHCl<sub>3</sub>/MeOH, gave purple needles of **11** (11 mg, 34%): NMR  $\delta_{\text{H}}$  9.44 (s, 2H), 9.41 (s, 1H), 7.6 (m, 2H), 7.4 (m, 3H), 4.17 (q, 4H), *ca.* 3.8 (overlapping q, 12H), 1.84 (t, 6H), *ca.* 1.7 (overlapping t, 18H); vis  $\lambda_{\text{max}}$  437 nm ( $\epsilon$  174 300), 566 (12 300), 605 (13 200); IR (KBr) 2200w, 2134w cm<sup>-1</sup>; FAB MS 714. Anal. Calcd for C<sub>46</sub>H<sub>48</sub>N<sub>4</sub>Ni·CH<sub>3</sub>OH: C, 75.5; H, 7.0; N, 7.5. Found: C, 75.3; H, 6.9; N, 7.5.

**[2,3,7,8,12,13,17,18-Octaethyl-5-[(trimethylsilyl)butadiynyl]porphyrinato]nickel(II) (12).** (i) Alkyne **3** (43.5 mg, 0.071 mmol) was reacted with iodo(trimethylsilyl)acetylene (79 mg, 0.35 mmol) in NEt<sub>3</sub> (8 mL) using PdCl<sub>2</sub> (8.7 mg) and PPh<sub>3</sub> (17.4 mg). The reaction mixture was refluxed for 4 h under Ar. After 30 min, a black solid began to accumulate. After the usual workup, two flash columns, eluting with 15% CHCl<sub>3</sub>/hexane, were required for the purification of **12**. Compounds isolated in order of elution were **12**, **3**, and **1**. Fractions containing **12** were combined and recrystallized from CHCl<sub>3</sub>/MeOH to yield 13 mg (26%). (ii) Alkyne **3** (50 mg, 0.081 mmol), TMSA (0.175 mL, 1.24 mmol), and freshly prepared CuCl (2.25 g, 0.02 mol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 L) under dry air. TMEDA (3 mL, 0.02 mol) was added, and the mixture was stirred vigorously for 30 min. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated and washed with water until no more Cu(II) colour was extracted, dried, and evaporated to dryness. The crude product was purified by column chromatography, eluting with 15% CHCl<sub>3</sub>/hexane, and then recrystallization from CHCl<sub>3</sub>/MeOH to produce purple needles of **12** (39 mg, 67%): NMR  $\delta_{\text{H}}$  9.42 (s, 2H), 9.40 (s, 1H), 3.97 (q, 4H), *ca.* 3.8 (overlapping q, 12H), *ca.* 1.7 (overlapping t, 24H), 0.32 (s, 9H); vis  $\lambda_{\text{max}}$  402sh nm ( $\epsilon$  43 300), 431 (174 400), 567 (10 300), 603 (12 900); FAB MS 710. Anal. Calcd for C<sub>43</sub>H<sub>52</sub>N<sub>4</sub>NiSi·0.5H<sub>2</sub>O: C, 71.8; H, 7.4; N, 7.8. Found: C, 71.8; H, 7.7; N, 7.3.

**[5-Butadiynyl-2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II) (13).** The silyl-protected butadiyne **12** (19.5 mg, 0.027 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (6 mL), TBAF (12 mg, 46 mmol) was added, and the mixture was stirred at room temperature for 30 min. Treatment as for **10** above gave **13** (14 mg, 80%). This compound was used without further purification in subsequent reactions: NMR  $\delta_{\text{H}}$  9.42 (s, 2H),

9.41 (s, 1H), 3.95 (q, 4H), *ca.* 3.8 (overlapping q, 12H), 3.11 (s, 1H), *ca.* 1.75 (overlapping t, 24H).

**[2,3,7,8,12,13,17,18-Octaethyl-5-[(trimethylsilyl)hexatriynyl]porphyrinato]nickel(II) (14).** The butadiyne **13** (25 mg, 0.039 mmol), TMSA (90  $\mu$ L, 0.64 mmol), and CuCl (1 g, 0.01 mol) were mixed in CH<sub>2</sub>Cl<sub>2</sub> (500 mL) under dry air. TMEDA (1.5 mL, 0.01 mol) was added, and the mixture was stirred vigorously for 1 h. Water was added and the mixture was stirred for 30 min. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated, washed with water until no more Cu color remained, dried, and evaporated. The crude product was purified by column chromatography, eluting with 15% CHCl<sub>3</sub>/hexane, to give **14**, which was recrystallized from CHCl<sub>3</sub>/MeOH to yield purple needles (19.5 mg, 68%): NMR  $\delta_{\text{H}}$  9.41 (s, 2H), 9.40 (s, 1H), 4.08 (q, 4H), *ca.* 3.8 (overlapping q, 12H), *ca.* 1.75 (overlapping t, 24H), 0.29 (s, 9H); vis  $\lambda_{\text{max}}$  410sh nm ( $\epsilon$  54 400), 443 (164 800), 581 (14 200), 609 (15 200); FAB MS 734. Anal. Calcd for C<sub>45</sub>H<sub>52</sub>N<sub>4</sub>NiSi: C, 73.5; H, 7.1; N, 7.6. Found: C, 73.5; H, 7.15; N, 7.6.

**[2,3,7,8,12,13,17,18-Octaethyl-5-(phenylethynyl)porphyrinato]nickel(II) (15).** Alkyne **3** (30 mg, 0.049 mmol) was reacted with iodobenzene (30  $\mu$ L, 0.24 mmol) in NEt<sub>3</sub> (5 mL) using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1 mg). The reaction mixture was refluxed for 1 h under Ar. The usual workup, followed by column chromatography and recrystallization from CHCl<sub>3</sub>/MeOH, gave purple needles of **15** (28 mg, 83%): NMR  $\delta_{\text{H}}$  9.43 (s, 2H), 9.40 (s, 1H), 7.73 (d,  $J$  = 8.4 Hz, 2H), 7.45 (m, 3H), 4.23 (q, 4H), *ca.* 3.8 (overlapping q, 12H), *ca.* 1.78 (overlapping t, 24H); vis  $\lambda_{\text{max}}$  427 nm ( $\epsilon$  149 000), 556 (9700), 616 (9800); FAB MS 690. Anal. Calcd for C<sub>44</sub>H<sub>48</sub>N<sub>4</sub>Ni: C, 76.5; H, 7.0; N, 8.1. Found: C, 76.3; H, 7.05; N, 8.0.

**[2,3,7,8,12,13,17,18-Octaethyl-5-[(4-iodophenyl)ethynyl]porphyrinato]nickel(II) (16).** Alkyne **3** (29 mg, 0.048 mmol) was reacted with 1,4-diiodobenzene (78 mg, 0.24 mmol) in NEt<sub>3</sub> (5 mL) using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1 mg). The reaction mixture was refluxed for 4 h under Ar. The usual workup, followed by column chromatography and recrystallization from CHCl<sub>3</sub>/MeOH, gave purple needles of **16** (27 mg, 68%): NMR  $\delta_{\text{H}}$  9.45 (s, 2H), 9.43 (s, 1H), 7.82 (d,  $J$  = 8.1 Hz, 2H), 7.46 (d,  $J$  = 8.1 Hz, 2H), 4.20 (q, 4H), *ca.* 3.8 (overlapping q, 12H), *ca.* 1.76 (overlapping t, 24H); FAB MS 822. Anal. Calcd for C<sub>44</sub>H<sub>47</sub>IN<sub>4</sub>Ni: C, 64.7; H, 5.8; N, 6.9. Found: C, 64.7; H, 5.9; N, 6.85.

**[2,3,7,8,12,13,17,18-Octaethyl-5-[[4-[(trimethylsilyl)ethynyl]phenyl]ethynyl]porphyrinato]nickel(II) (17).** The previous compound **16** (14.4 mg, 0.018 mmol) was coupled with TMSA (20  $\mu$ L, 0.088 mmol) in NEt<sub>3</sub> (5 mL) using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1 mg) as catalyst. The reaction mixture was refluxed for 3 h under Ar. The usual workup, followed by column chromatography and recrystallization from CHCl<sub>3</sub>/MeOH, gave **17** as a purple powder (10 mg, 75%): NMR  $\delta_{\text{H}}$  9.43 (s, 2H), 9.40 (s, 1H), 7.65 (d,  $J$  = 8.7 Hz, 2H), 7.55 (d,  $J$  = 8.7 Hz, 2H), 4.20 (q, 4H), *ca.* 3.8 (overlapping q, 12 H), *ca.* 1.76 (overlapping t, 18H), 0.29 (s, 9H); vis  $\lambda_{\text{max}}$  432 nm ( $\epsilon$  105 300), 558 (8300), 595 (8400); FAB MS 786. A satisfactory elemental analysis was not obtained.

**[2,3,7,8,12,13,17,18-Octaethyl-5-(thiophene-2-yl-ethynyl)porphyrinato]nickel(II) (18).** Alkyne **3** (20 mg, 0.033 mmol) was reacted with 2-iodothiophene (36  $\mu$ L, 0.033 mmol) in NEt<sub>3</sub> (3 mL) using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1 mg) as catalyst. The reaction mixture was refluxed for 3 h under Ar. The usual workup, followed by column chromatography and recrystallization from CHCl<sub>3</sub>/MeOH, gave purple needles of **18** (16 mg, 70%): NMR  $\delta_{\text{H}}$  9.43 (s, 2H), 9.40 (s, 1H), 7.46 (dd,  $J$  = 3.6, 1.1 Hz, 1H), 7.42 (dd,  $J$  = 5.1, 1.1 Hz, 1H), 7.15 (dd,  $J$  = 5.1, 3.6 Hz, 1H), 4.20 (q, 4H), *ca.* 3.8 (overlapping q, 12H), *ca.* 1.8 (overlapping t, 24H); vis  $\lambda_{\text{max}}$  431 nm ( $\epsilon$  149 000), 556 (9700), 616 (9800); FAB MS 696. Anal. Calcd for C<sub>42</sub>H<sub>46</sub>N<sub>4</sub>NiS: C, 72.85; H, 6.85; N, 7.9. Found: C, 72.5; H, 6.6; N, 8.0.

**[2,3,7,8,12,13,17,18-Octaethyl-5-[(5-iodothiophene-2-yl)ethynyl]porphyrinato]nickel(II) (19).** Alkyne **3** (36 mg, 0.059 mmol) was reacted with 2,5-diiodothiophene (100 mg, 0.3 mmol) in NEt<sub>3</sub> (6 mL) using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2 mg) as catalyst. The reaction mixture was refluxed for 4 h under Ar. The usual workup, followed by column chromatography, gave **19** (13 mg, 27%): NMR  $\delta_{\text{H}}$  9.43 (s, 2H), 9.40 (s, 1H), 7.27 (d,  $J$



= 3.9 Hz, 1H), 7.09 (d,  $J = 3.9$  Hz, 1H), 4.14 (q, 4H), *ca.* 3.8 (overlapping q, 12H), *ca.* 1.75 (overlapping t, 24H). FAB MS 822.

**[2,3,7,8,12,13,17,18-Octaethyl-5-[[5-[(trimethylsilyl)ethynyl]thiophene-2-yl]ethynyl]porphyrinato]nickel(II) (20).** The previous compound **19** (13 mg, 0.016 mmol) was coupled with TMSA (10  $\mu$ L, 0.035 mmol) in  $\text{NEt}_3$  (4 mL) using  $\text{PdCl}_2(\text{PPh}_3)_2$  (1 mg). The reaction mixture was refluxed for 3 h under Ar. The usual workup, followed by column chromatography and recrystallization from  $\text{CHCl}_3/\text{MeOH}$ , gave **20** as a purple powder (10 mg, 80%): NMR  $\delta_{\text{H}}$  9.43 (s, 2H), 9.40 (s, 1H), 7.27 (d,  $J = 3.9$  Hz, 1H), 7.24 (d,  $J = 3.9$  Hz, 1H), 4.15 (q, 4H), *ca.* 3.8 (overlapping q, 12H), *ca.* 1.77 (overlapping t, 24H), 0.29 (s, 9H); vis  $\lambda_{\text{max}}$  425sh nm ( $\epsilon$  64 900), 447 (84 900), 559 (8 000), 592 (9200); FAB MS 792. A satisfactory elemental analysis was not obtained.

**[2,3,7,8,12,13,17,18-Octaethyl-5-(2-oxoethyl)porphyrinato]nickel(II) (21).** Alkyne **3** (6.5 mg, 0.011 mmol) was dissolved in pyrrolidine (5 mL) under Ar, and stirred at 50  $^{\circ}\text{C}$  for 30 min. The mixture was evaporated to dryness and the residue was extracted with  $\text{CHCl}_3$ . The extracts were washed with 2 M HCl and then water, dried, and evaporated to give a residue which was recrystallized from  $\text{CHCl}_3/\text{MeOH}$  to give a purple powder of **21** (5 mg, 71%): NMR  $\delta_{\text{H}}$  9.42 (s, 2H), 9.41 (s, 1H), 8.61 (t,  $J = 2.1$  Hz, 1H), 5.43 (d,  $J = 2.1$  Hz, 2H), *ca.* 3.8 (overlapping q, 12H), *ca.* 1.77 (overlapping t, 24H); vis  $\lambda_{\text{max}}$  405 nm ( $\epsilon$  131 000), 530 (6400), 570 (10 800). Anal. Calcd for  $\text{C}_{38}\text{H}_{46}\text{N}_4\text{NiO} \cdot 0.5\text{CH}_3\text{OH}$ : C, 71.2; H, 7.45; N, 8.6. Found: C, 71.1; H, 7.5; N, 8.4.

**trans-5,5'-Buten-3-yne-1,4-diylbis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] (23).** Alkyne **3** (30 mg, 0.049 mmol) was reacted with **5** (100 mg, 0.14 mmol) in  $\text{NEt}_3$  (5 mL), using  $\text{PdCl}_2(\text{PPh}_3)_2$  (1 mg). The mixture was refluxed for 5 h. Products identified after column chromatography were **5**, **1**, and **23**. Fractions containing only **23** were combined and recrystallized from  $\text{CHCl}_3/\text{MeOH}$  to yield green microcrystals of **23** (22 mg, 74%): NMR  $\delta_{\text{H}}$  9.43 (d,  $J = 15.6$  Hz, 1H), 9.42 (s, 4H), 9.39 (s, 2H), 5.37 (d,  $J = 15.6$  Hz, 1H), 4.22 (q, 4H), 4.19 (q, 4H), *ca.* 3.9 (overlapping q, 24H), 1.85 (t, 6H), *ca.* 1.77 (overlapping t, 42H); vis  $\lambda_{\text{max}}$  409 nm ( $\epsilon$  114 000), 440 (123 000), 480sh (83 000), 530 (25 000), 566 (30 000), 606 (30 000); FAB MS 1228. Anal. Calcd for  $\text{C}_{76}\text{H}_{88}\text{N}_8\text{Ni}_2$ : C, 74.2; H, 7.2; N, 9.1. Found: C, 74.4; H, 7.2; N, 9.1.

**trans,trans-5,5'-Hexa-1,5-dien-3-yne-1,6-diylbis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] (24).** Enyne **10** (30 mg, 0.046 mmol) was reacted with **5** (100 mg, 0.14 mmol) in  $\text{NEt}_3$  (5 mL), using  $\text{PdCl}_2(\text{PPh}_3)_2$  (1 mg). The mixture was refluxed for 2 h. Products identified after column chromatography were **5**, **24**, and **25**. Fractions containing only **24** were combined and recrystallized from  $\text{CHCl}_3/\text{MeOH}$  to yield green microcrystals (13 mg, 20%): NMR  $\delta_{\text{H}}$  9.45 (s, 4H), 9.44 (s, 2H), 9.30 (d,  $J = 14.7$  Hz, 2H), 5.03 (d,  $J = 14.7$  Hz, 2H), *ca.* 3.86 (overlapping q, 32H), *ca.* 1.77 (overlapping t, 48H); vis  $\lambda_{\text{max}}$  408 nm ( $\epsilon$  194 000), 457 (77 000), 532 (27 000), 564 (33 000), 616sh (17 000); FAB MS 1254. Anal. Calcd for  $\text{C}_{78}\text{H}_{90}\text{N}_8\text{Ni}_2$ : C, 74.6; H, 7.2; N, 8.9. Found: C, 74.0; H, 7.0; N, 8.9.

**trans,trans-5,5'-Octa-1,7-diene-3,5-diyne-1,8-diylbis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] (25).** (i) The enyne **10** (17 mg, 0.024 mmol) was dissolved in pyridine (10 mL),  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (8.5 mg) was added, and the mixture was stirred at 60  $^{\circ}\text{C}$  for 2 h. The mixture was poured into 2 M HCl (50 mL) and extracted with  $\text{CHCl}_3$ . The organic layer was washed with water, dried, and evaporated to dryness. The product was recrystallized from  $\text{CHCl}_3/\text{MeOH}$  to yield **25** as brown microcrystals (11 mg, 70%). (ii) The silyl-protected enyne **8** (20 mg, 0.028 mmol) was treated as above with  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (25 mg) in pyridine (20 mL). Product **25** was isolated as above in 88% yield: NMR  $\delta_{\text{H}}$  9.43 (s, 4H), 9.42 (s, 2H), 9.37 (d,  $J = 15.3$  Hz, 2H), 4.91 (d,  $J = 15.3$  Hz, 2H), *ca.* 3.85 (overlapping q, 32H), *ca.* 1.75 (overlapping t, 48H); vis  $\lambda_{\text{max}}$  409 nm ( $\epsilon$  114 000), 440 (123 000), 480sh (83 000), 531 (25 000), 566 (30 000), 606 (30 000); FAB MS 1280. Anal. Calcd for  $\text{C}_{80}\text{H}_{90}\text{N}_8\text{Ni}_2$ : C, 75.1; H, 7.1; N, 8.8. Found: C, 75.0; H, 7.0; N, 8.8.

**trans-[2-[1-[2,3,7,8,12,13,17,18-Octaethylporphyrin-5-**

**yl]buten-3-yn-4-yl]-3,7,8,12,13,17,18-heptaethylporphyrinato]dinickel(II) (26).** A mixture of **5** (38 mg, 0.055 mmol),  $\text{Pd}(\text{OAc})_2$  (1.7 mg),  $\text{PPh}_3$  (3.6 mg),  $\text{CuI}$  (1 mg), and **27** (40 mg, 25% excess) in  $\text{NEt}_3$  (12 mL), was stirred for 5 h at room temperature. Workup gave a crude residue which was applied to preparative TLC plates (nine of 20  $\times$  20 cm  $\times$  1 mm) and eluted several times with 25%  $\text{CHCl}_3/\text{hexane}$ . The bands due to the starting porphyrins were followed by the major red-brown band of the required product, which was recovered and recrystallized from  $\text{CHCl}_3/\text{MeOH}$  to give almost black microcrystals (19 mg, 29%): NMR  $\delta_{\text{H}}$  10.14 (s, 1H), 9.83 (s, 1H), 9.76 (s, 1H), 9.75 (s, 1H), 9.74 (d,  $J = 15.6$  Hz, 1H), 9.52 (s, 2H), 9.47 (s, 1H), 5.53 (d,  $J = 15.6$  Hz, 1H), *ca.* 4.15 (overlapping q, 6H), *ca.* 3.9 (overlapping q, 24H), *ca.* 1.95 (overlapping t, 9H), *ca.* 1.8 (overlapping t, 36H); vis  $\lambda_{\text{max}}$  405 nm ( $\epsilon$  218 200), 525 (21 900), 571 (48 400); IR (KBr) 2176vw  $\text{cm}^{-1}$ ; FAB MS 1201. Anal. Calcd for  $\text{C}_{74}\text{H}_{84}\text{N}_8\text{Ni}_2 \cdot \text{CH}_3\text{OH}$ : C, 72.9; H, 7.2; N, 9.1. Found: C, 72.7; H, 6.9; N, 8.7.

**trans-[2-[1-[2,3,7,8,12,13,17,18-Octaethylporphyrin-5-yl]-buten-3-yn-4-yl]-5,10,15,20-tetraphenylporphyrinato]dinickel(II) (28).** A mixture of **5** (38 mg, 0.055 mmol),  $\text{Pd}(\text{OAc})_2$  (1 mg),  $\text{PPh}_3$  (2.3 mg),  $\text{CuI}$  (1 mg), and **29** (47 mg, 25% excess) in  $\text{NEt}_3$  (12 mL) was stirred for 1 h at room temperature, then additional amounts of catalysts as above were added, followed by stirring for a further 48 h. After workup, the residue was applied to preparative TLC plates (five of 20  $\times$  20 cm  $\times$  1 mm) and eluted several times with 25%  $\text{CHCl}_3/\text{hexane}$ . The major bands were identified by NMR spectra as (in order of elution): **5**, **29**, butenyne **28**, and bis( $\text{NiTPP}$ )butadiyne. Crude **28** was recrystallized from  $\text{CHCl}_3/\text{MeOH}$  to give almost black microcrystals (10 mg, 14%): NMR  $\delta_{\text{H}}$  (500 MHz) 9.45 (s, 2H), 9.43 (s, 1H), 9.00 (d,  $J = 15.6$  Hz, 1H), 8.97 (s, 1H), *ca.* 8.70 (overlapping dd, 4H), 8.65, 8.62 (AB quartet, 2H,  $J = 5.1$  Hz), *ca.* 7.95 (overlapping dd, 6H), 7.88 (dd, 1H), *ca.* 7.65 (m, 9H), 7.42 (t, 2H), 7.27 (tt, 1H), 4.75 (d,  $J = 15.6$  Hz, 1H), 3.87 (q, 4H), *ca.* 3.8 (overlapping q, 12H), 1.79, 1.78, 1.75, 1.70 (overlapping t, 24H); vis  $\lambda_{\text{max}}$  411sh nm ( $\epsilon$  124 000), 426 (168 500), 538 (27 900), 571 (24 900); IR (KBr) 2171vw  $\text{cm}^{-1}$ ; FAB MS 1310. Anal. Calcd for  $\text{C}_{84}\text{H}_{72}\text{N}_8\text{Ni}_2$ : C, 77.0; H, 5.5; N, 8.6. Found: C, 76.8; H, 5.5; N, 8.0.

**5,5'-(1,4-Phenylenediethynediyl)bis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] (30).** This preparation was described in our preliminary communication.<sup>22</sup> IR (KBr) 2189w  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{82}\text{H}_{90}\text{N}_8\text{Ni}_2 \cdot \text{H}_2\text{O}$ : C, 74.4; H, 7.0; N, 8.5. Found: C, 74.2; H, 6.8; N, 8.3.

**5,5'-(1,3-Phenylenediethynediyl)bis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] (31).** The alkyne **3** (48.5 mg, 0.079 mmol) was reacted with 1,3-diiodobenzene (13 mg, 0.039 mmol) in  $\text{NEt}_3$  (8 mL) using  $\text{PdCl}_2(\text{PPh}_3)_2$  (1 mg). The reaction mixture was refluxed for 6 h under Ar. Column chromatography using 25%  $\text{CHCl}_3/\text{hexane}$  yielded the *m*-iodophenylethynyl monomer, butadiyne **1**, and the required **31**. Fractions containing **31** were combined and recrystallized from  $\text{CHCl}_3/\text{MeOH}$  (15 mg, 30%): NMR  $\delta_{\text{H}}$  9.44 (s, 4H), 9.41 (s, 2H), 8.10 (s, 1H), 7.76 (d, 2H), 7.58 (t, 1H), 4.27 (q, 8H), *ca.* 3.8 (overlapping q, 24H), 1.88 (t, 12H), *ca.* 1.75 (overlapping q, 36H); vis  $\lambda_{\text{max}}$  435 nm ( $\epsilon$  229 300), 558 (20 900), 593 (22 500); FAB MS 1302. Anal. Calcd for  $\text{C}_{82}\text{H}_{90}\text{N}_8\text{Ni}_2$ : C, 75.0; H, 7.1; N, 8.75. Found: C, 75.0; H, 7.1; N, 8.7.

**[2,3,7,8,12,13,17,18-Octaethyl-5-[(2-iodophenyl)ethynyl]porphyrinato]nickel(II) and 5,5'-(1,2-Phenylenediethynediyl)bis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] (32).** A mixture of alkyne **3** (31 mg, 0.05 mmol), *o*-diiodobenzene (8.3 mg, 0.025 mmol),  $\text{PdCl}_2$  (6 mg), and  $\text{PPh}_3$  (12 mg) in  $\text{NEt}_3$  (5 mL) was stirred and refluxed for 2 h. More alkyne (15 mg),  $\text{PdCl}_2$  (2 mg), and  $\text{PPh}_3$  (4 mg) were added, and stirring was continued overnight at room temperature. Workup gave a crude residue, which was separated by column chromatography, eluting with 25%  $\text{CHCl}_3/\text{hexane}$ , into four fractions. The first gave fine dark red needles of the monomer, after recrystallization from  $\text{CHCl}_3/\text{MeOH}$  (7 mg, 34%): NMR  $\delta_{\text{H}}$  9.44 (s, 2H), 9.41 (s, 1H), 7.94 (dd,  $J = 7.8$ , 1.1 Hz, 1H), 7.69 (dd,  $J = 7.8$ , 1.5 Hz, 1H), 7.44 (dt,  $J = 7.8$ , 1.1 Hz, 1H), 7.07 (dt,  $J = 7.8$ , 1.5 Hz, 1H), 4.20 (q, 4H), *ca.* 3.8 (overlapping q, 12H), *ca.* 1.8 (overlapping t, 24H); vis  $\lambda_{\text{max}}$  423 nm ( $\epsilon$  151 900), 555 (10 100), 594 (11 200); IR (KBr) 2200w

cm<sup>-1</sup>; FAB MS 816. Anal. Calcd for C<sub>44</sub>H<sub>47</sub>IN<sub>4</sub>Ni: C, 64.7; H, 5.8; N, 6.9. Found: C, 64.7; H, 5.9; N, 6.8. The second fraction consisted mainly of the butadiyne **1**. The third fraction was subjected to a second column in 25% CHCl<sub>3</sub>/hexane, but the original major component was observed to diminish in intensity, with apparent formation of butadiyne **1** and more polar, golden-brown products. The required dimer **36** was isolated as dark red microcrystals after recrystallization from CHCl<sub>3</sub>/MeOH (2.2 mg): NMR δ<sub>H</sub> 9.38 (s, 2H), 9.15 (s, 4H), 7.86 (dd, *J* = 6.2, 3.7 Hz, 2H), 7.50 (dd, *J* = 6.2, 3.7 Hz, 2H), *ca.* 3.8 (overlapping q, 16H), 3.74 (q, 8H), 3.02 (q, 8H), 1.77 (t, 12H), 1.70 (t, 12H), 1.53 (t, 12H), 1.02 (t, 12H); FAB MS 1304.5. The polar fractions from both columns (eluted with increasing proportions of CHCl<sub>3</sub>) were combined and shown by NMR to consist of numerous presently unidentified products.

**5,5'-(Thiophene-2,5-diyl-diethynediyl)bis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] (33)**. This preparation was described in our communication.<sup>23</sup> NMR δ<sub>H</sub> 9.43 (s, 4H), 9.39 (s, 2H), 7.45 (s, 2H), 4.22 (q, 8H), *ca.* 3.8 (overlapping q, 24H), 1.92 (t, 12H), *ca.* 1.75 (overlapping t, 36H); vis λ<sub>max</sub> 425 nm (ε 120 500), 460sh (114 200), 482 (129 000), 563sh (26 400), 607 (47 800); FAB MS 1310. Anal. Calcd for C<sub>80</sub>H<sub>88</sub>N<sub>8</sub>Ni<sub>2</sub>S: C, 73.4; H, 6.8; N, 8.6. Found: C, 72.7; H, 6.9; N, 8.2.

**5,5'-Hex-3-ene-1,5-diyne-1,6-diylbis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] [34 (*cis*) and 35 (*trans*)]**. The alkyne **3** (50 mg, 0.081 mmol) was reacted with 1,2-dibromoethylene (*cis/trans* mixture, 3.4 μL, 0.041 mmol) in NEt<sub>3</sub> (10 mL) using PdCl<sub>2</sub> (10 mg) and PPh<sub>3</sub> (20 mg). The mixture was refluxed for 4 h under argon. The residue from the usual workup was subjected to two flash columns and radial chromatography which yielded monocoupled products, **1**, and a mixture of **34** and **35**. A sample of this mixture was refluxed in benzene for 8 h. The residue after evaporation was shown by NMR to be exclusively the *trans* isomer **35**. Recrystallization from CHCl<sub>3</sub>/MeOH gave dark green microcrystals of **35**: NMR δ<sub>H</sub> 9.42 (s, 4H), 9.38 (s, 2H), 6.83 (s, 2H), 4.19 (q, 8H), *ca.* 3.8 (overlapping q, 24H), 1.84 (t, 12H), *ca.* 1.75 (overlapping t, 36H); vis λ<sub>max</sub> 425 nm (ε 120 500), 460sh (114 000), 482 (129 000), 563sh (26 400), 607 (47 800); FAB MS 1254 (recorded on mixture of *cis* and *trans*).

**5,5'-Hexatriynediylbis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] (36)**. (i) The alkyne **3** (60 mg, 0.098 mmol) was reacted with tetraiodoethylene (26 mg, 0.049 mmol)

in NEt<sub>3</sub> (6 mL) using PdCl<sub>2</sub> (12 mg) and PPh<sub>3</sub> (24 mg). The mixture was refluxed for 2 h under argon. After column chromatography, the dimeric fractions were shown by NMR to be mixtures of hexatriyne **36** and butadiyne **1**. These compounds could not be cleanly separated by chromatography. The presence of **36** was confirmed by FAB MS (*m/z* 1250). (ii) Butadiyne **13** (4.5 mg, 0.007 mmol), alkyne **3** (4.1 mg, 0.007 mmol), and CuCl (0.17 g, 1.7 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) under dry air. TMEDA (0.26 mL, 0.01 mol) was added, and the mixture was stirred for 30 min. Workup as for **12** (ii) above gave a crude product which was subjected to column chromatography, eluting unreacted monomers with 15% CHCl<sub>3</sub>/hexane, then a mixture of dimers **1**, **36**, and **38** with 25% CHCl<sub>3</sub>/hexane. Further chromatography separated **38**, but **1** and **36** could not be separated completely. A fraction containing a *ca.* 50/50 mixture of **1** and **36** was collected and used for our spectroelectrochemical experiments.<sup>26</sup>

**5,5'-Octatetraynediylbis[[2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)] (38)**. (i) The butadiyne **13** (14 mg, 0.022 mmol) was dissolved in pyridine (5 mL) and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (4 mg) was added. Treatment as for **25** above gave **38** as green microcrystals (22 mg, 80%) after recrystallization from CHCl<sub>3</sub>/MeOH. (ii) The silyl-protected butadiyne **12** (12 mg, 0.017 mmol) was treated with Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (5 mg) in pyridine (7 mL) at 60 °C for 1 h. Workup as in (i) gave 10 mg (95%) of **38** after recrystallization: NMR δ<sub>H</sub> 9.40 (s, 4H), 9.38 (s, 2H), 4.09 (q, 8H), *ca.* 3.8 (overlapping q), *ca.* 1.75 (overlapping t, 48H); vis λ<sub>max</sub> 387sh nm (ε 50 000), 417sh (87 100), 450 (116 500), 468 (130 800), 490 (141 600), 621 (66 100); FAB MS 1274. Anal. Calcd for C<sub>80</sub>H<sub>86</sub>N<sub>8</sub>Ni<sub>2</sub>: C, 75.3; H, 6.8; N, 8.8. Found: C, 75.15; H, 7.0; N, 8.3.

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