Stepwise Syntheses of Bisporphyrins, Bischlorins, and Biscorroles, and of Porphyrin−Chlorin and Porphyrin−Corrole Heterodimers

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Abstract: The stepwise syntheses and characterization of a series of symmetrical and unsymmetrical bisporphyrins, bischlorins, and biscorroles, and of porphyrin−chlorin and porphyrin−corrole dyads possessing ethylene, phenyl, and stilbene linking units are described. The methodology for synthesis of 10-substituted corroles **2** and their cobalt complexes **9** via *a,c*-biladiene salts **1** was first developed, and then extended to provide biscorroles (e.g., **4** and **5**) linked through the 10-positions with phenyl linker units. Using a similar methodology, phenyl-linked corrole−porphyrin dyads **28** and **30** were also prepared. By way of intermediate phenyl-linked unsymmetrical bisdipyrromethanes, a completely unsymmetrical heterobimetallic bisporphyrin system, **45**, was synthesized. Low-valent titanium coupling (McMurry) reactions were used to prepared stilbene-linked bisdipyrromethanes (e.g., **46**) which were subsequently transformed into stilbene-linked bisporphyrins (e.g., **48**). McMurry cross-coupling reactions of porphyrins bearing *p*-formylphenyl substituents also afforded an unsymmetrically substituted bisporphyrinylstilbene, **60**, as well as the corresponding homodimers **56** and **59**. Likewise, McMurry cross-coupling of a *p*-formylphenyl-substituted porphyrin, **62**, with a formylchlorin, **63**, afforded a stilbene-linked bisporphyrin, **64**, a bischlorin, **66**, and a novel porphyrin−chlorin heterodimer, **65**. All novel products were characterized by ^{1}H NMR, UV−vis, and mass spectroscopy and elemental analysis. X-ray structural information was also obtained for the zinc/nickel bisporphyrin **45** and for the bis-nickel porphyrin−chlorin **65**.

Introduction

Publications of the X-ray data on the bacterial photosynthetic reaction centers in *Rhodopseudomonas viridis*[1ab] and *Rhodobacter spheroides*,[1b,c] and on the integral membrane light-harvesting complex from *Rhodopseudomonas acidophila*,[1d] have spurred interest in the synthesis of monomeric and dimeric porphyrin systems which can act as mimics of the reaction centers and antenna systems in photosynthetic bacteria and plants.[2,3] It has been shown[4,5] that close proximity, along with geometry, orientation, and redox properties, is an intrinsic quality for efficient energy transfer. In addition, the potential catalytic properties[6−8] of face-to-face bisporphyrin systems, such as the "PacMan" porphyrins,[2a] have further increased the interest of synthetic groups. Additionally, in the natural photosynthetic reaction centers different reduced tetrapyrroles are present, in order to minimize the back-reaction following initial charge separation. Opportunities to mimic this feature have stimulated interest in heterodimers, where two different macrocycles are covalently linked.[9,10]

Many different tetrapyrrolic macrocycles (other than porphyrin) have been reported in the literature, each with its own unique chemistry and spectroscopic signature; in recent times our

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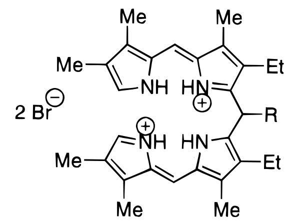
interest has focused on corrole. This tetrapyrrole has experienced a revival of interest, after decades of minimal attention since its first synthesis by Johnson and Kay in 1965.[11] Corroles exhibit both unexpected steric flexibility of the planar conformation of the macrocycle and the ability to stabilize higher oxidation states of certain coordinated metals[12] compared with porphyrins. This is presumably due, in part, to the smaller size of the corrole core compared with porphyrins.

Among bisporphyrin systems, there appear to be relatively few general and efficient synthetic approaches for the preparation of unsymmetrical porphyrin dimers. Unsymmetrical porphyrin dimers create redox gradients, with one porphyrin subunit being more easily oxidized or reduced than the other. Perhaps most impressive is the work of Sessler et al.[13] who reported the synthesis and characteristics of a variety of selectively monometalated monoquinone-substituted zinc containing octaalkylporphyrin dimers designed to mimic certain key electronic and structural aspects of the photosynthetic reaction centers. Maruyama et al.[14] reported an approach to unsymmetrical porphyrin dimers via condensation of an *a,c*-biladiene dihydrobromide with isophthaldehyde (to give a porphyrin bearing a formyl group), followed by its reaction with 2 equiv of a 2-unsubstituted pyrrole; finally condensation with a dipyrromethane gave a low yield of an unsymmetrical bisporphyrin. Sauvage and co-workers[15] have prepared a molecular triad consisting of a zinc(II)−gold(II)−bisporphyrin connected by a ruthenium(II) bis(2,2′:6′,2′′-terpyridyl) spacer.

Covalently-linked bisporphyrins have yielded much information as models for electron transfer in reaction centers as functions of geometry and energetics. Because both chromophores in these systems are porphyrins, selective excitation or metalation is often problematic. In natural systems (photosynthetic reaction centers) interactions with the surrounding protein matrix modulate the physical properties of each macrocycle in the array. These differences allow vectorial transport along an energy gradient down which an electron can travel. In model systems the difference in physical (optical and redox) properties between chromophores can be created by linking two different chromophores. This was elegantly shown by Wasielewski et al.[9] who reported a series of porphyrin−chlorin molecules. Gust et al. have described an ingenious carotenoid−zinc porphyrin−pyropheophorbide triad,[10a] and Osuka et al.[10b] have prepared a porphyrin−oxochlorin−pyromellitimide triad which showed a long-lived charge-separated state. In this way either macrocycle can be selectively excited. In the present paper we present synthetic methodology for synthesis of biscorrole, porphyrin−corrole, bisporphyrin, bischlorin, and porphyrin−chlorin heterodimers. Novel systems possessing the corrole nucleus present a particular challenge since the synthetic chemistry of corrole is far from developed[16] (compared with the corresponding porphyrin and chlorin systems).[17] To our knowledge no examples of dimeric systems involving corrole have been reported so far in the literature, and moreover, only *meso*-phenyl-substituted complexes have been prepared as peripherally functionalized systems.[18]

Results and Discussion

Corrole-Containing Systems. Meso-Functionalized Corroles. The base-catalyzed cyclization of 1,19-diunsubstituted *a,c*-biladiene dihydrobromide **1a** is the method of choice[19] for synthesis of corroles **2**, and we used this methodology for the preparation of our corrole-containing synthetic targets. We chose first to investigate meso-position functionalization of *a,c*-biladienes (and eventually corroles). Subsequently, we expanded our approach to phenyl-linked biscorroles **3**, and **4** and to a phenyl-linked corrole−porphyrin heterodimer system, **5**.



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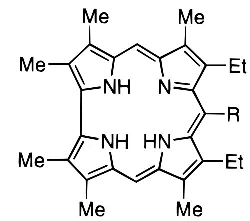

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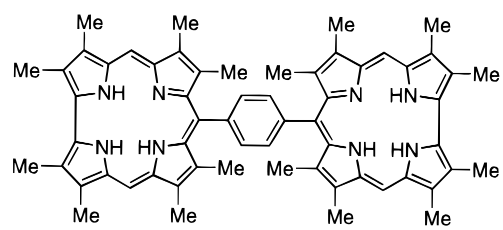
a R = H
b R = CO_2Me
c R = CH_2CO_2Me
d R = CH_2CH_2Cl



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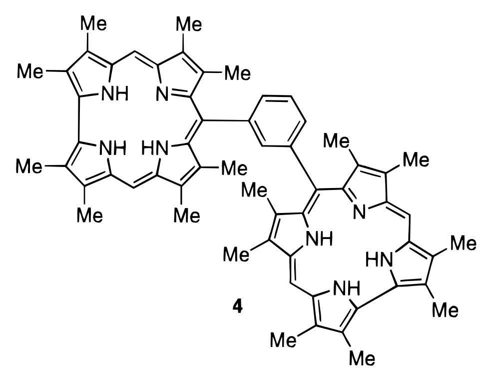

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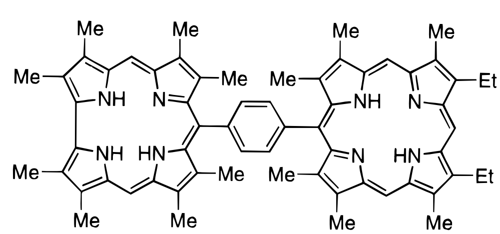

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Monomeric *a,c*-biladienes have been synthesized by decarboxylation of the corresponding dipyrromethane **6** in trifluoroacetic acid followed by reaction with 2-formylpyrrole **7** in

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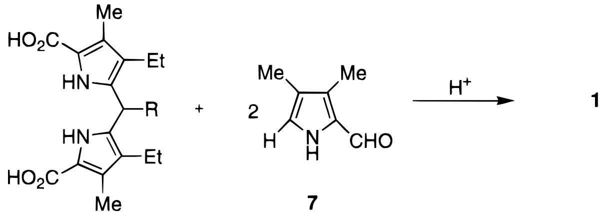
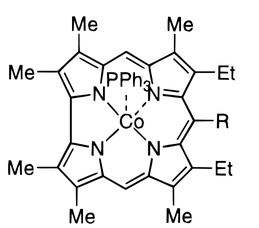
methanol. Hydrobromic acid was added to provide good yields (70−85%) of the corresponding crystalline *a*,*c*-biladiene dihydrobromides **1**. In the case of the reaction of **7** with the



6 **7**

a R = H
b R = CO_2Me
c R = CH_2CO_2Me
d R = CH_2CH_2Cl

5-(methoxycarbonyl)dipyrromethane **6b**, the formation of the *a*,*c*-biladiene **1b** was very slow and the yield was lower than for the other *a*,*c*-biladienes. Spectrophotometry showed almost immediate formation of a tripyrrene species, **8**, followed by a slow addition reaction of the second formylpyrrole presumably to give **1b**. This unusual observation is possibly due to the electron-withdrawing nature of the meso-substituent. Cyclizations of the *a*,*c*-biladiene hydrobromides **1** to give corroles **2** were carried out in methanol (containing sodium acetate to catalyze the ring closure);[20] the presence of the meso-substituents did not affect the yields in the reactions, which were comparable, if not higher than, with those reported in the literature.[21−23] The product corroles **2** were usually transformed into the corresponding (triphenylphosphine)cobalt complexes **9** in order to

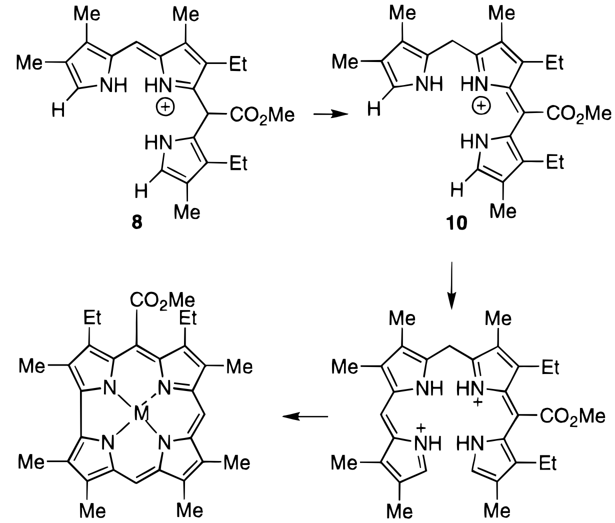


9

a R = H
b R = CO_2Me
c R = CH_2CO_2Me
d R = CH_2CH_2Cl
e R = $CH{=}CH_2$

avoid the ^{1}H NMR line-broadening which normally affects corrole free bases.[24] In the case of the *meso*-(methoxycarbonyl)-corrole, the ^{1}H NMR spectrum of the product unexpectedly showed the presence of three different resonances in the meso-proton region. One resonance (9.02 ppm) is assigned to the expected product **9b**, while the other two (9.44 and 8.82 ppm) are attributed to the cobalt(III) complex **12** of the isomeric 5-(methoxycarbonyl)corrole **13**. Production of the unexpected mixture of meso-substituted corroles **2b** + **13** presumably results from the fact that the very slow formation of the biladiene **1b** permitted the intermediate tripyrrene **8** to undergo tautomeric equilibrium with **10** (Scheme 1); addition of the second formylpyrrole **7** would then afford the *a*,*c*-biladiene **11**, isomeric with **1b**, which upon base-catalyzed cyclization and cobalt insertion would yield the 5-substituted corrole complex **12**.

Scheme 1



12 M = Co(PPh_3)
13 M = 3H

No tripyrrene intermediates were observed in the other *a*,*c*-biladiene syntheses, and cyclizations afforded pure corroles. In the case of the 10-[(methoxycarbonyl)methyl]corrole **9c**, the rigidity of the meso-substituent does not allow free rotation about the C(10)−C(10^1) bond because of the steric interaction with the 8- and 12-ethyl substituents; thus, in the ^{1}H NMR spectrum, the resonance of the 10^1-CH_2 group is broadened. A similar phenomenon has been noted in the corresponding porphyrin.[25] In addition we observed a splitting of the ^{1}H NMR signal attributed to the *o*-phenyl protons of the PPh_3 ligand, as also observed in (triphenylphosphine)[5,10,15-tris(*o*-chlorophenyl)-2, 3,7,8,12,13,17,18-octamethylcorrolato]cobalt(III) where a similar restricted rotation of the *meso*-phenyl groups induces the same effect.[26] This hypothesis was confirmed by variable temperature NMR measurements (not shown), in which we observed thermal interconversion at 323 K, with a coalescence of these signals. The 10-(2-chloroethyl)corrole complex **9d** was subjected to dehydrohalogenation in pyridine/NaOH (aqueous) to afford the 10-vinylcorrole complex **9e** in good yield.

Biscorroles. Phenyl-linked *a*,*c*-biladiene salts **14** and **15** were synthesized in good yields from the 1,4-bis[bis(3,4-dimethylpyrryl)methyl]benzenes **16** and **17** and 2-formyl-3,4-dimethylpyrrole (**7**). Metal-free biscorroles **3** and **4** were obtained by cyclization of **14** and **15**, respectively, in methanolic solution, using chloranil as oxidant.

Optical spectra of these biscorrole compounds were similar to those of an octaalkylcorrole, with no significant modifications either in the Soret or Q band regions. FAB mass spectra showed the molecular peak and M^{2+} peaks. Due to the low solubility and the significant line-broadening that usually affect metal-free corroles, we were unable to obtain well-resolved ^{1}H NMR spectra of these metal-free dimers. In order to overcome these problems, we synthesized the biscorrole **18**, via the bis-*a*,*c*-biladiene **19** using the bisdipyrromethane **16** and 3,4-diethyl-2-formylpyrrole (**20**); in this case the ^{1}H NMR spectra strongly depended on the solvent used. In $CDCl_3$, in fact, we obtained more resonances than expected for the biscorrole. The visible spectrum of the solution showed the appearance of a new absorbance, red shifted to the Soret band of the starting dimer, that seems to indicate the formation of a monocation of the

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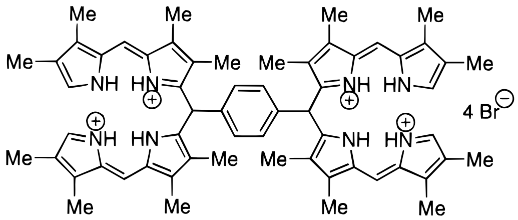

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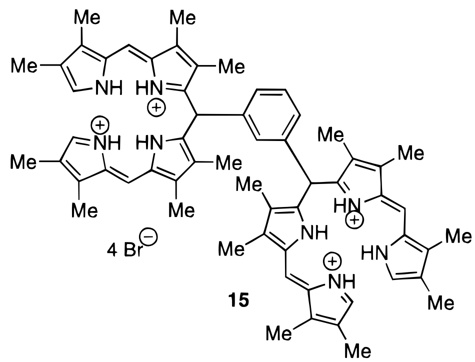

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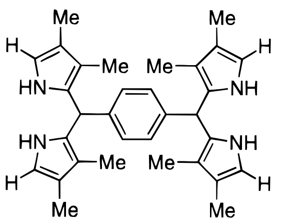

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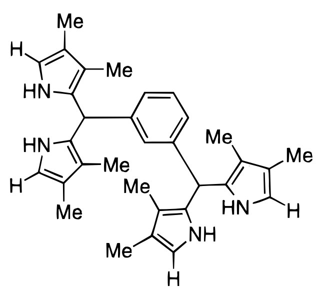

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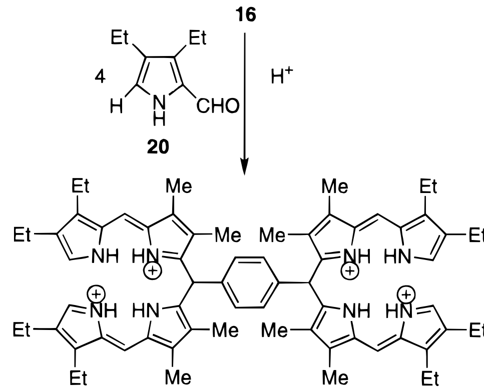

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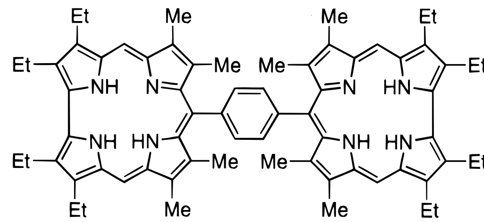

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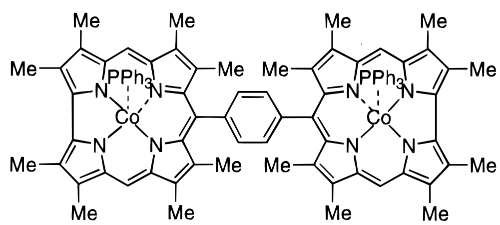

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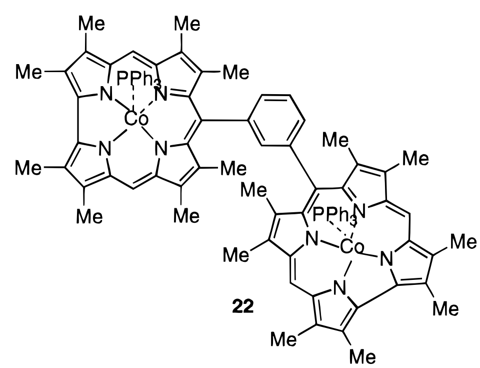

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corrole ring, probably due to the traces of acid that normally are present in this solvent. This hypothesis was confirmed by measuring the spectrum in pyridine, whereupon these additional resonances disappeared.

To avoid problems affecting the ^{1}H NMR characterization of free-base corrole dimers, we also synthesized the corresponding (triphenylphosphine)cobalt(III) complexes **21** and **22**. The synthesis of these complexes was performed by cyclization of the corresponding *a,c*-biladiene using the same methodology as in the case of a monomeric corrole, but there was a significant decrease in the yield of the reaction in the case of the cobalt(III) *m*-phenylbiscorrole, presumably due to instability of the complex during the purification procedure. As in the case with metal-free dimers, electronic spectra were similar to those of monomeric Co(III) corrole complexes, with no significant shifts of the absorbances. FAB mass spectra revealed the M^{+} peak along with a more abundant peak at $M^{+} - PPh_3$, indicating the lability of the axial ligand. For both complexes, ^{1}H NMR spectra showed a single resonance for the meso protons. In the case of the *p*-phenylbiscorrole **21**, the proton resonances for the bridging phenyl group were complex, presumably due to the triphenylphosphine ligands removing the magnetic degeneracy of these hydrogen atoms which was observed for the metal-free dimer. The presence of multiple resonances can be ascribed to the existence of isomers generated by restricted rotation around the bridging phenyl group; the two triphenylphosphine ligands render the two faces of the complex inequivalent. VT experiments revealed coalescence of the resonances at 350 K, and the activation energy barrier for the rotation was calculated to be 68.8 kJ/mol.

Porphyrin-Corroles. A corrole−porphyrin system, **5**, was synthesized by treatment of terephthaldehyde with ethyl 3,4-dimethylpyrrole-2-carboxylate (**23**),[27] to give the 5-aryldipyrromethane **24**. The dipyrromethane−porphyrin **25** was first obtained by acid-catalyzed condensation of the 1,19-unsubstituted *a,c*-biladiene salt **1a** with **24**. Subsequent hydrolysis and decarboxylation[13] afforded the corresponding dipyrromethane−porphyrin **26a**, which was condensed with 2 equiv of 2-formyl-3,4-dimethylpyrrole (**7**) to give the *a,c*-biladiene−porphyrin unit **27**. All attempts to isolate **27** in pure form failed, so in situ cyclization with chloranil was performed, to afford the pseudodimer **5** in acceptable yield.

The electronic absorption spectrum of **5** showed superimposed characteristic absorbances of porphyrin and corrole macrocycles in the Q band region; the Soret band of the porphyrin overwhelmed the corresponding absorbance of corrole due to the larger extinction coefficient of the former. FAB mass

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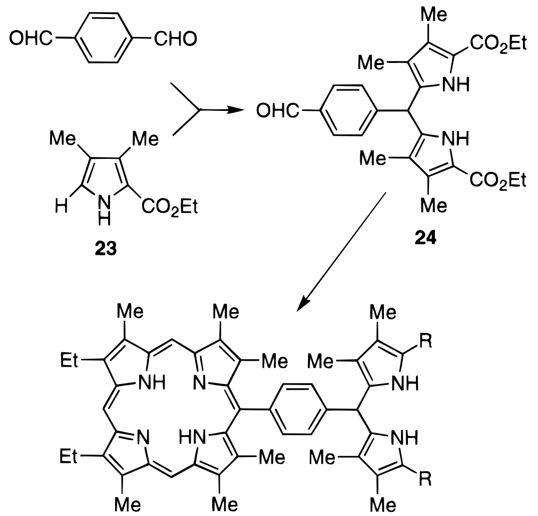
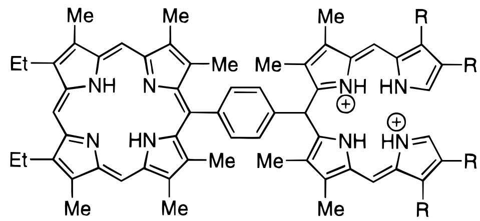
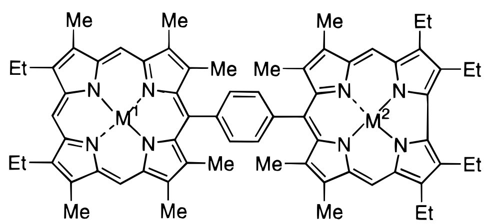


25 R = CO_2Et; M = 2H
26a R = H; M = 2H
26b R = H; M = Ni



27 R = Me
29 R = Et

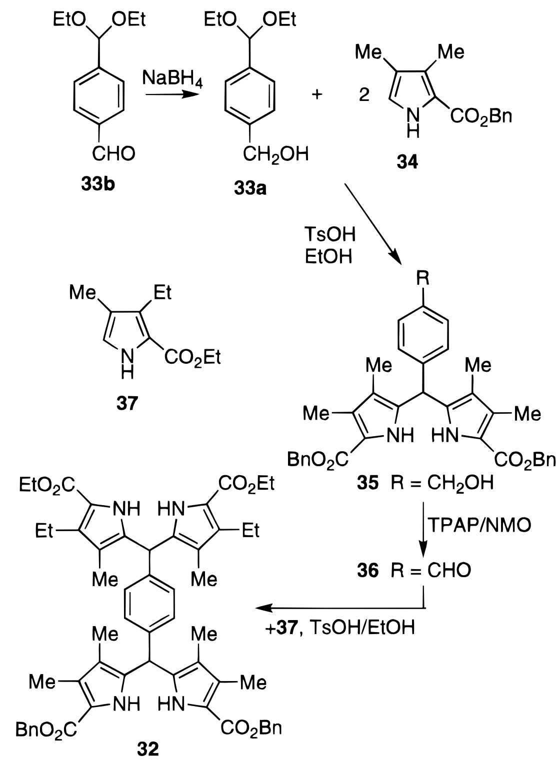


28 M^1 = 2H; M^2 = 3H
30 M^1 = Ni; M^2 = Co(PPh_3)

spectra showed the molecular peak, as well as the corresponding porphyrin and corrole fragments. Yet again, the low solubility and the broadening of the resonances attributable to the corrole moiety in **5** did not permit us to obtain a suitable ^{1}H NMR spectrum of this bis system. Also in this case, the synthesis of the tetraethyltetramethylcorrole−porphyrin dimer **28** (from **26** and 2 equiv of **20** to give **28**, followed by corrole ring cyclization) allowed us to obtain a well-resolved ^{1}H NMR spectrum, where the resonances attributable to both fragments could be distinguished. In **28** the meso-protons were observed as a 2:1:2 pattern, with chemical shifts similar to those of the corresponding monomeric macrocycles, and the bridging phenyl group protons were apparent as a singlet, similar to the case of the corresponding homobiscorroles.

The successful synthesis of the porphyrin−corrole pseudodimer **28** led us to prepare a heterobimetallic complex. The porphyrin−dipyrromethane **26** was metalated with nickel(II) (to give **26b**), and the resulting complex was condensed with 2 equiv of 2-formyl-3,4-diethylpyrrole (**20**); formation of the porphyrin−*a*,*c*-biladiene **29** was monitored by spectrophotometry. When the reaction was complete, addition of cobalt(II) acetate, triphenylphosphine, and sodium acetate to **30** afforded the corresponding Ni(II) porphyrin−Co(III) corrole complex **30** in

Scheme 2



good yield. In the visible absorption spectrum of the complex, the absorbances of the corrole moiety were overwhelmed by the porphyrin bands; the FAB mass spectrum showed the molecular peak, and as before, a more abundant peak at $M^+ - PPh_3$. In addition, the fragmentation pattern of **30** showed low abundance peaks attributable to the [Ni porphyrin]$^+$ and [Co corrole]$^+$ species. In the ^{1}H NMR spectrum of **30**, the resonance of the bridging phenyl group was split due to the presence of the triphenylphosphine ligand, as observed in the case of the biscorrole systems.

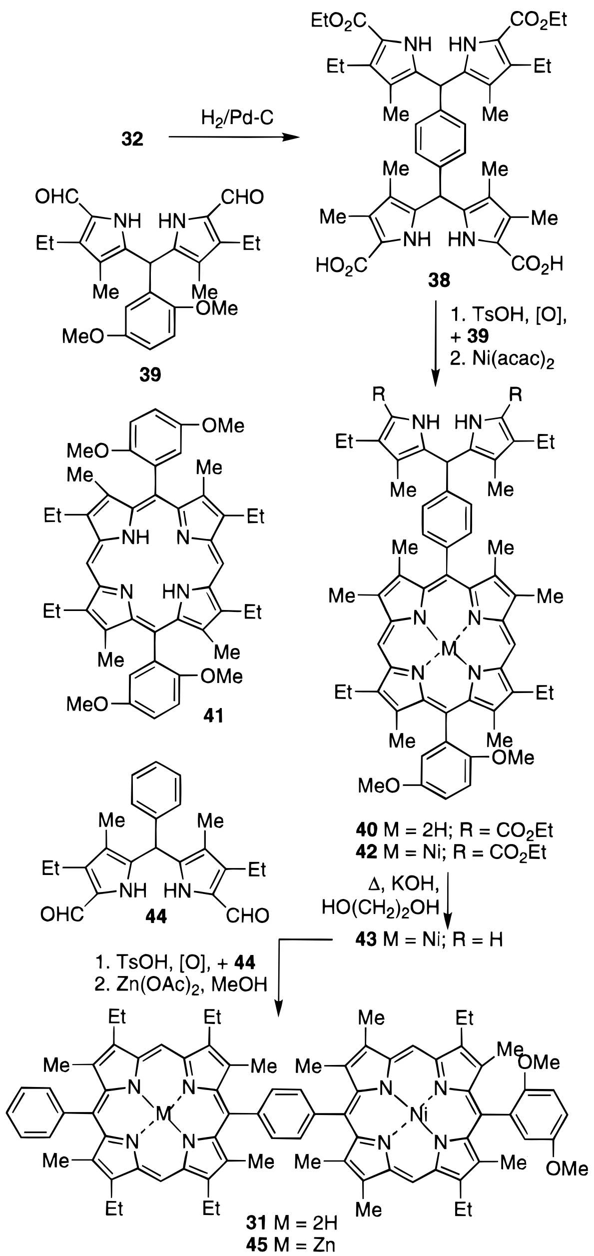
Non-corrole Bis Macrocyclic Systems. Bisporphyrins. We sought to establish a general methodology whereby unsymmetrical bisporphyrins with rigid linkages could be prepared. Two ways to achieve this goal are (a) the initial preparation of one porphyrin and further stepwise elaboration to append the second and (b) a heterocoupling reaction of two intact porphyrins. Several approaches using both (a) and (b) will be described which yield bisporphyrins. We chose to focus on bisporphyrins with stilbene and phenyl linkages as they have well-defined geometries. In general, molecules that possess more well-defined structural relationships between the donor and the acceptor yield more subtle insights into electron-transfer reactions.[28] Symmetrical bisporphyrins bearing a *p*- or *m*-phenyl interporphyrin tether have previously been reported, first by McClendon and co-workers[29] and later by Sessler and co-workers,[2c,13] using terephthaldehyde or isophthaldehyde as interporphyrin linking units.

We first attempted the synthesis of the completely unsymmetrical monometalated bisporphyrin dimer **31** (Schemes 2 and 3). The unsymmetrical bisdipyrromethane dimer intermediate **32**, containing both benzyl and ethyl ester protecting groups, was prepared as the key intermediate (Scheme 2). Thus, the linking unit **33a** was first obtained by reduction of commercially available terephthaldehyde mono(diethyl acetal) (**33b**) using

(28) (a) Wasielewski, M. R. *Chem. Rev.* **1992**, 435. (b) Kurreck, H.; Huber, M. *Angew. Chem., Intl. Ed. Engl.* **1995**, *34*, 849.

(29) Heiler, D.; McClendon, G. L.; Rogalskyj, P. *J. Am. Chem. Soc.* **1987**, *109*, 604.

Scheme 3



LAH[30a] or $NaBH_4$. This was condensed with benzyl 3,4-dimethylpyrrole-2-carboxylate (**34**)[31] to give **35**. Reaction with tetrapropylammonium perruthenate (TPAP) in CH_2Cl_2/NMO[32,33] afforded the 5-(formylphenyl)dipyrromethane **36** which was then condensed with 2 equiv of pyrrole **37** to give the target unsymmetrical bisdipyrromethane **32** in 82% yield. Catalytic debenzylation of **32** gave the bis(dipyrromethanedicarboxylic acid) **38** in quantitative yield. Further reaction of **38** with diformyldipyrromethane **39**[34] gave the porphyrinyldipyrromethane **40** in 29% yield, along with porphyrin **41** as a minor contaminant.[35] Treatment of **40** with Ni(acac)$_2$ in refluxing *o*-xylene produced the corresponding metal complex **42**, which was subjected to hydrolysis by refluxing with ethylene glycol/KOH[13] to give **43**, and then condensed with diformyldipyrromethane **44** (MacDonald conditions); the bisporphyrin **31** was treated in situ with zinc(II) acetate to give **45** in 15% yield. Crystals of **31** suitable for X-ray crystallography could not be obtained, but the zinc(II) complex **45** did satisfactorily crystallize from CH_2Cl_2/MeOH. The molecular structure of **45** is shown in Figure 1. The compound crystallized with a MeOH molecule in the axial position of the zinc center [Zn−O1A = 2.187(6) Å] and contains another MeOH molecule of solvation. The zinc center, easily identified by its axial MeOH molecule, shows an average Zn−N bond length of 2.064(5) Å, and the zinc porphyrin macrocycle shows only moderate deviations from planarity with an average deviation of 0.078 Å for the 24 macrocycle atoms from their least-squares plane. The nickel(II) porphyrin macrocycle, on the other hand, shows considerable deviation from planarity with an average deviation of 0.239 Å from the least-squares plane, typical of the situation found in other nickel(II) porphyrins. The average Ni−N bond length is 1.920(5) Å. Overall, the zinc(II) and nickel(II) porphyrin components have structural characteristics similar to those of related (monomeric) porphyrins.[38] The bisporphyrin **45** is not truly linear, but is more bow-shaped with an angle of 24.3° between the two 4N planes.

In order to obtain the symmetrical bisdipyrromethane **46**, formyldipyrromethane **47** was dimerized with low-valent titanium under McMurry conditions.[39] We have previously shown that this methodology can also be applied successfully to the self-condensation of porphyrins bearing formyl substituents.[40] Bisdipyrromethane **46** was then converted into the porphyrin dimer **48** in 18% yield by first refluxing with ethylene glycol/KOH (to give **49**) and then condensing with diformyldipyrromethane **50** following the modified[41a] MacDonald protocol.[41b] The structure of **48** was further confirmed and the trans stereochemistry of the central double bond established by a preliminary single-crystal X-ray structure (not shown) of the bisnickel(II) complex **51**.[42]

Bisporphyrins linked by stilbene groups have been previously reported by Mullen and co-workers.[43] In addition Ono et al.[44] have prepared a series of bisporphyrins where the number of stilbene linkers was varied between one and four. As we have had much success with low-valent titanium coupling reactions (McMurry) to prepare bisporphyrins,[40] we chose to examine the McMurry coupling of 5-(4-formylphenyl)octaalkylporphyrins to form the stilbene-linked systems. Porphyrins **52** and **53**

(30) (a) See citation 13 in ref 30b. (b) Sessler, J. L; Capuano, V. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1134.

(31) Smith, K. M.; Kehres, L. A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2329.

(32) Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1625. See also: *Aldrichim. Acta* **1988**, *21*, 16.

(33) (a) Pandey, R. K.; Smith, K. M.; Dougherty, T. J. *J. Med. Chem.* **1990**, *33*, 2032. (b) Shiau, F.-Y.; Pandey, R. K.; Ramaprasad, S.; Smith, K. M. *J. Org. Chem.* **1990**, *55*, 2190.

(34) Compound **39** was prepared by reaction of pyrrole **37** with 2,5-dimethoxybenzaldehyde, followed by saponification of the ethyl esters and double Vilsmeier formylation.

(35) Interestingly, previous syntheses of 5,15-diphenylporphyrins such as **41** have usually involved reaction of 2 mol of a dipyrromethane with 2 mol of benzaldehyde.[2d,30b,36,37] In this case the approach is reversed, and involves serendipitous condensation of 2 mol of a 1,9-diformyl-5-aryl-dipyrromethane.

(36) Gunter, M. J.; Mander, L. N. *J. Org. Chem.* **1981**, *46*, 4792.

(37) Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898.

(38) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 1.

(39) McMurry, J. E.; Lectka, T.; Rico, J. G. *J. Org. Chem.* **1989**, *54*, 3748. McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513.

(40) Vicente, M. G. H.; Smith, K. M. *J. Org. Chem.* **1991**, *56*, 4407.

(41) (a) Cavaleiro, J. A. S.; Gonsalves, A. M. d'A. R.; Kenner, G. W.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1771. (b) Arsenault, G. P.; Bullock, E.; MacDonald, S. F. *J. Am. Chem. Soc.* **1960**, *82*, 4384.

(42) Senge, M. O.; Gerzevske, K. R.; Smith, K. M. Unpublished results.

(43) (a) Cosmo, R.; Kautz, C.; Meerholz, K.; Heinze, J.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 604. (b) Hammel, C.; Kauzt, C.; Mullen, K. *Chem. Ber.* **1990**, *123*, 1353.

(44) Ono, N.; Tomita, H.; Maruyama, K. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2453.

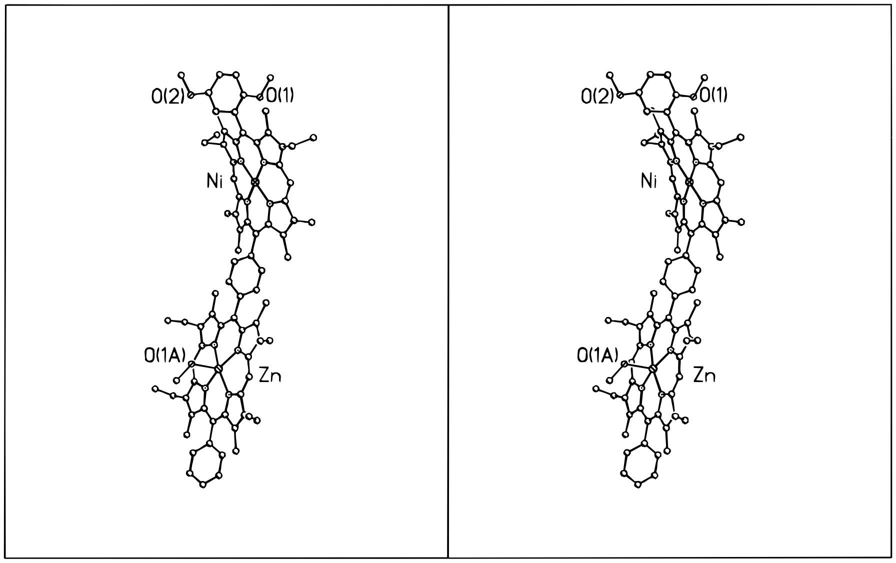
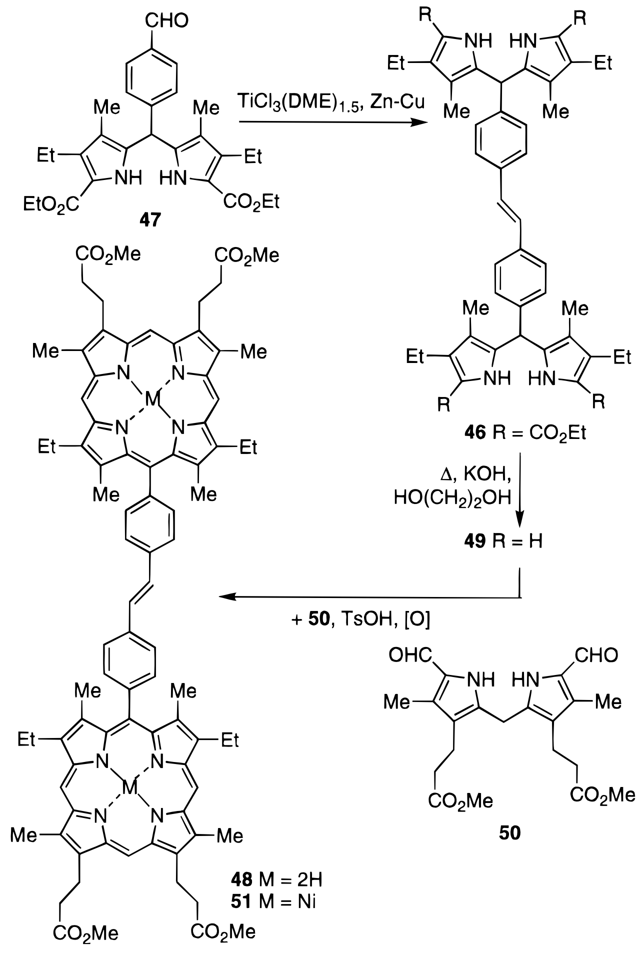


Figure 1. Stereopair showing the molecular structure of **45**. Hydrogen atoms and disordered positions have been omitted for clarity. All dihedral angles between the aryl rings and the mean porphyrin planes are 90°.

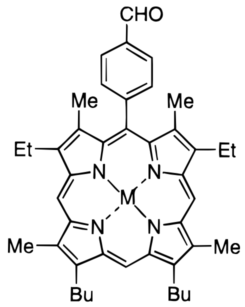


were synthesized according to literature procedures.[45] We chose first to characterize the corresponding McMurry-coupled homodimers, before preparing a heterodimer by cross-coupling (from which the homodimers would need to be separated). Nickel(II) was inserted smoothly into the two porphyrins using nickel(II) acetylacetonate in xylenes to generate nickel(II) porphyrin−benzaldehydes **54** and **55**. When (4-formyl phenyl)-porphyrins were previously coupled under McMurry conditions by Mullen and co-workers,[43] they reported obtaining only the trans isomer. However, when porphyrin **54** was subjected to the McMurry coupling conditions [$(TiCl_3)(DME)_{1.5}$, Zn−Cu couple], two less polar products were obtained in a 6:1 ratio with respect to the inverse order of chromatographic elution. Both products had a molecular ion at *m/z* 1356.6 and had ^{1}H NMR resonances attributable to a bridging CH═CH group (7.69 and 7.13 ppm, respectively). The predominant more polar product (λ_{max} = 404 nm) was assigned structure **56** with the trans orientation, while the fastest running product (λ_{max} = 400 nm, in lesser amount) was assigned the cis configuration **57**. Bathochromic shifts for face-to-face porphyrins have been noted by ourselves[46] and others.[2b] While it was assumed that the McMurry coupling conditions gave predominantly the trans configuration about the double bond, we have previously shown that porphyrin−aldehydes give a 1:1 mixture of *cis*- and *trans*-ethylenebisporphyrins. This arises presumably through a $\pi-\pi$ preassociation of the macrocycles in a transition state or at the pinacol intermediate stage. A $\pi-\pi$ preassociation can also explain the predominance of the *cis*-stilbene product arising from the McMurry coupling of acetophenone.[47] When nickel(II) porphyrin−benzaldehyde **55** was coupled under standard McMurry conditions, the major product was the porphyrin−benzyl alcohol **58** due to reduction of the aldehyde. A very small (ca. 8%) amount of the stilbene dimer **59** could be isolated, and this was assigned the *trans* configuration. A faster running spot on TLC (presumably the *cis*-stilbene dimer) could be seen, but the amount was too small to be characterized. With the two homocoupled standards in hand the heterocoupling could now be attempted. McMurry coupling of porphyrins **54** and **55** yielded, after separation from the homocoupled and other products **56**−**59**, compound **60** with meso-proton NMR resonances at 9.41, 9.52, and 9.60 ppm in a 2:1:2 ratio. The mass spectrum confirmed the structural assignment as **60**. These bisnickel(II) dimers can be easily demetalated by treatment with dilute trifluoroacetic acid in CH_2Cl_2 as shown in the conversion of **59** into **61**. Work with similar compounds by Sessler et al.[13] has shown that bisporphyrins with hydroquinol dimethyl ether groups can be demethylated by treatment with BBr_3 and oxidized to quinone with DDQ or lead(IV) oxide. In addition they have shown, remarkably, that one can selectively insert

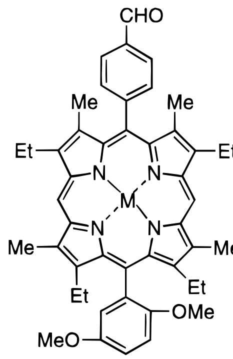
(45) Sessler, J. L.; Capuano, V. L.; Harriman. A. *J. Am. Chem. Soc.* **1993**, *115*, 4618.

(46) Senge, M. O.; Gerzevske, K. R.; Vicente, M. G. H.; Forsyth, T. P.; Smith, K. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 750.

(47) Andersson, P. G. *Tetrahedron Lett.* **1994,** *35*, 2609.

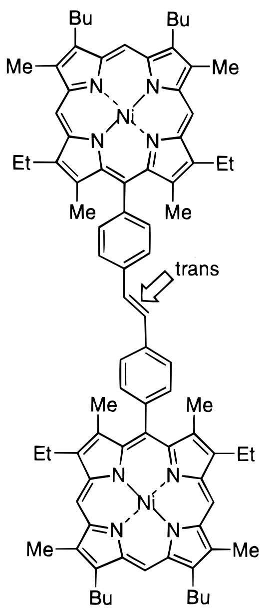


52 M = 2H
54 M = Ni

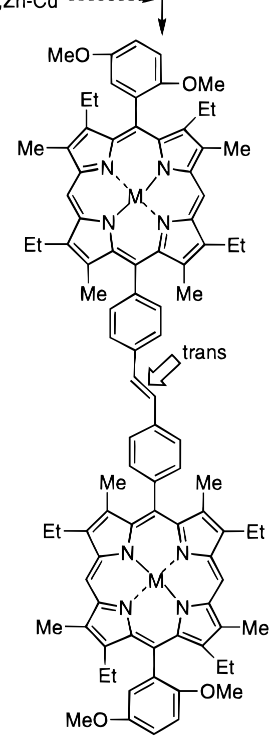


53 M = 2H
55 M = Ni

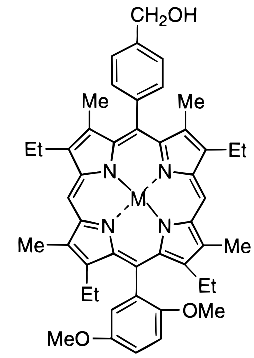
$TiCl_3(DME)_{1.5}$,Zn-Cu



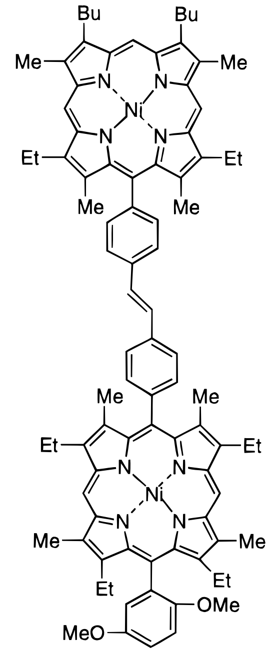
56
57 (cis double bond at arrow)



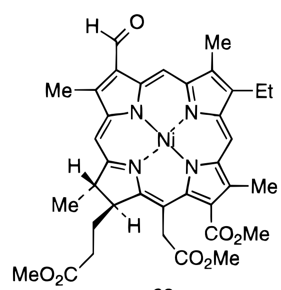
59 M = Ni
61 M = 2H



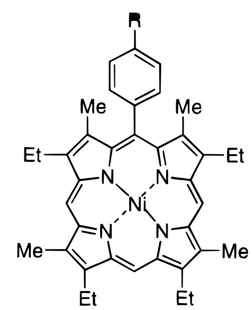
58



60



63



62 R = CHO
67 R = CH_2OH

zinc into the macrocycle proximal or distal to the quinone by titrating the bisporphyrin with dilute solutions of zinc(II) acetate. If titration is attempted at the quinone stage, the zinc insertion occurs preferentially at the macrocycle distal to the quinone subunit; conversely if metalation with zinc is done with the hydroquinone, the zinc is incorporated in the macrocycle proximal to the hydroquinone. Thus, **61** represents a formal intermediate in the synthesis of a rigid H_2-porphyrin−zinc(II) porphyrin−quinone triad, which according to Kurreck and Huber,[28b] represents a realistic model of the reaction center in *R. viridis*.

Chlorin-Containing Bis Systems. The heterocoupling reaction of porphyrins was also expanded to include chlorin macrocycles. Porphyrin **62** was prepared using methodology similar to that employed in the syntheses of **54** and **55**. When a 2:1 mixture of nickel(II) 3-formylchlorin-e_6 trimethyl ester **63** and **62** was subjected to the McMurry coupling as described above, the bisporphyrin **64** (6% yield, based on **63**), the porphyrin−chlorin dimer **65** (41%), and the bischlorin **66** (42%) were obtained. The alcohol−porphyrin byproduct **67** was also isolated (14%), but the reduction of the formyl group was no longer the main reaction as it was in the coupling of **55**. When the porphyrin was used in excess (2.5 equiv relative to **63**), the amount of porphyrin−chlorin dimer isolated was similar (35%) but the formation of the alcohol−porphyrin byproduct became predominant (40%) and no increase in the bisporphyrin yield was observed. The 3-formylchlorin-e_6 trimethyl ester clearly reacts before the reduction of the formyl group in **62** occurs. The visible absorption spectrum of **65** (Figure 2) shows a superposition of the spectra of the porphyrin and the chlorin. Figure 3 shows the molecular structure of this novel bisnickel complex **65**, and represents the first reported crystal structure of a porphyrin−chlorin dimer. Crystals were grown by slow diffusion of *n*-hexane into a $CHCl_3$ solution of **65**. The overall 3-D structure resembles a bowed shape with an angle of 35.7° between the two 4N planes. An absolute stereochemical determination based upon anomalous scattering was successful and further confirmed the absolute stereochemistry of chlorophyll-*a* derivatives. In common with other nickel(II) chlorins, the chlorin-e_6 trimethyl ester macrocycle in **65** adopts a ruffled conformation with a mean deviation from the least-squares plane (calculated for the 24 core carbon and nitrogen atoms) of 0.313 Å. In the saturated ring of the chlorin a C_β−C_β bond length of 1.52(2) Å is observed, in good agreement with data from other chlorin structural determinations. The carbons of the saturated ring in the chlorin macrocycle have a torsion angle of 26.0° which is high but falls within the normal range. The Ni−N

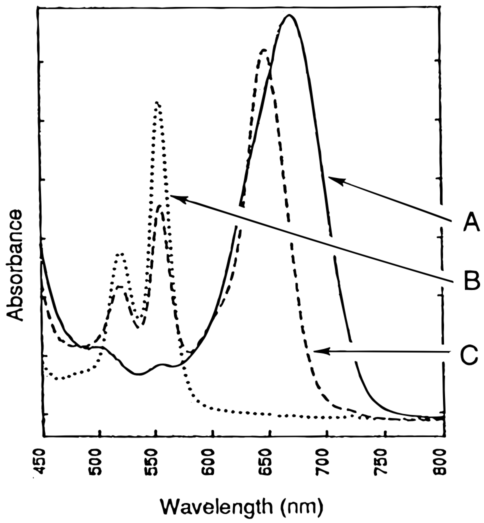


Figure 2. Visible absorption spectra (in CH_2Cl_2) of (A) nickel(II) chlorin−chlorin **66**, (B) nickel(II) porphyrin−porphyrin **64**, and (C) nickel(II) porphyrin−chlorin **65**.

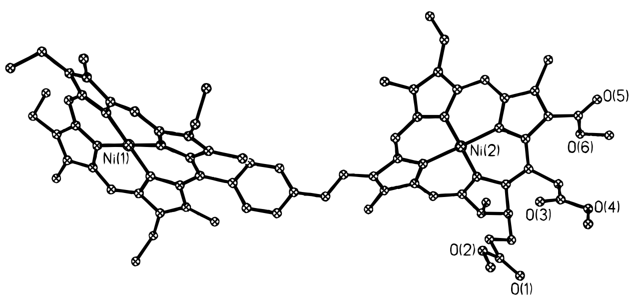
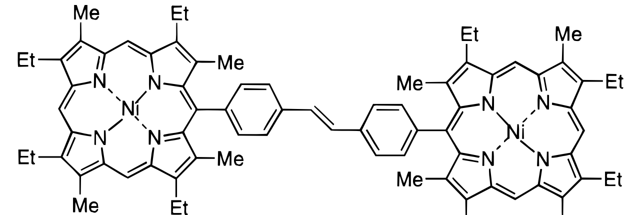
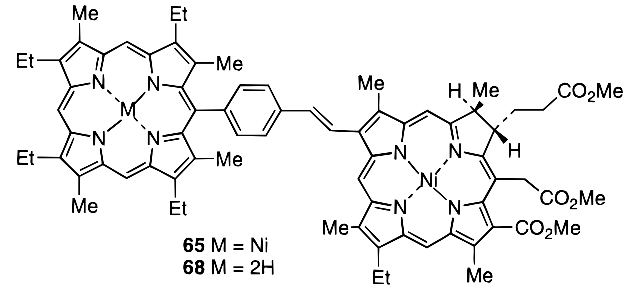


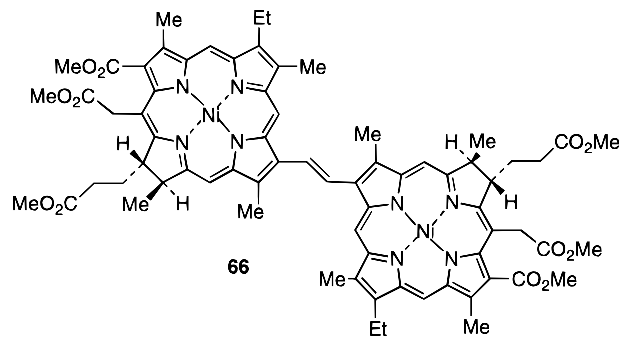
Figure 3. Molecular structure of **65**. Hydrogen atoms and disordered positions have been omitted for clarity.



64



65 M = Ni
68 M = 2H



66

bond lengths for the chlorin macrocycle were 1.953(7) (reduced ring), 1.928(7), 1.920(7), and 1.911(7) Å, showing the Ni−N bond length to the reduced ring to be elongated compared with those bonds to the fully aromatized pyrrole rings. The nickel etioporphyrin macrocycle portion of **65** adopts a ruffled conformation with a mean deviation from the least-squares plane (calculated as above) of 0.244 Å. Finally, the average Ni−N bond length for the porphyrin macrocycle is 1.941(6) Å.

Treatment of **65** with TFA in CH_2Cl_2 (1:1) accomplished selective removal of the nickel from the porphyrin, and produced the monometalated bis system **68**. Since zinc chlorins appear to be more easily demetalated than nickel chlorins,[48] their utilization to prepare heterometalated porphyrin−chlorin dimers allows an extension of the scope of the McMurry reaction as it is applied to tetrapyrrole systems.[49] The ethylenic protons in the porphyrin−chlorin dimers **65** and **68** resonate as a pair of doublets with a coupling constant of 16.5 Hz, suggesting a trans configuration about the double bond. The chlorin−chlorin dimer **66** also adopts a trans configuration.

Experimental Section

Melting points are uncorrected and were measured on a Thomas/Bristoline microscopic hot stage apparatus. Silica gel 60 (70−230 and 230−400 mesh, Merck) or neutral alumina (Merck; usually Brockmann Grade III, i.e., deactivated with 6% water) was used for column chromatography. Preparative scale thin layer chromatography was carried out on 20 cm × 20 cm glass plates coated with Merck G 254 silica gel (2 mm thick). Reactions were monitored by thin layer chromatography and spectrophotometry, and were carried out under nitrogen in the dark (aluminum foil). ^{1}H NMR spectra were measured in $CDCl_3$ solution at 300 MHz using a General Electric QE300 spectrometer, or at 400 MHz using a Bruker AM 400 instrument; chemical shifts are expressed in parts per million relative to residual $CHCl_3$ (7.258 ppm). Mass spectra were obtained in Rome using a VG Quattro spectrometer (FAB) or at the University of California, San Francisco, Mass Spectrometry Resource. Elemental analyses were obtained from Mid West Analytical Laboratory, Indianapolis, IN. Electronic absorption spectra were measured in CH_2Cl_2 using a Hewlett-Packard 8450A or a Philips PU8700 spectrophotometer.

8,12-Diethyl-2,3,7,13,17,18-hexamethyl-10-(2-chloroethyl)-*a,c*-biladiene Dihydrobromide (1d). 3,7-Diethyl-2,8-dimethyl-5-(2-chloroethyl)-dipyrromethane-1,9-dicarboxylic acid (**6d**) (200 mg) was dissolved in trifluoroacetic acid (20 mL) and stirred for 5 min. 2-Formyl-3,4-dimethylpyrrole (**7**) (130 mg) in MeOH (20 mL) was added, and the red solution was stirred for 15 min, before addition of 30% HBr in acetic acid (5 mL). After dropwise addition of diethyl ether (50 mL) the title *a,c*-biladiene salt precipitated as a dark red powder (296 mg, 85% yield). Mp: 300 °C. UV−vis: λ_{max} 445 nm (ϵ 132 000), 521 (75 000). ^{1}H NMR: δ 13.58 (s, 2 H), 12.60 (s, 2 H), 7.68 (s, 2 H), 7.32 (s, 2 H), 5.60 (br t, 1 H), 3.80, 3.38 (each br t, 2 H), 2.68 (m, 4 H), 2.30 (s, 12 H), 2.05 (s, 6 H), 1.60 (t, 6 H). Anal. Calcd for $C_{31}H_{41}Br_2ClN_4$: C, 55.99; H, 6.21; N, 8.43. Found: C, 56.12; H, 6.11; N, 8.31.

8,12-Diethyl-2,3,7,13,17,18-hexamethyl-10-[(methoxycarbonyl)-methyl]-*a,c*-biladiene Dihydrobromide (1c). This compound was similarly prepared in 82% yield from 3,7-diethyl-2,8-dimethyl-5-[(methoxycarbonyl)methyl]dipyrromethane-1,9-dicarboxylic acid (**6c**) and **7**. Mp: >300 °C. UV−vis: λ_{max} 444 nm (ϵ 121 000), 520 (70 400). ^{1}H NMR: δ 13.47 (s, 2 H), 12.85 (s, 2 H), 7.52 (s, 2 H), 7.38 (s, 2 H), 5.46 (br t, 1 H), 5.12 (s, 2 H), 3.66 (s, 3 H), 2.82 (m, 4 H), 2.36 (s, 12 H), 2.00 (s, 6 H), 1.32 (t, 6 H). Anal. Calcd for $C_{32}H_{42}$-

(48) See also ref 9.

(49) However, the coupling has to be carried out[50] in the presence of pyridine to neutralize some chemisorbed HCl formed during the reduction of $TiCl_3$.

(50) Jaquinod, L.; Pandey, R. K.; Forsyth, T. P.; Nurco, D. J.; Smith, K. M. Unpublished results.

$Br_2N_4O_2$: C, 56.98; H, 6.28; N, 8.31. Found: C, 57.03; H, 6.16; N, 8.47.

8,12-Diethyl-2,3,7,13,17,18-hexamethyl-10-(methoxycarbonyl)-*a,c*-biladiene Dihydrobromide (1b) and 8,12-Diethyl-2,3,7,13,17,-18-hexamethyl-5-(methoxycarbonyl)-*a,c*-biladiene Dihydrobromide (11). This presumed mixture of compounds (see text) was prepared as above, from 3,7-diethyl-2,8-dimethyl-5-(methoxycarbonyl)dipyrromethane-1,9-dicarboxylic acid (**6b**), but the reaction needed 24 h to be complete. Subsequently, diethyl ether was added dropwise to precipitate the mixture of isomeric biladienes **1b** and **11** (in 48% yield). Anal. Calcd for $C_{31}H_{40}Br_2N_4O_2$: C, 56.37; H, 6.10; N, 8.48. Found: C, 56.87; H, 6.24; N, 8.12.

1,4-Bis(2,3,7,8,12,13,17,18-octamethyl-*a,c*-biladien-10-yl)benzene Tetrahydrobromide (14). 1,4-Bis[2,2-bis(3,4-dimethylpyrryl)-methyl]benzene (**16**) (0.5 g) and **7** (0.51 g) were dissolved in acetic acid (50 mL), and 2 mL of 30% HBr in acetic acid was added. After 10 min diethyl ether (100 mL) was added dropwise to precipitate the product as red-green crystals (1.00 g, 78%). UV−vis: λ_{max} 455 nm (ϵ 57 700), 465 (66 300), 516 (133 600). Anal. Calcd for $C_{60}H_{70}Br_4N_8$: C, 58.93; H, 5.77; N, 9.16. Found: C, 59.01; H, 5.70; N, 9.02.

1,3-Bis(2,3,7,8,12,13,17,18-octamethyl-*a,c*-biladien-10-yl)benzene Tetrahydrobromide (15). This compound was prepared, as described for **14**, from 1,3-bis[2,2-bis(3,4-dimethylpyrryl)methyl]benzene (**17**) in 76% yield. UV−vis: λ_{max} 456 nm (ϵ 51 900), 467 (50 300), 515 (118 300). Anal. Calcd for $C_{60}H_{70}Br_4N_8$: C, 58.93; H, 5.77; N, 9.16. Found: C, 59.33; H, 5.94; N, 8.96.

1,4-Bis(2,3,17,18-tetraethyl-7,8,12,13-tetramethyl-*a,c*-biladien-10-yl)benzene Tetrahydrobromide (19). This compound was prepared as above starting from **16** and 2-formyl-3,4-diethylpyrrole (**20**) in 76% yield. UV−vis: λ_{max} 452 nm (ϵ 66 300), 461 (51 000), 519 (ϵ 132 700). Anal. Calcd for $C_{68}H_{86}Br_4N_8$: C, 61.18; H, 6.49; N, 8.39. Found: C, 60.91; H, 6.93; N, 8.15.

(Triphenylphosphine)[8,12-diethyl-2,3,7,13,17,18-hexamethyl-10-(2-chloroethyl)corrolato]cobalt(III) (9d). *a,c*-Biladiene dihydrobromide **1d** (200 mg) was added to a solution of cobalt(II) acetate (200 mg), sodium acetate (500 mg), and triphenylphosphine (200 mg) in boiling MeOH. The mixture was refluxed for 2 h, then the solution was cooled to room temperature (rt), and the solvent was evaporated under vacuum. The solid was dissolved in CH_2Cl_2 and chromatographed on neutral grade III alumina (CH_2Cl_2 eluent); the first red band afforded the title compound which was crystallized from CH_2Cl_2/MeOH as dark-red crystals (208 mg, 84%). Mp 201−203 °C dec. UV−vis: λ_{max} 372 nm (ϵ 69 200), 567 (14 400). ^{1}H NMR: δ 9.04 (s, 2 H), 7.01 (m, 3 H), 6.67 (m, 6 H), 4.64 (m, 6 H), 4.40 (t, 2 H), 3.69 (m, 4 H), 3.18 (t, 2 H), 3.14 (s, 12 H), 3.09 (s, 6 H), 1.61 (t, 6 H). Anal. Calcd for $C_{49}H_{49}CoClN_4P$: C, 71.83; H, 6.03; N, 6.84. Found: C, 71.68; H, 5.92; N, 6.99.

(Triphenylphosphine)[8,12-diethyl-2,3,7,13,17,18-hexamethyl-10-[(methoxycarbonyl)methyl]corrolato]cobalt(III) (9c). This compound was similarly prepared in 79% yield from **1c**. Mp: 264−266 °C dec. UV−vis: λ_{max} 369 nm (ϵ 53 100), 569 (10 500). ^{1}H NMR: δ 9.02 (s, 2 H), 6.98 (m, 3 H), 6.62 (m, 6 H), 5.32 (s, 2 H), 4.75−4.66 (m, 6 H), 3.75 (s, 3 H), 3.60 (br m, 4 H), 3.14 (s, 12 H), 3.10 (s, 6 H), 1.57 (t, 6 H). Anal. Calcd for $C_{50}H_{50}CoN_4O_2P$: C, 72.45; H, 6.08; N, 6.76. Found: C, 72.32; H, 6.10; N, 6.79.

(Triphenylphosphine)(8,12-diethyl-2,3,7,13,17,18-hexamethyl-10-(methoxycarbonyl)corrolato)cobalt(III) (9b) and (Triphenylphosphine)(8,12-diethyl-2,3,7,13,17,18-hexamethyl-5-(methoxycarbonyl)-corrolato)cobalt(III) (12). A mixture of **1b** and **11** obtained as previously described (see text) was used as above to synthesize the corresponding cobalt complexes (53% total yield). UV−vis: λ_{max} 372, 570 nm. ^{1}H NMR: δ 9.440, 9.02, 8.82 (each s, 1 H), 6.59 (m, 3 H), 6.42 (m, 6 H), 4.76 (m, 6 H), 4.05, 4.01 (each s, 3 H), 3.54 (m, 4 H), 3.12−2.93 (s, 18 H), 1.64 (t, 6 H). Anal. Calcd for $C_{49}H_{48}CoN_4O_2P$: C, 72.14; H, 6.05; N, 6.87. Found: C, 72.01; H, 5.97; N, 6.92

(Triphenylphosphine)(8,12-diethyl-2,3,7,13,17,18-hexamethyl-10-vinylcorrolato)cobalt(III) (9e). Corrole **9d** (100 mg) was dissolved in pyridine (50 mL) and refluxed for 10 min, then 10% NaOH (5 mL) and water (4 mL) were added, and the solution was further refluxed for 1.5 h. The mixture was cooled to rt, and 25% acetic acid (4 mL) was added. The solvent was evaporated under vacuum, and the residue was chromatographed on neutral alumina (grade V, CH_2Cl_2 eluent) to obtain the vinyl derivative **9e**. Crystallization from CH_2Cl_2/MeOH afforded purple crystals (74 mg, 77%). Mp: 198−200 °C dec. UV−vis: λ_{max} 372 nm (ϵ 61 300), 570 (16 800). ^{1}H NMR: δ 9.01(s, 2 H), 7.72−7.69 (dd, 1 H), 6.99 (m, 3 H), 6.66 (m, 6 H), 5.65 (d, 1 H), 4.85 (d, 1 H), 4.67 (m, 6 H), 3.64 (m, 4 H), 3.17 (s, 12 H), 3.10 (s, 6 H), 1.47 (t, 6 H). Anal. Calcd for $C_{49}H_{48}CoN_4P$: C, 75.16; H, 6.18; N, 7.16. Found: C, 74.91; H, 6.32; N, 6.84.

1,4-Bis(2,3,7,8,12,13,17,18-octamethylcorrol-10-yl)benzene (3). Bis-*a,c*-biladiene tetrahydrobromide **14** (500 mg) was dissolved in MeOH saturated with $NaHCO_3$, and chloranil (500 mg) was added. The solution was stirred for 5 min at rt, and then 2 mL of 15% N_2H_4 in water was added. The solvent was evaporated under vacuum, the solid was redissolved in CH_2Cl_2 and chromatographed on neutral alumina (grade III, CH_2Cl_2 eluent), and the first red-green band was collected to give the title corrole dimer. It was crystallized from CH_2Cl_2/hexane (168 mg, 46%). Mp: >300 °C. UV−vis: λ_{max} 400 nm (ϵ 112 000), 411 (82 000), 542 (24 000), 597 (28 000). FAB-MS: *m/z* 895 (M^+), 447 (M^{2+}). Anal. Calcd for $C_{60}H_{62}N_8$: C, 80.50; H, 6.98; N, 12.52. Found: C, 80.42; H, 6.86; N, 12.29.

1,3-Bis(2,3,7,8,12,13,17,18-octamethylcorrol-10-yl)benzene (4). This biscorrole (mp >300 °C; 140 mg, 39%) was similarly prepared from **15**. UV−vis: λ_{max} 402 nm (ϵ 105 000), 415 (80 000), 543 (25 000), 598 (26 000). FAB-MS: *m/z* 895 (M^+), 447 (M^{2+}). Anal. Calcd for $C_{60}H_{62}N_8$: C, 80.50; H, 6.98; N, 12.52. Found: C, 80.31; H, 7.03; N, 12.19.

1,4-Bis(2,3,17,18-tetraethyl-7,8,12,13-tetramethylcorrol-10-yl)benzene (18). This biscorrole (mp >300 °C; 210 mg, 49%) was similarly prepared from **19**. UV−vis: λ_{max} 403 nm (ϵ 116 000), 410 (78 000), 545 (26 000), 598 (28 000). ^{1}H NMR ($C_5{}^2H_5N$): δ 9.42 (s, 4 H), 8.37 (s, 4 H), 3.95−3.80 (q, 16 H), 3.30−2.74 (s, 24 H), 1.70−1.68 (t, 24 H). FAB-MS: *m/z* 1007 (M^+), 504 (M^{2+}). Anal. Calcd for $C_{68}H_{78}N_8$: C, 81.06; H, 7.81; N, 11.13. Found: C, 80.83; H, 7.25; N, 11.01.

1,4-Bis[[(Triphenylphosphino)cobalt(III)]-2,3,7,8,12,13,17,18-octamethylcorrol-10-yl]benzene (21). Bis-*a,c*-biladiene **14** (500 mg) was added to a refluxing solution of cobalt(II) acetate (500 mg), sodium acetate (1 g), and triphenylphosphine (500 mg) in MeOH. The solution was refluxed for 3 h, the solvent was evaporated under vacuum, the residue was chromatographed on neutral alumina (grade III; CH_2Cl_2 elution), and the first red band afforded the title product, recrystallized from CH_2Cl_2/hexane (326 mg, 52%). Mp: >300 °C. UV−vis: λ_{max} 378 nm (ϵ 80 400), 576 (21 000). ^{1}H NMR ($C_6{}^2H_6$): δ 9.52 (s, 4 H), 8.18, 8.05 (each br s, 1 H), 7.73 (br s, 2 H), 6.96 (m, 6 H), 6.73 (m, 12 H), 5.25 (m, 12 H), 3.45 (s, 12 H), 3.36 (s, 24 H), 3.12 (s, 12 H). FAB-MS: *m/z* 1532 (M^+), 1270 ($M^+ - PPh_3$). Anal. Calcd for $C_{96}H_{86}Co_2N_8P_2$: C, 75.28; H, 5.66; N, 7.32. Found: C, 75.34; H, 5.83; N, 7.13.

1,3-Bis[[(Triphenylphosphino)cobalt(III)]-2,3,7,8,12,13,17,18-octamethylcorrol-10-yl]benzene (22). This complex (mp > 300 °C; 175 mg, 28% yield) was prepared as above from **15** . UV−vis: λ_{max} 374 nm (ϵ 81 000), 573 (20 500). ^{1}H NMR: δ 9.12 (s, 4 H), 7.80, 7.62, 7.48 (br m, 4 H), 6.98 (m, 6 H), 6.74 (m 12 H), 4.82 (m, 12 H), 3.24−3.02 (each s, 48 H). FAB-MS: *m/z* 1532 (M^+), 1270 ($M^+ - PPh_3$), 1008 ($M^+ - 2PPh_3$). Anal. Calcd for $C_{96}H_{86}Co_2N_8P_2$: C, 75.28; H, 5.66; N, 7.32. Found: C, 75.12; H, 5.91; N, 7.04.

1-(13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-4-[1,9-bis(ethoxycarbonyl)-2,3,7,8-tetramethyldipyrromethan-5-yl]benzene (25). 8,12-Diethyl-2,3,7,13,17,18-hexamethyl-*a,c*-biladiene salt **1a** (500 mg), 1-formyl-4-[1,9-bis(ethoxycarbonyl)-2,3,7,8-tetramethyldipyrromethan-5-yl]benzene (**24**) (500 mg) and TsOH (1 g) were dissolved in ethanol and refluxed for 4 h. Sodium acetate was added to neutralize the solution, and then the solvent was evaporated under vacuum. The residue was dissolved in CH_2Cl_2 and chromatographed on neutral alumina (grade III, CH_2Cl_2 elution). After elution of traces of unrecognized porphyrin, a red-violet band afforded 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole (33 mg, 9%). A second, red-brown band gave the title product (224 mg, 31%), which was crystallized from CH_2Cl_2/MeOH. Mp: 289−291 °C dec. UV−vis: λ_{max} 402 nm (ϵ 235 000), 502 (41 500), 534 (31 200), 570 (30 300), 623 (25 200). ^{1}H NMR: δ 10.18 (s, 2 H), 9.98 (s, 1 H), 8.52 (br s, 2 H), 7.82 (dd, 4 H), 5.92 (s, 1 H), 4.36, 4.12 (each q, 4 H), 3.62 , 3.48 , 2.62, 2.48, 2.02

(each s, 6 H), 1.62, 1.20 (each t, 6 H), −3.12 (br, 2 H). Anal. Calcd for $C_{55}H_{62}N_6O_4$: C, 75.83; H, 7.17; N, 9.65. Found: C, 75.72; H, 7.05; N, 9.58.

1-(13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl]-4-(2,3,7,8-tetramethyldipyrromethan-5-yl)benzene (26a). The foregoing diethyl ester **25** (120 mg) was suspended in diethylene glycol (25 mL) containing KOH (1 g).[13] The mixture was heated at 190 °C under N_2 for 2 h and then allowed to cool to rt. The resulting solid was filtered, washed with H_2O, and dried to give the title product (85 mg, 85%). Mp: 275−277 °C dec. UV−vis: λ_{max} 403 nm (ϵ 225 000), 502 (40 700), 534 (33 400), 571 (29 600), 623 (24 800). ^{1}H NMR: δ 10.22 (s, 2 H), 9.92 (s, 1 H), 8.46 (br s, 2 H), 7.85 (dd, 4 H), 6.84 (s, 2 H), 4.02 (q, 4 H), 3.53, 3.36, 2.51, 2.24, 2.03 (each s, 6 H), 1.46 (t, 6 H), −3.06 (br, 2 H). Anal. Calcd for $C_{49}H_{54}N_6$: C, 80.95; H, 7.49; N, 11.56. Found: C, 80.80; H, 7.61; N, 11.31.

1-(13,17-Diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl]-4-(2,3,7,8,-12,13,17,18-octamethylcorrol-10-yl)benzene (5). Porphyrinyldipyrromethane **26a** (80 mg) and formylpyrrole **7** (25 mg) were dissolved in MeOH (50 mL), and 30% HBr in acetic acid (0.5 mL) was added (to give **27**). After 15 min $NaHCO_3$ (500 mg) and chloranil were added, and the mixture was stirred for 15 min. Next, 15% N_2H_4 in water (1 mL) was added, the solvent evaporated under vacuum, and the residue chromatographed on grade III neutral alumina. The appropriate fraction was collected to give the product, which was recrystallized from CH_2Cl_2/hexane to give 27 mg (26%). Mp: >300 °C. UV−vis: λ_{max} 404 nm (ϵ 354 000), 505 (67 000), 537 (49 100), 573 (50 000), 598 (43 000), 624 (42 000). FAB-MS: *m/z* 934 (M^+). Anal. Calcd for $C_{63}H_{66}N_8$: C, 80.91; H, 7.11; N, 11.98. Found: C, 80.73; H, 7.43; N, 11.66.

1-(13,17-Diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl]-4-(2,3,-17,18-tetraethyl-7,8,12,13-tetramethylcorrol-10-yl)benzene (28). This heterodimer (26 mg, 31%; mp > 300 °C) was synthesized from **26a** and **20** as described above. UV−vis: λ_{max} 406 nm (ϵ 333 100), 505 (64 000), 539 (48 300), 571 (52 100), 599 (48 000), 624 (39 000). ^{1}H NMR: δ 10.22 (s, 2 H), 9.95 (s, 1 H), 9.58 (s, 2 H), 8.45 (s, 4 H), 4.10 (q, 8 H), 3.95 (q, 4 H), 3.70 , 3.67, 3.46 , 3.08, 2.95 (each s, 6 H), 1.88, 1.80 (each t, 9 H), −2.80 (br, 3 H), −3.00 (br, 2 H). Anal. Calcd for $C_{67}H_{74}N_8$: C, 81.16; H, 7.53; N, 11.31. Found: C, 80.95; H, 7.92; N, 11.12.

1-(Nickel(II)-13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-4-(2,3,7,8-tetramethyldipyrromethan-5-yl)benzene (26b). Porphyrinyldipyrromethane **26a** (100 mg) was dissolved in $CHCl_3$ (50 mL), and a saturated solution of nickel(II) acetate in MeOH (20 mL) was added. The mixture was refluxed for 1 h, after which spectrophotometry showed complete formation of the metal complex. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 and crystallized by addition of MeOH to afford 96 mg of the title complex (89%). Mp: 176−178 °C dec. UV−vis: λ_{max} 407 nm (ϵ 164 000), 530 (28 000), 559 (30 100). ^{1}H NMR: δ 10.22 (s, 2 H), 9.95 (s, 1 H), 9.58 (s, 2 H), 8.45 (s, 4 H), 4.10 (q, 8 H), 3.95 (q, 4 H), 3.70 , 3.67, 3.46 , 3.08, 2.95 (each s, 6 H), 1.88, 1.80 (each t, 9 H), −2.80 (br, 3 H), −3.00 (br, 2 H). Anal. Calcd for $C_{49}H_{52}N_6Ni$: C, 75.16; H, 6.70; N, 10.74. Found: C, 74.95; H, 6.92; N, 10.48.

1-(Nickel(II)-13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-4-[[(triphenylphosphino)cobalt(III)-2,3,17,18-tetraethyl-7,8,12,-13-tetramethylcorrol-10-yl]benzene (30). The foregoing nickel(II) porphyrinyldipyrromethane **26b** (80 mg) and formylpyrrole **20** (18 mg) were dissolved in MeOH (50 mL), and 30% HBr in acetic acid (0.5 mL) was added. After 15 min cobalt(II) acetate (200 mg), sodium acetate (1 g), and triphenylphosphine (200 mg) were added, and the solution was refluxed for 1 h. The solvent was evaporated under vacuum, and the residue was chromatographed on neutral alumina (Brockmann Grade III, CH_2Cl_2 elution); the first red band afforded the title product (63 mg, 41%), crystallized from CH_2Cl_2/hexane. Mp: >300 °C. UV−vis: λ_{max} 408 nm (ϵ 288 400), 538 (31 000), 578 (41 200). ^{1}H NMR: δ 9.62 (s, 2 H), 9.50 (s, 1 H), 9.12 (s, 2 H), 8.20, 8.18, 7.28, 7.20 (each d, 1 H), 6.98 (m, 3 H), 6.72 (m, 6 H), 4.79 (m, 6 H), 3.88 (q, 4 H), 3.58 (q, 8 H), 3.53, 3.49, 3.21 (each s, 6 H), 2.91 (s, 12 H), 1.78 (t, 6 H), 1.65 (t, 12 H). FAB-MS: *m/z* 1366 (M^+), 1104 ($M^+ - PPh_3$). Anal. Calcd for $C_{85}H_{84}CoN_8NiP$: C, 74.72; H, 6.20; N, 8.20. Found: C, 75.44; H, 5.91; N, 7.81.

Dibenzyl 5-[4-(Hydroxymethyl)phenyl]-2,3,7,8-tetramethyldipyrromethane-1,9-dicarboxylate (35). To a 500 mL flask were added acetal **33a**[30] (1.46 g, 6.94 mmol), benzyl 3,4-dimethylpyrrole-2-carboxylate (**34**)[31] (3.18 g, 13.9 mmol), and 200 mL of absolute EtOH. The flask was purged with N_2, and TsOH (0.1 g) was added. The mixture was then heated at reflux for 3 h under N_2 with magnetic stirring. At this time triethylamine (2.0 mL) was added, and the ethanol was removed in vacuo. The light-yellow solid was recrystallized from MeOH to yield dipyrromethane **35** (3.00 g, 5.2 mmol, 75% yield). Mp: 70−72 °C. ^{1}H NMR ($CDCl_3$): δ 1.77 (s, 3 H), 1.90 (br s, 1 H), 2.25 (s, 3 H), 4.68 (s, 2 H), 5.24 (s, 4 H), 5.48 (s, 1 H), 7.17 (dd, 4 H), 8.32 (br s, 2 H). MS: *m/z* (relative intensity) 576 (15), 348 (20), 91 (100). Anal. Calcd for $C_{36}H_{36}N_2O_5$: C, 74.97; H, 6.30; N, 4.86. Found: C, 74.81; H, 6.40; N, 4.92.

Dibenzyl 5-(4-Formylphenyl)-2,3,7,8-tetramethyldipyrromethane-1,9-dicarboxylate (36). Tetrapropylammonium perruthenate (TPAP) (183 mg 0.520 mmol) was added to the dipyrromethane **35** (3.0 g, 5.2 mmol), 4-methylmorpholine *N*-oxide (NMO) (0.73 g, 6.24 mmol), and CH_2Cl_2 (50 mL) with stirring at room temperature under N_2. The solution immediately turned a dark-green color, and stirring was continued for 2 h. It was poured into water and extracted with CH_2Cl_2 (3 × 50 mL). The organic extracts were combined, washed with water and brine, and dried over Na_2SO_4. The solvent was removed in vacuo, and the resulting light-brown solid was purified by column chromatography using silica gel (CH_2Cl_2 eluent). The fastest running band was collected, the solvent was removed in vacuo, and the product was crystallized from CH_2Cl_2/MeOH to yield **36** (2.54 g, 4.42 mmol, 85% yield) as an off-white powder. Mp: 147 °C. ^{1}H NMR ($CDCl_3$): δ 1.80 (s, 3 H), 2.25 (s, 3 H), 5.22 (s, 4 H), 5.63 (s, 1 H), 7.43 (dd, 4 H), 8.63 (br s, 2 H), 9.98 (s, 1 H). MS: *m/z* (relative intensity) 574 (M^+, 20), 346 (15), 91 (100). Anal. Calcd for $C_{36}H_{34}N_2O_5$: C, 75.24; H, 5.96; N, 4.89. Found: C, 74.98; H, 6.10; N, 4.87.

1-[Bis[5-(ethoxycarbonyl)-4-ethyl-3-methyl-2-pyrryl]methyl]-4-[bis[[(benzyloxy)carbonyl]-4-ethyl-3-methyl-2-pyrryl]methyl]benzene (32). (Formylphenyl)dipyrromethane **36** (650 mg, 1.13 mmol), pyrrole **37**[27,51,52] (410 mg, 2.27 mmol), and TsOH (100 mg) were dissolved in in absolute EtOH (20 mL), and the resulting solution was refluxed for 2 h. The solution was placed in the refrigerator for 12 h. The white precipitate was filtered off, washed with cold EtOH, and dried under vacuum to yield bisdipyrromethane **32** (0.990 mg, 1.07 mmol, 88% yield). Mp: 199−201 °C. ^{1}H NMR ($CDCl_3$): δ 1.11 (t, 6 H), 1.29 (t, 6 H), 1.78 (s, 12 H), 2.25 (s, 6 H), 2.74 (q, 4 H), 4.11 (q, 4 H), 5.24 (s, 4 H), 5.47 (s, 2 H), 7.03 (s, 4 H), 7.34 (m, 10 H), 8.25 (br s, 2 H), 8.39 (br s, 2 H). MS: *m/z* (relative intensity) 918 (M^+, 45), 151 (29), 108 (95). Anal. Calcd for $C_{56}H_{62}N_4O$: C: 73.18; H, 6.80; N, 6.10. Found: C, 72.79; H, 6.83; N, 5.99.

Porphyrin−Dipyrromethane Conjugate 40. The bis unsymmetrical dipyrromethanedicarboxylic acid **38** (738 mg, 1.01 mmol) was obtained in quantitative yield after catalytic hydrogenation of dipyrromethane **32** (1.05 g) in THF (200 mL) containing 10% palladized charcoal (150 mg) and triethylamine (1 mL). Compound **38** was mixed with diformyldipyrromethane **39**[13] (422 mg, 1.01 mmol) and dissolved in CH_2Cl_2 (200 mL). TsOH (20 mg dissolved in 50 mL of MeOH) was added, and the reaction mixture was stirred under nitrogen for 12 h. A saturated solution of zinc(II) acetate in MeOH (50 mL) was added, and the reaction mixture was stirred while a gentle stream of air was bubbled through the solution. The solution was poured into H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with $NaHCO_3$, deionized water, and brine before being dried over Na_2SO_4. After removal of the solvent in vacuo, the residue so obtained was dissolved in 15% H_2SO_4/TFA (15 mL) and stirred at rt for 1 h. The dark-green solution was cooled to 0 °C and cautiously diluted with water, then CH_2Cl_2 was added, the mixture was neutralized with a saturated solution of $NaHCO_3$, the organic phase was dried over Na_2SO_4, and the solvent was removed in vacuo. The residue so obtained was chromatographed on an alumina column (CH_2Cl_2 eluent). The appropriate eluents were collected, concentrated, and crystallized from CH_2Cl_2/cyclohexane to yield **40** (300 mg, 0.29 mmol, 29% yield) as a purple solid. Mp: 290−295 °C. UV−vis: λ_{max} 406 nm (ϵ 258 000), 506 (47 900), 546 (34 000), 574 (35 500), 624 (28 000). ^{1}H NMR

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($CDCl_3$): δ −2.85 (br s, 2 H), 1.26 (t, 6 H), 1.45 (t, 6 H), 1.80 (t, 6 H), 2.06 (s, 6 H), 2.57 (s, 6 H), 2.64 (s, 6 H), 2.89 (q, 4 H), 3.56 (s, 6 H), 3.71 (s, 3 H), 3.89 (s, 3 H), 4.05 (q, 4 H), 4.49 (q, 4 H), 5.89 (s, 1 H), 8.49 (s, 2 H), 10.22 (s, 2 H). MS: *m/z* (relative intensity) for $C_{65}H_{74}N_6O_6$, calcd 1034.6, found 1034.6 (M^+, 65), 1035.6 (M + 1, 100). Anal. Calcd for $C_{65}H_{74}N_6O_6$: C, 75.41; H, 7.20; N, 8.12. Found: C, 75.29; H, 7.30; N, 8.12.

Nickel(II) Porphyrin−Dipyrromethane Diester Conjugate 42. Free base porphyrin **40** (275 mg, 0.265 mmol) was dissolved in *o*-xylene (50 mL), and nickel(II) acetylacetonate (680 mg, 2.65 mmol) was added. The mixture was refluxed until spectrophotometry indicated complete conversion of starting material to product (ca. 4 h). The solvent was removed in vacuo to yield a dark-red residue which was chromatographed on grade III neutral alumina (CH_2Cl_2 eluent). The appropriate fractions were collected, and the solvent was evaporated to yield a red powder which was crystallized from CH_2Cl_2/cyclohexane to give **42** (260 mg, 0.239 mmol) in 90% yield. Mp: 164−166 °C. UV−vis: λ_{max} (CH_2Cl_2) 406 nm (ϵ 230 000), 526 (30 800), 562 (34 500). ^1H NMR ($CDCl_3$): δ 1.21 (t, 6 H), 1.40 (t, 6 H), 1.61 (t, 6 H), 1.98 (s, 6 H), 2.30 (s, 6 H), 2.39 (s, 6 H), 2.85 (q, 4 H), 3.25 (s, 6 H), 3.71 (s, 3 H), 3.80 (s, 3 H), 4.36 (q, 4 H), 5.78 (s, 1 H), 6.79 (d, 1 H), 7.03−7.16 (m, 2 H), 8.38 (s, 4 H), 9.42 (s, 2 H). MS: *m/z* (relative intensity) 1090 (M^+, 95), 1091 (M + 1, 100). Anal. Calcd for $C_{65}H_{72}N_6NiO_6$: C, 71.49; H, 6.65; N, 7.70. Found: C, 71.66; H, 6.30; N, 7.89.

Nickel Porphyrin−Diunsubstituted Dipyrromethane Conjugate 43. Porphyrin−dipyrromethane conjugate **42** (240 mg, 0.219 mmol) was dissolved in THF (100 mL), and NaOH (0.5 g) was added. The resulting solution was refluxed until all starting material was consumed (TLC). At this time the condenser was removed, and the THF was evaporated until a dark-purple viscous oil remained. At this time ethylene glycol (200 mL) was added, and the material was heated at 180 °C for 1.5 h. The solution was poured into ice−water and extracted with CH_2Cl_2 until the organic layer was clear. The combined organic layers were washed with water and brine and dried over Na_2SO_4. The solvent was removed, and the dark residue was chromatographed on a silica gel column (1:1 CH_2Cl_2/cyclohexane eluent). The appropriate fractions were combined, the solvent was removed in vacuo, and the residue was crystallized from CH_2Cl_2/MeOH to yield **43** (90 mg, 0.095 mmol, 43% yield) as a dark-purple powder. Mp: 173−174 °C. UV−vis: λ_{max} 406 nm (ϵ 133 600), 526 (22 000), 562 (23 300). ^1H NMR ($CDCl_3$): δ 1.25 (t, 6 H), 1.59 (t, 6 H), 2.52 (q, 4 H), 1.98 (s, 6 H), 2.27 (s, 6 H), 2.38 (s, 6 H), 3.22 (s, 6 H), 3.70 (m, 7 H), 3.79 (s, 3 H), 5.78 (s, 1 H), 6.52 (d, 2 H), 6.79 (d, 1 H), 7.53−7.12 (m, 6 H), 9.41 (s, 2 H). MS: *m/z* (relative intensity) 946 (M^+, 100), 945 (30) 838 (25). Anal. Calcd for $C_{59}H_{64}N_6NiO_2\cdot 2H_2O$: C 72.02; H, 6.97; N, 8.54. Found: C, 72.34; H, 6.78; N, 8.77.

Zinc/Nickel Heterometalated Bisporphyrin 45. Porphyrin−dipyrromethane conjugate **43** (70 mg, 0.074 mmol) and 1,9-diformyldipyrromethane **44**[2a] (27 mg, 0.074 mmol) were dissolved in CH_2Cl_2 (50 mL). TsOH (280 mg) was added, and the reaction mixture was stirred at rt under nitrogen for 12 h. A saturated solution of zinc(II) acetate in MeOH (15 mL) was added, and the mixture was stirred while a gentle stream of air was bubbled through the solution. The solution was poured into water and extracted with CH_2Cl_2. The combined organic layers were washed with $NaHCO_3$, deionized H_2O, and brine before being dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was chromatographed on a silica gel column (2% MeOH/CH_2Cl_2 eluent). The appropriate eluents were collected, concentrated in vacuo, and crystallized from CH_2Cl_2/cyclohexane to yield **45** (20 mg, 0.014 mmol, 19% yield) as a dark-red solid. Mp: > 300 °C. UV−vis: λ_{max} 410 nm (ϵ 402 000), 536 (59 300), 570 (50 400), 622 (33 900). ^1H NMR ($CDCl_3$): δ 1.64 (m, 6 H), 1.84 (m, 12 H), 2.42 (s, 6 H), 2.48 (s, 6 H), 3.36 (s, 6 H), 3.80 (m, 10 H), 4.08 (m, 8 H), 9.42 (s, 2 H), 10.22 (s, 2 H). FAB-MS: *m/z* (relative intensity) for $C_{82}H_{82}N_8NiO_2Zn$, calcd 1332.5 (M^+, 100), found 1334.3. Anal. Calcd for $C_{82}H_{82}N_8NiO_2Zn\cdot H_2O$: C 73.74; H, 6.19; N, 8.39. Found C, 73.95; H, 6.30; N, 7.89.

***trans*-4,4′-Bis[1,9-bis(ethoxycarbonyl)-2,8-diethyl-3,7-dimethyldipyrromethan-5-yl]stilbene (46).** $TiCl_3(DME)_{1.5}$ (5.31 g, 0.0183 mol) and Zn−Cu couple (5.09 g) were added to a dry nitrogen filled flask in a drybox. Dry DME (100 mL) was added, and the mixture was refluxed under nitrogen for 2 h to activate the Ti° reagent. Diethyl 1,9-bis(ethoxycarbonyl)-2,8-diethyl-5-(4-formylphenyl)-3,7-dimethyldipyrromethane-1,9-dicarboxylate (**47**) (2.20 g, 459 mmol) in DME (40 mL) was added, and the mixture was refluxed for an additional 1 h; TLC indicated complete reaction of starting material. The solution was cooled to rt before filtering through a bed of Celite and washing with CH_2Cl_2 to remove residual metals and salts. The solution turned a pink-red color (probably through partial dipyrromethene formation). To remove the colored impurities, a small amount of montmorillonite K-10 clay was added to the solution and then filtered off. The filtrate was evaporated under reduced pressure. Crystallization from CH_2Cl_2/petroleum ether afforded 1.52 g of yellow-white crystals. The mother liquor was concentrated, and a second crop (90 mg) was obtained from CH_2Cl_2 and MeOH, for a combined yield of 76%. Mp: 126−134 °C. ^1H NMR ($CDCl_3$): δ 8.25 (br s, 4 H), 7.47, 7.09 (each d, 4 H), 7.08 (s, 2 H), 5.48 (s, 2 H), 4.25 (q, J = 7.0 Hz, 8 H), 2.73 (q, J = 7.5 Hz, 8 H), 1.80 (s, 12 H), 1.31 (t, J = 7.1 Hz, 12 H), 1.11 (t, J = 7.5 Hz, 12 H). MS: *m/z* for $C_{65}H_{68}N_4O_8$, calcd 924.5, found 924.6. Anal. Calcd for $C_{56}H_{68}N_4O_8\cdot 0.5H_2O$ C, 72.00; H, 7.44; N, 6.00. Found: C, 72.07; H, 7.40; N, 6.00.

***trans*-4,4′-Bis[2,8-diethyl-13,17-bis[2-(methoxycarbonyl)ethyl]-3,7,12,18-tetramethylporphyrin-5-yl]stilbene (48).** Bisdipyrromethane **46** (393 mg, 0.425 mmol) was suspended in ethylene glycol (32 mL) with NaOH (673 mg). The solution was heated at 100 °C for 0.5 h to saponify the ethyl esters before refluxing at 195 °C for decarboxylation[13] to afford **49**. The reaction was monitored (TLC); mono-, di-, tri-, and tetra-α-free bisdipyrromethanes were observed. The reaction was complete after 25 min. During cooling to rt, an orange precipitate formed, and *trans*-4,4′-bis(2,8-diethyl-3,7-dimethyldipyrromethan-5-yl)-stilbene (**57**) (221 mg, 82% yield) was collected, dried, and used without further purification. A portion (185.2 mg, 0.291 mmol) of the foregoing bisdipyrromethane **57** and 1,9-diformyl-3,7-bis[2-(methoxycarbonyl)-ethyl]-2,8-dimethyldipyrromethane[53] (**50**) (232 mg, 0.576 mmol) were diluted with CH_2Cl_2 (105 mL); the suspension was purged with N_2 for 5 min before adding a mixture of TsOH (560 mg) in MeOH (20 mL) (previously purged by bubbling N_2 through the solution for 5 min). The solution was allowed to stir at rt for 18 h before adding DDQ (200 mg) and refluxing for 25 min. The solution was cooled to rt before washing several times with water (100 mL) (to eliminate remaining DDQ), once with aqueous saturated $NaHCO_3$ (100 mL), and once with brine (100 mL) before drying over anhydrous Na_2SO_4 and filtering. After evaporation of the solvent, the residue was subjected to two silica gel columns, eluting with 3% MeOH in CH_2Cl_2. The isolated product was crystallized from CH_2Cl_2/*n*-hexane to give 72 mg (18% yield) of the title compound **48**. Mp: >300 °C. UV−vis: λ_{max} 408 nm (ϵ 436 000), 502 (32 800), 536 (11 100), 570 (12 400), 624 (2200). ^1H NMR ($CDCl_3$): δ 10.21 (s, 4 H), 9.99 (s, 2 H), 8.16, 8.10 (each d, 4 H), 7.84 (s, 2 H), 4.43, 3.33 (each t, J = 7.7 Hz, 8 H), 4.07 (q, J = 7.2 Hz, 8 H), 3.70 (s, 24 H), 2.63 (s, 12 H), 1.81 (t, J = 7.7 Hz, 12 H), −3.16, −3.24 (each br s, 2 H). MS: *m/z* for $C_{86}H_{92}N_8O_8$, calcd 1364.7, found 1365.8. Anal. Calcd for $C_{86}H_{92}N_8O_8\cdot 0.5H_2O$: C, 75.14; H, 6.82; N, 8.15. Found: C, 75.08; H, 6.84; N, 8.07.

***trans*-4,4′-Bis[nickel(II)-2,8-diethyl-13,17-bis[2-(methoxycarbonyl)ethyl]-3,7,12,18-tetramethylporphyrin-5-yl]stilbene (51).** Free base bisporphyrin **48** (10 mg, 7.34 mmol) was dissolved in *o*-xylene (5 mL) with nickel(II)(acac)$_2$ (9.3 mg, 36.2 mmol). The solution was refluxed for 20 min before cooling to rt. The mixture was diluted with CH_2Cl_2 (50 mL) and washed three times with water (50 mL) before drying over anhydrous Na_2SO_4 and filtering. After concentration to a red solid, preparative TLC, eluting with 2% MeOH in CH_2Cl_2, afforded the title product. Crystallization from CH_2Cl_2 and MeOH afforded the pure dimetalated dimer **51** (8.5 mg, 79% yield), mp >300 °C. UV−vis: λ_{max} 404 nm (ϵ 353 000), 522 (23 800), 556 (40 500). ^1H NMR ($CDCl_3$): δ 9.64 (s, 4 H), 9.57 (s, 2 H), 7.94 (m, 8 H), 7.69 (s, 2 H), 4.22, 3.16 (each t, J = 7.7 Hz, 8 H), 3.81 (q, J = 8.1 Hz, 8 H), 3.71, 3.46, 2.43 (each s, 12 H), 1.67 (t, J = 7.5 Hz, 12 H). MS: *m/z* for $C_{86}H_{90}N_8Ni_2O_8$, calcd 1478.6, found 1478.4.

Nickel(II) 5-(4-Formylphenyl)-13,17-dibutyl-2,8-diethyl-3,7,12,-17-tetramethylporphyrin (54). Porphyrin **52**[45] (226 mg, 0.325 mmol), xylenes (50 mL), and nickel(II)(acac)$_2$ (0.834 g, 3.25 mmol) were mixed

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together. The solution was refluxed until spectrophotometry indicated the complete conversion of starting material to product (1 h). The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2, washed with water, brine, and dried over Na_2SO_4. The resulting solid was dissolved in CH_2Cl_2 (15 mL), and MeOH was added to precipitate the porphyrin **52** (204 mg, 2.93 mmol, 90% yield) as an orange-red solid. Mp: 280−281 °C. UV−vis: λ_{max} 400 (ϵ 202 900), 522 (20 700), 556 (31 600). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, 6 H), 1.63 (t, 6 H), 2.22 (m, 14 H), 3.41 (2, 6 H), 3.79 (m, 8 H), 8.12 (dd, 4 H), 9.55 (s, 1 H), 9.61 (s, 2 H), 10.32 (s, 1 H). MS: *m/z* (relative intensity) 694 (M^+, 100), 651 (20). HRMS: *m/z* for $C_{43}H_{48}N_4NiO$, calcd 694.3181, found 694.3220. Anal. Calcd for $C_{43}H_{48}N_4NiO$: C, 74.36; H, 6.82; N, 8.30. Found C, 74.40; H, 6.79; N, 8.30.

Nickel(II) 5-(2,5-Dimethoxyphenyl)-15-(4-formylphenyl)-2,8,12,-18-tetraethyl-3,7,13,17-tetramethylporphyrin (55). Porphyrin **53**[45] (410 mg, 0.528 mmol), xylenes (50 mL), and nickel(II)(acac)$_2$ (1.36 g, 5.28 mmol) were mixed together and treated as described for the synthesis of porphyrin **54** to give the title porphyrin **55** (368 mg, 0.475 mmol, 90% yield) as an orange-red solid. Mp: >300 °C. UV−vis: λ_{max} 406 nm (ϵ 209 800), 528 (22 350), 562 (26 200). ^{1}H NMR ($CDCl_3$): δ 1.55 (overlapping t, 12 H), 2.22 (s, 6 H), 2.41 (s, 6 H), 3.73 (m, 11 H), 3.81 (s, 3 H), 6.80 (d, 1 H), 7.20 (m, 2 H), 8.16 (m, 4 H), 9.44 (s, 2 H), 10.31, (s, 1 H). MS: *m/z* (relative intensity) 775 (M + 1, 75), 774 (M^+, 100). Anal. Calcd for $C_{47}H_{48}N_4NiO_3$: C, 72.78; H, 6.24; N, 7.22. Found: C, 72.72; H, 6.25; N, 7.19.

***trans*- and *cis*-4,4′-Bis(nickel(II)-13,17-dibutyl-2,8-diethyl-3,7,12,-18-tetramethylporphyrin-5-yl)stilbene (56 and 57).** $TiCl_3(DME)_{1.5}$ (459 mg, 1.58 mmol), Zn−Cu couple[39,40] (445 mg, 6.26 mmol), and anhydrous DME (20 mL) were mixed under rigorously anhydrous conditions. The mixture was refluxed for 2 h under argon. At this time nickel porphyrin **54** (110 mg, 0.167 mmol) was added, and the mixture was refluxed for 3 h. The solution was cooled and filtered through a neutral alumina (grade III) plug. The dark-red solution was chromatographed on a silica gel column (2:1 cyclohexane/CH_2Cl_2 eluent). The first and second red bands were assigned the cis and trans product configurations, respectively. These bands were collected, and the solvent was removed in vacuo. Each of the respective red bands was dissolved in a minimum volume of CH_2Cl_2 and precipitated by the addition of MeOH to yield bisporphyrins **56** and **57**.

First Band. *cis*-Bisporphyrin 57. 11 mg, 8.1 mmol, 5% yield. Mp: >300 °C. UV−vis: λ_{max} 400 nm (ϵ 345 000), 520 (46 800), 556 (66 300). ^{1}H NMR ($CDCl_3$): δ 1.08 (t, 12 H), 1.51 (t, 12 H), 1.68 (m, 8 H), 2.13 (m, 8 H), 2.43 (s, 12 H), 3.36 (s, 12 H), 3.67 (q, 8 H), 3.82 (t, 8 H), 7.13 (s, 2 H), 7.79 (dd, 8 H), 9.52 (s, 2 H), 9.54 (s, 4 H). MS: *m/z* (relative intensity) 1356.6 (M^+, 100), 692.3 (40). Anal. Calcd for $C_{86}H_{96}N_8Ni_2{\cdot}3H_2O$: C, 73.09; H, 7.28; N 7.93. Found: C, 72.86; H, 7.30; N, 7.87.

Second Band. *trans*-Bisporphyrin 56. 60 mg, 0.044 mmol, 53% yield. Mp: >300 °C. UV−vis: λ_{max} 404 nm (ϵ 318 000), 518 (60 000), 554 (73 300). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, 12 H), 1.70 (m, 20 H), 2.17 (m, 8 H), 2.42 (s, 12 H), 3.42 (s, 12 H), 3.84 (m, 16 H), 7.69 (s, 2 H), 7.94 (s, 8 H), 9.55 (s, 2 H), 9.62 (s, 4 H). MS: *m/z* (relative intensity) 1356.6 (M^+, 100), 692.3 (40). Anal. Calcd for $C_{86}H_{96}N_8Ni_2{\cdot}3H_2O$: C, 73.09; H, 7.28; N, 7.93. Found: C, 72.79; H,7.07; N, 7.67.

***trans*-4,4′-Bis[nickel(II)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(2,5-dimethoxyphenyl)porphyrin-5-yl]stilbene (59) and Nickel-(II) 2,8,12,18-Tetraethyl-5-[4-(hydroxymethyl)phenyl]-15-(2,5-dimethoxyphenyl)-3,7,13,17-tetramethylporphyrin (58).** $TiCl_3(DME)_{1.5}$ (459 mg, 1.58 mmol), Zn−Cu couple (445 mg, 6.26 mmol), anhydrous DME (20 mL), and nickel porphyrin **55** (129 mg, 0.166 mmol) were refluxed for 3 h as described above in the synthesis of **56** and **57**. The dark-red product solution after passage through an alumina plug was chromatographed on silica gel (2:1 cyclohexane/CH_2Cl_2 eluent). The leading red band was collected, and the solvent was removed in vacuo to yield a red orange residue which was crystallized from CH_2Cl_2/cyclohexane to give **59** (10 mg, 6.61 mmol, 8% yield). Mp: >300 °C. UV−vis: λ_{max} 412 nm (ϵ 309 000), 528 (41 700), 562 (43 400). ^{1}H NMR ($CDCl_3$): δ 1.65 (t, 24 H), 2.38 (s, 12 H), 2.40 (s, 12 H), 3.72 (s, 19 H) 3.82 (s, 3 H), 6.80 (d, 2 H), 7.17−7.24 (m, 4 H), 7.66 (s, 2 H), 7.81 (br m, 8 H), 9.43 (s, 4 H). MS: *m/z* (relative intensity) 1512.9 (M^+, 100). There was not enough material available for a combustion analysis. The major product in this reaction was determined to be benzyl alcohol−porphyrin **58** (65 mg, 0.083 mmol; 50% yield). Mp: >300 °C. UV−vis: λ_{max} 406 nm (ϵ 211 800), 526 (21 500), 562 (26 400). ^{1}H NMR ($CDCl_3$): δ 1.55 (t, 12 H), 2.24 (s, 6 H), 2.34 (s, 6 H) 3.73 (m, 11 H), 3.81 (s, 3 H), 5.01 (s, 2 H), 6.78 (d, 1 H), 7.20 (m, 2 H), 7.68 (m, 4 H), 9.41 (s, 2 H). MS: *m/z* (relative intensity) 777 (M + 1, 75), 776 (M^+, 100). Anal. Calcd for $C_{47}H_{50}N_4NiO_3$: C, 72.59; H, 6.48; N, 7.20. Found: C, 72.31; H, 6.30; N, 7.25.

***trans*-4-(Nickel(II)-13,17-dibutyl-2,8-diethyl-3,7,12,18-tetramethylporphyrin-5-yl)-4′-[nickel(II)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(2,5-dimethoxyphenyl)porphyrin-5-yl]stilbene (60).** $TiCl_3(DME)_{1.5}$ (918 mg, 3.17 mmol), Zn−Cu couple (890 mg, 12.5 mmol), anhydrous DME (20 mL), and nickel porphyrins **54** (110 mg, 0.167 mmol) and **55** (129 mg, 0.167 mmol) were mixed under rigorously anhydrous conditions, and the mixture was refluxed for 3 h. The solution was cooled and filtered through a grade III neutral alumina plug. The dark-red solution was chromatographed on silica gel (2:1 cyclohexane/CH_2Cl_2 eluent). The second major band was collected, and the solvent was removed in vacuo. The resulting orange-red residue was crystallized by dissolving it in a minimum amount of CH_2Cl_2 and adding MeOH to isolate **60** (25 mg, 0.017 mmol, 20% yield). Mp: >300 °C. UV−vis: λ_{max} 408 nm (ϵ 336 000) 524 (64 500), 558 (73 400). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 6 H), 1.65 (m, 22 H), 2.25 (m, 4 H), 2.38 (s, 6 H), 2.40 (s, 6 H), 2.42 (s, 6 H), 3.43 (s, 6 H), 3.72−3.82 (s + s + overlapping m, 22 H), 6.82 (d,1 H), 7.14−7.26 (m, 2 H) 7.67 (s, 2 H), 7.93 (s, 4 H), 9.41 (s, 2 H), 9.52 (s, 1 H), 9.60 (s, 2 H). MS: *m/z* (relative intensity) 1436.6 (M^+, 25) 1410.6 (100). Anal. Calcd for $C_{90}H_{96}N_8Ni_2O_2{\cdot}2H_2O$: C, 73.28; H, 6.83; N, 7.60. Found: C, 72.99; H, 6.99; N, 7.34.

***trans*-4,4′-Bis[2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(2,5-dimethoxyphenyl)porphyrin-5-yl]stilbene (61).** Dinickel bisporphyrin **59** (10 mg, 6.67 mmol) was dissolved in CH_2Cl_2 (15 mL), and trifluoroacetic acid (2 mL) was added. This solution was stirred in the dark under nitrogen. After 15 min, the solution was cooled to 0 °C, poured into ice−H_2O, and neutralized by the careful addition of dilute NH_4OH. The organic layer was separated, and the aqueous layer was washed with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried over Na_2SO_4 and removed in vacuo, yielding a purple residue which was crystallized by dissolving the residue in CH_2Cl_2 and carefully layering the solution with MeOH to yield **61** (8 mg, 5.69 mmol, 86% yield) as a dark purple solid. Mp: >300 °C. UV−vis: λ_{max} 412 nm (ϵ 396 000), 508 (29 800), 540 (11 100), 574 (10 700), 626 (2700). ^{1}H NMR ($CDCl_3$): δ −2.34 (br s, 2 H), 1.81 (t, 24 H), 2.67 (s, 24 H), 4.09 (br m, 16 H), 7.15−7.32 (m, 6 H), 7.76 (s, 2 H), 8.04−8.21 (m, 8 H), 10.29 (s, 4 H). MS: *m/z* for $C_{94}H_{100}N_8O_4$, calcd 1405.9, found 1405.8. Anal. Calcd for $C_{94}H_{100}N_8O_4{\cdot}H_2O$: C, 79.18; H, 7.35; N, 7.86. Found: C, 79.08; H, 7.19; N, 8.07.

***trans*-4,4′-Bis(nickel(II)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin-5-yl)stilbene (64), 1-[*trans*-3^1-(Nickel(II)-chlorin-e_6 trimethyl ester)]-4-(nickel(II)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin-5-yl)benzene (65), and *trans*-1,2-Bis[nickel(II)-2-chlorin-e_6 trimethyl ester]ethene (66).** $TiCl_3(DME)_{1.5}$ (1.01 g, 3.5 mmol) and Zn−Cu couple (0.92 g, 12.9 mmol) were added to a dry flask in a drybox. Anhydrous DME (20 mL) was added to the reaction flask, and the resulting mixture was refluxed for 2 h under argon. A powder made up of nickel(II) 3-formylchlorin-e_6 trimethyl ester (**63**) (165 mg, 0.24 mmol) and nickel(II) 5-(4-formylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**62**) (75 mg, 0.12 mmol) was then added, and the mixture was refluxed for 2.5 h. After being cooled to rt, the reaction mixture was filtered through a plug of neutral alumina [grade III, CH_2Cl_2/MeOH (10:1) elution]. The solvents were removed, and the residue was further purified by chromatography on a silica gel column [elution with CH_2Cl_2/cyclohexane (3:1)] to give successively a red band containing the bisporphyrin along with some impurities, a brown-green fraction, and a red fraction characterized by ^{1}H NMR and FAB MS as the nickel(II) 5-[4-(hydroxymethyl)phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**67**) (10 mg, 14%). Further elution with CH_2Cl_2 gave the bischlorin **66** (62 mg, 42%). The brown-green fraction was rechromatographed on a neutral alumina (grade III) column [CH_2Cl_2/cyclohexane (2:1) elution] to yield the mixed dimer **65** which was recrystallized twice from CH_2Cl_2/cyclohexane to give 30 mg (41% yield). The porphyrin dimer **64** was rechromatographed on a silica gel column [elution with CH_2Cl_2/cyclohexane (2:3)] and recrystallized from CH_2Cl_2/cyclohexane to give 5 mg (6%) of **64**. Mp: 261−262 °C; UV−vis: λ_{max} 404 nm (ϵ 324 000), 520 (35 500), 556 (52 300). ^{1}H NMR ($CDCl_3$): δ 9.62 (s, 4 H), 9.56 (s, 2 H), 7.93 (s, 8 H), 7.68 (s, 2 H), 3.85 (m, 16 H), 3.43 (s, 12 H), 2.42 (s, 12 H), 1.75 (t, 12H, J = 7.5 Hz), 1.67 (t, 12H, J = 7.5 Hz). MS: *m/z* 1244.5 (100). Anal. Calcd for $C_{72}H_{76}N_8Ni_2O_{12}\cdot 2H_2O$: C, 73.02; H, 6.60; N, 8.73. Found: C, 72.66; H, 6.51; N, 8.54. The following are data for porphyrin−chlorin dimer **65**. Mp: >330 °C. UV−vis: λ_{max} 402 (ϵ 240 600), 520 (12 100), 556 (22 400), 650 (43 800). ^{1}H NMR ($CDCl_3$): δ 9.65 (s, 2 H), 9.58 (s, 1 H), 9.29 (s, 1 H), 9.11 (s, 1 H), 8.49 (d, 1H, J = 16.5 Hz), 8.10 (d + s, 3 H), 8.02 (d, 2H, J = 8.1 Hz), 7.71 (d, 1H, J = 16.5 Hz), 4.81, 4.74, 4.61, 4.55 (ABq, 2H, J = 18.3 Hz), 4.18, 3.83, 3.69, 3.36, 3.28, 3.22 (each s, 3 H), 4.12 (m, 1 H), 3.88 (m, 8 H), 3.61 (m, 2 H), 3.45, 2.53 (each s, 6 H), 2.52 (m, 2 H), 1.77 (t + sh, 8 H), 1.68 (t, 6H, J = 7.5 Hz), 1.58 (t + d, 6 H). MS: *m/z* 1304.7 (100). Anal. Calcd for $C_{75}H_{78}N_8Ni_2O_6$: C, 69.03; H, 6.03; N, 8.52. Found: C, 69.00; H, 5.76; N, 8.17. The following are data for bischlorin **66**. Mp: 284−285 °C. UV−vis: λ_{max} 409 nm (ϵ 135 600), 500 (10 000), 556 (7700), 672 (63 000). ^{1}H NMR ($CDCl_3$): δ 9.34, 9.09, 8.38, 8.12 (each s, 2 H), 4.77, 4.56 (ABq, J = 18.4 Hz, 4 H), 4.16, 3.81, 3.68, 3.39, 3.26, 3.08 (each s, 6 H), 3.58 (q, 4 H), 2.42 (m, 4 H), 1.84 (m, 4 H), 1.61 (m, 12 H). MS: *m/z* 1361.4 (100). Anal. Calcd for $C_{72}H_{76}N_8Ni_2O_{12}$: C, 63.46; H, 5.62; N, 8.61. Found: C, 63.38; H, 5.66 ; N, 8.23.

1-[*trans*-3^2-(Nickel(II)-chlorin-e_6 trimethyl ester)]-4-(2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin-5-yl)benzene (68). The porphyrin−chlorin dimer **71** (20 mg) was dissolved in CH_2Cl_2 (10 mL). TFA (10 mL) was added, and the mixture was stirred for 3 h at rt. CH_2Cl_2 (50 mL) was added, and the mixture was washed with H_2O, saturated aqueous Na_2CO_3, and H_2O again. The organic phase was dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on an alumina column [Brockmann Grade III, elution with CH_2Cl_2/cyclohexane (25:15)]. The slower moving band was collected and evaporated to give 14 mg (73%) of the title compound. Mp: >330 °C. UV−vis: λ_{max} 406 (ϵ 238 000), 502 (18 400), 534 (8100), 570 (8700), 648 (41 600). ^{1}H NMR ($CDCl_3$): δ 10.21 (s, 2 H), 9.99 (s, 1 H), 9.33 (s, 1 H), 9.11 (s, 1 H), 8.56 (d, 1H, J = 16.5 Hz), 8.21 (m, 4 H), 8.13 (s, 1 H), 7.78 (d, 1H, J = 16.5 Hz), 4.78, 4.58 (ABq, J = 18.4 Hz, 2 H), 4.18, 3.83, 3.69, 3.40, 3.28, 3.24 (each s, 3 H), 4.11 (m, 9 H), 3.61 (m, 3 H), 3.68, 2.70 (each s, 6 H), 2.52 (m, 2 H), 1.92 (t + sh, 8 H), 1.82 (t, 6H, J = 7.5 Hz), 1.64 (t + d, 6 H), −3.11 (s, 1 H), −3.22 (s, 1 H). MS: *m/z* 1247.5 (100).

Crystal Structures. Compound 45. $C_{81}H_{82}N_8NiO_3Zn\cdot CH_3OH$, blue parallelepipeds were grown from CH_2Cl_2/MeOH, crystal size 0.6 × 0.5 × 0.1 mm, monoclinic, space group $C2/m$, a = 39.62(2) Å, b = 15.190(6) Å, c = 12.406(6) Å, β = 104.83(3)°, V = 7217(6) Å^3, FW = 1399.68, ρ_{calc} = 1.288 mg·m^{-3}, μ = 0.650 mm^{-1}, $2\theta_{max}$ = 50°, Mo Kα radiation (λ = 0.710 73 Å), ω scans, T = 130 K, 6601 independent reflections. The structure was solved via a Patterson synthesis followed by structure expansion (SHELXS-87: Sheldrick, G. M., University of Göttingen, 1990). An absorption correction was applied,[54] hydrogen atoms were included in calculated positions, and the structure was refined against $|F^2|$ (Siemens SHELXTL V. 5.02, 1995). The final cycle of refinement included 476 independent parameters and converged with $R1$ = 0.089, $wR2$ = 0.231 ($I > 2\sigma(I)$) and $R1$ = 0.1263, $wR2$ = 0.2855 (all data). The structure suffers from disorder of the side chain ethyl groups, crystallographically required disorder of the axial MeOH carbon, and high thermal motion of some side chain atoms.

Compound 65. Dark purple blocks of $C_{75}H_{78}N_8O_6Ni_2\cdot 0.70(CHCl_3)$ were grown from *n*-hexane/$CHCl_3$, dimensions 0.46 × 0.32 × 0.16 mm, monoclinic $C2$, a = 23.019(3) Å, b = 9.4780(11) Å, c = 30.798(3) Å, β = 94.528(8)°, V = 6698.4(13) Å^3, Z = 4, FW = 1388.43, ρ_{calc} = 1.412 g·cm^{-3}, μ = 2.29 mm^{-1}, Siemens P4 diffractometer with a rotating anode [λ(Cu Kα) = 1.541 78 Å] at 130(2) K in the $\theta/2\theta$ scan mode to $2\theta_{max}$ = 112°. Of 5619 reflections measured 5074 were independent, and 4525 had $I > 2\sigma$. The structure was solved by direct methods and refined (based on F^2 using all independent data) by full matrix least-squares methods (Siemens SHELXTL V. 5.02, 1995); the number of parameters is 872. Hydrogen atom positions were located by their idealized geometry and refined using a riding model. An absorption correction was performed using XABS2.[54] An absolute structure determination based upon anomalous scattering was successful. Final R values were $R1$ = 0.0582 (based on observed data) and $wR2$ = 0.1900 (based on all data).

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Supporting Information Available: Tables listing of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for compounds **45** and **65** (25 pages); structure factors for compounds **45** and **65** (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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