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Synthesis of Isomeric Angularly Annealed Dinaphthoporphyrin Systems: Examination of the Relative Positioning and Orientation of Ring Fusion as Factors Influencing the Porphyrin Chromophore†

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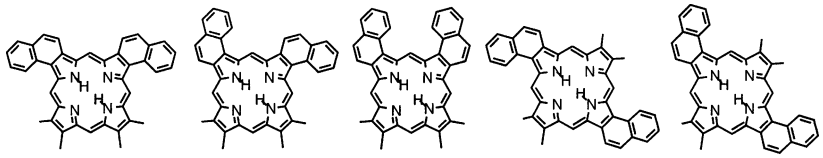

Porphyrins built up from two naphtho[1,2-*c*]pyrrole subunits and two β-substituted pyrroles can produce five isomeric dinaphthoporphyrin systems. To gain insights into the effects of ring fusion on extended porphyrin chromophores, all five of these systems were synthesized in isomerically pure form. In four of these syntheses, dihydronaphthopyrroles were used to introduce one or both of the naphthalene subunits, and dehydrogenation with DDQ in refluxing toluene later produced the fully conjugated systems. Naphthopyrroles were also prepared by reacting isocyanoacetate esters with 1-nitronaphthalene in the presence of a phosphazene base. These compounds proved to be less stable than their dihydronaphthopyrrolic counterparts but could still be utilized in these synthetic studies. Three isomeric *adj*-dinaphthoporphyrin systems were prepared using the MacDonald "2 + 2" condensation or by the cyclization of *a*,*c*-biladiene intermediates with copper(II) chloride or $AgIO_3-Zn(OAc)_2$. A dinaphthoporphyrin with two naphthalene units pointing toward one another could only be obtained in low yields due to a combination of stability and steric factors, but the other two *adj*-difused systems were isolated in good overall yields. However, the final dehydrogenation step occurred in moderate yields (50−60%) and could only be performed when the porphyrins bore propionate ester side chains that produced sufficient solubility in organic solvents. The two related *opp*-dinaphthoporphyrins were synthesized by a "head-to-tail" self-condensation of a dipyrrylmethane aldehyde, or a "3 + 1" synthesis using a tripyrrane intermediate bearing two fused dihydronaphthalene moieties, in excellent yields. In both cases, a final dehydrogenation step was required, but the *opp*-dinaphthoporphyrins were consistently formed in virtually quantitative yields. The *opp*-dinaphthoporphyrin series gave UV−vis spectra with relatively strong Soret bands at 425 nm, and the visible region was dominated by an unusually strong Q-band III. The *adj*-dinaphthoporphyrins produced broader less intense Soret bands and four well-defined Q-bands, including a relatively strong absorption at 645 nm. However, the relative orientation of the naphthalene rings had no significant effects on these spectra. On the other hand, the dications produced in TFA-chloroform solutions showed more discrimination between the individual porphyrin systems, and the metallo derivatives also displayed significant variations in their electronic absorption spectra.

Introduction

Porphyrins with extended chromophores are being investigated for applications that range from material science to medicine.[1,2] In some cases, ring fusion results in highly red-shifted chromophores that could have value in photodynamic therapy.[3,4] Other structural units are being utilized to act as bridging units in the production of nanoscale systems, including molecular wires and arrays.[5,6] Porphyrins with fused benzene or naphthalene rings are structurally analogous to the phthalocyanines

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† Porphyrins with Exocyclic Rings. 17. For part 16, see: Lash, T. D.; Werner, T. M.; Thompson, M. L.; Manley, J. M. *J. Org. Chem.* **2001**, *66*, 3152−3159.

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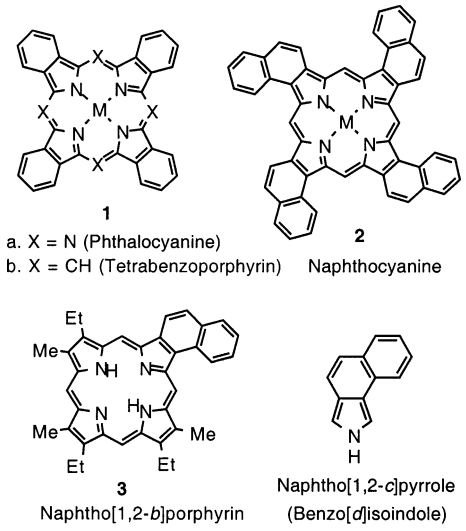
CHART 1



(**1a**) and naphthocyanines (e.g., **2**), families of tetraazaporphyrinoids that show a wide range of industrial applications (Chart 1). Although mono-, di-, and tetrabenzoporphyrins **1b** are presently receiving considerable attention,[8−11] far less work has been carried out on the naphthoporphyrins.[12,13] In earlier work, we reported the first synthesis of a naphtho[1,2-*b*]porphyrin **3** for use as a standard for geochemical studies.[8a,14] Porphyrin **3** showed a distinctive UV−vis spectrum, but only small bathochromic shifts were noted.[14] This observation led us to develop syntheses of porphyrins fused to other types of aromatic rings so that we could investigate the influence of these different ring systems on the electronic absorption spectra.[1−3,15−17] Not surprisingly, porphyrins with two or more fused units showed larger effects, and for the doubly fused structures substantial differences were observed between the oppositely and adjacently difused systems.[15a,c,16b] To date, little theoretical work has been conducted on these important extended porphyrin structures.[18] Phthalocyanine-type systems have been more thoroughly studied, and the differences between adjacent versus opposite diaromatic ring fused tetraazaporphyrin derivatives have been probed by synthesis, spectroscopy, and molecular orbital calculations.[19] In addition to the relative positioning of the fused rings, the orientation of asymmetrical units can also be a factor. To gain a better understanding of these factors, a series of dinaphthoporphyrins related to naphthoporphyrin **3** were targeted for synthesis (Chart 2).[20−22] When two angularly annealed naphthalene rings are present, five different structural types are possible (A−E, Chart 2).[23] Three of these dinaphthoporphyrins have adjacent ring fusion (*adj*-dinaphthoporphyrins), while the other two feature naphthalenes at the opposite positions (*opp*-dinaphthoporphyrins). The synthesis of all five of these isomeric systems proved to be a considerable challenge that required the application of several different methodologies.[24] In this paper, the synthesis and spectroscopic characterization of all five structural types of dinaph-

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(6) (a) Jaquinod, L.; Siri, O.; Khoury, R. G.; Smith, K. M. *Chem. Commun.* **1998**, 1261. (b) Vicente, M. G. H.; Cancilla, M. T.; Lebrilla, C. B.; Smith, K. M. *Chem. Commun.* **1998**, 2355.

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(12) For examples of naphtho[2,3-*b*]porphyrins and related linearly annealed systems, see: (a) Kopranenkov, V. N.; Vorotnikov, A. M.; Luk'yanets, E. A. *J. Gen. Chem. USSR* **1979**, *49*, 2467. (b) Rein, M.; Hanack, M. *Chem. Ber.* **1988**, *121*, 1601. (c) Kobayashi, N.; Nevin, W. A.; Mizunuma, S.; Awaji, H.; Yamaguchi, M. *Chem. Phys. Lett.* **1993**, *205*, 51. (d) Tomé, A. C.; Lacerdo, P. S. S.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S. *Chem. Commun.* **1997**, 1199. (e) Ito, S.; Ochi, N.; Uno, H.; Murashima, T.; Ono, N. *Chem. Commun.* **2000**, 893. (f) Finikova, O. S.; Cheprakov, A. V.; Carroll, P. J.; Vinogradov, S. A. *J. Org. Chem.* **2003**, *68*, 7517.

(13) For examples of porphyrins with porphyrins with four angularly annealed naphthalenes, see: (a) Kopranenkov, V. N.; Vorotnikov, A. M.; Dashkevich, S. N.; Luk'yanets, E. A. *J. Gen.Chem. USSR* **1985**, *55*, 803. (b) Vorotnikov, A. M.; Krasnokut-skii, S. N.; Braude, E. V.; Kopranenkov, V. N. *Chem. Heterocyclic Comp.* **1990**, *26*, 1314. (c) Ono, N.; Hironaga, H.; Ono, K.; Kaneko, S.; Murashima, T.; Ueda, T.; Tsukamura, C.; Ogawa, T. *J. Chem. Soc., Perkin Trans. 1* **1996**, 417. Although these porphyrins can exist in four isomeric forms, some preparations appear to favor one specific isomer over the others.[13b,c]

(14) Lash, T. D.; Denny, C. P. *Tetrahedron* **1995**, *51*, 59.

(15) (a) Lash, T. D.; Novak, B. H. *Tetrahedron Lett.* **1995**, *36*, 4381. (b) Lash, T. D.; Novak, B. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 683. (c) Novak, B. H.; Lash, T. D. *J. Org. Chem.* **1998**, *63*, 3998.

(16) (a) Chandrasekar, P.; Lash, T. D. *Tetrahedron Lett.* **1996**, *37*, 4873. (b) Lash, T. D.; Chandrasekar, P.; Osuma, A. T.; Chaney, S. T.; Spence, J. D. *J. Org. Chem.* **1998**, *63*, 3, 8455.

(17) (a) Lash, T. D.; Wijesinghe, C.; Osuma, A. T.; Patel, J. R. *Tetrahedron Lett.* **1997**, *38*, 2031. (b) Lash, T. D.; Werner, T. M.; Thompson, M. L.; Manley, J. M. *J. Org. Chem.* **2001**, *66*, 3152. (c) Lash, T. D.; Gandhi, V. *J. Org. Chem.* **2000**, *65*, 8020.

(18) Kobayashi, N.; Konami, H. *J. Porphyrins Phthalocyanines* **2001**, *5*, 233.

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(20) Preliminary communication: Lash, T. D.; Roper, T. J. *Tetrahedron Lett.* **1994**, *35*, 7715.

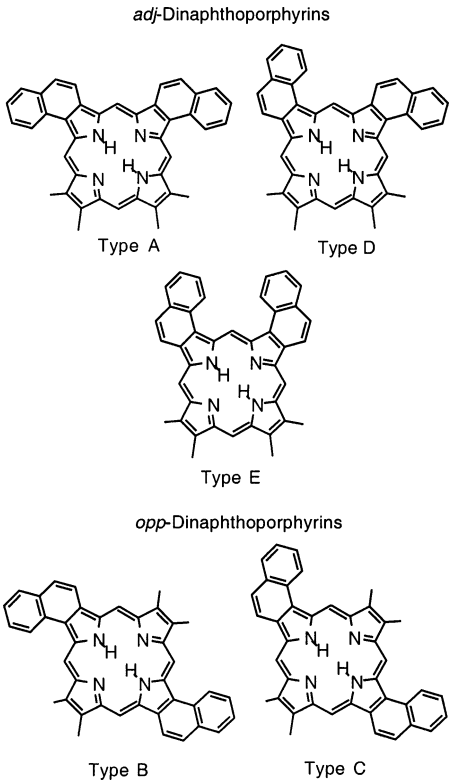
(21) These results were presented, in part, at the following meetings: 85th Annual Meeting of the Illinois State Academy of Science, Springfield, IL, Oct 1992 (Roper, T. J.; Denny, C. P.; Lash, T. D. *Trans. Illinois State Acad. Sci.* **1992**, *85* (Suppl.), 46, Abstract No. 45); 207th National ACS Meeting, San Diego, CA, March 1994 (Lash, T. D.; Roper, T. J.; Novak, B. H.; Lin, Y. *Book of Abstracts*, ORGN 154); 34th Midwest Regional ACS Meeting, Quincy, IL, Oct. 1999 (Manley, J. M.; Lash, T. D. *Program and Abstracts*, Abstract No. 164); 219th National ACS Meeting, San Francisco, CA, March 2000 (Manley, J. M.; Lash, T. D. *Book of Abstracts*, ORGN 357).

(22) Results taken, in part, from: Manley, J. M. M.S. Thesis, Illinois State University, 2001.

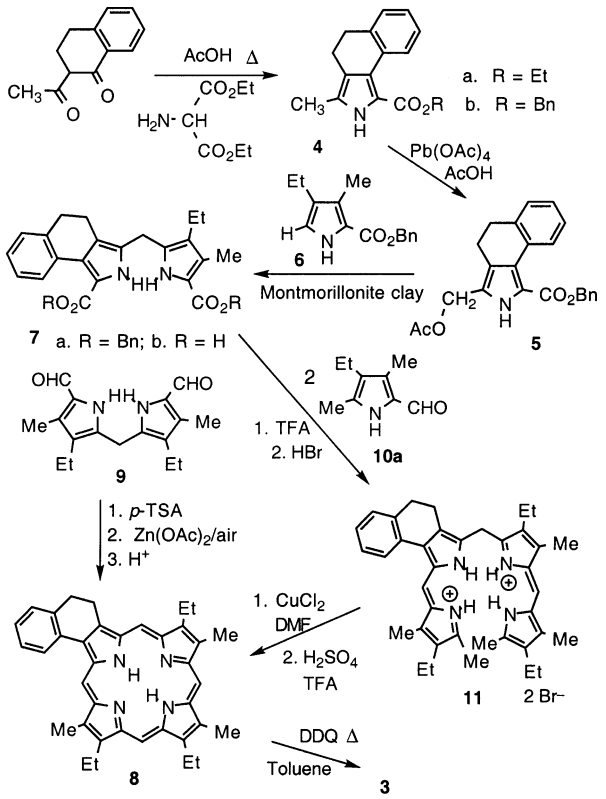
(23) Series A−E were assigned in the order that they were synthesized, which also provides the most logical sequence for discussing the syntheses of these five dinaphthoporphyrin systems.

(24) For recent reviews on porphyrin synthesis, see: (a) Smith, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 1, pp 1−43. (b) Smith, K. M. *J. Porphyrins Phthalocyanines* **2000**, *4*, 319−324.

CHART 2. Dinaphthoporphyrins



SCHEME 1



thoporphyrins and their nickel(II), copper(II), and zinc metalloderivatives are reported. A preliminary communication on the type A and B systems was published some time ago,[20] but syntheses of the type C−E systems were accomplished more recently.[21,22]

Results and Discussion

The synthesis of dinaphthoporphyrins requires the availability of suitably substituted pyrrolic precursors that can introduce the naphthalene units. As isoindole structures are relatively unstable and poorly suited for porphyrin synthesis,[25] we initially favored the use of dihydronaphthopyrroles rather than the fully unsaturated systems (Chart 1) that might not stand up to the reaction conditions.[14,20] In addition, a fused naphthalene unit could significantly alter the reactivity of the pyrrolic intermediates, and this might interfere with macrocycle formation. In the earlier synthesis of a mononaphthoporphyrin **3**, dihydronaphthopyrrole esters **4** were used as the key intermediates (Scheme 1).[14] Condensation of diethyl aminomalonate with 2-acetyl-1-tetralone in acetic acid gave the ethyl ester **4a**, and this is transesterified with sodium benzyloxide in benzyl alcohol to give the benzyl ester **4b**.[14] Further reaction with lead tetraacetate afforded the acetoxymethyl derivative **5** and this reacted with α-unsubstituted pyrrole **6** to give dipyrrylmethane **7a**.[14] Cleavage of the benzyl esters with hydrogen over palladium−charcoal gave the corresponding dicarboxylic acid **7b**, and this was taken on via two different routes to the dihydronaphthoporphyrin **8**.[14] Reaction of **7b** with dipyrrylmethane dialdehyde **9a** in the presence of *p*-toluenesulfonic acid, followed by air oxidation in the presence of zinc acetate, gave porphyrin **8** in 44% yield.[14] Alternatively, reaction of **7b** with 2 equiv of pyrrole aldehyde **10a** in the presence of HBr gave *a*,*c*-biladiene **11** and subsequent cyclization with copper(II) chloride in DMF, followed by demetalation with H_2SO_4−TFA, gave **8** in 25% yield for the two steps combined.[14] Dehydrogenation with DDQ then gave the required naphtho[1,2-*b*]porphyrin **3** (Scheme 1).[14,26] The success of this strategy led us to adapt the principles used in the synthesis of **3** to prepare the type A and type B dinaphthoporphyrin systems.[20]

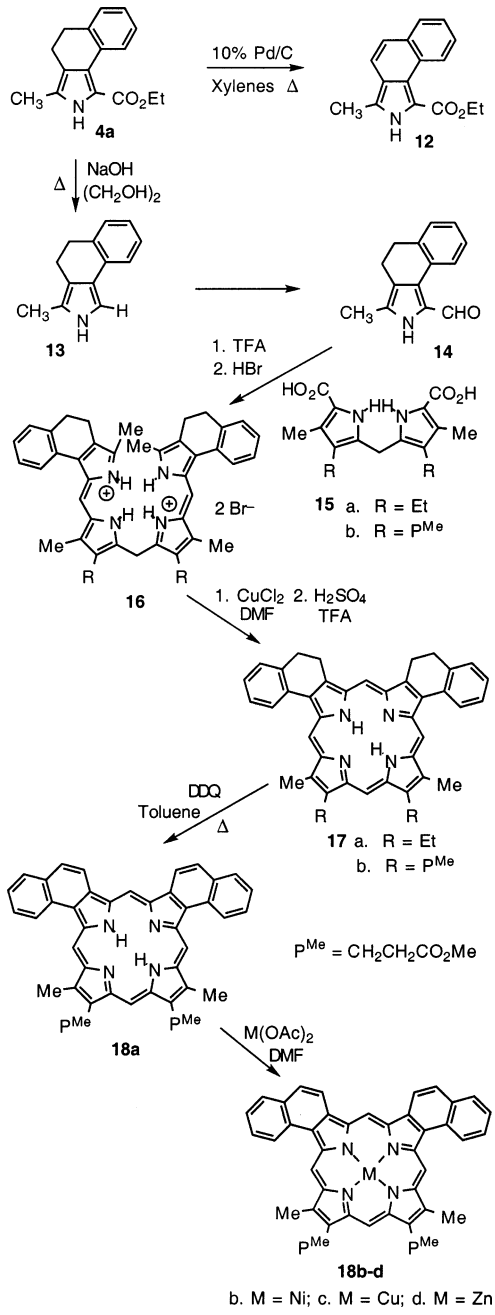
Synthesis of Type A Dinaphthoporphyrins. The synthesis of the type A *adj*-dinaphthoporphyrin system was accomplished by using the *a*,*c*-biladiene strategy[27] (Scheme 2). Although the final step of the dehydrogenation strategy had been satisfactory, we also investigated the use of naphthopyrrole intermediates as well. Dihydronaphthopyrrole **4a** was found to be easily dehydrogenated with 10% Pd/C in refluxing xylenes to give naphthopyrrole **12** in excellent yield, but this compound proved to be too reactive to be used as an intermediate for naphthoporphyrin synthesis. Attempts to saponify or transesterify the ester goup for **12** led to decomposition, while reactions with lead tetraacetate afforded complex mixtures. However, precursor **4a** is far more robust and

(25) Remy, D. E. *Tetrahedron Lett.* **1983**, *24*, 1451.

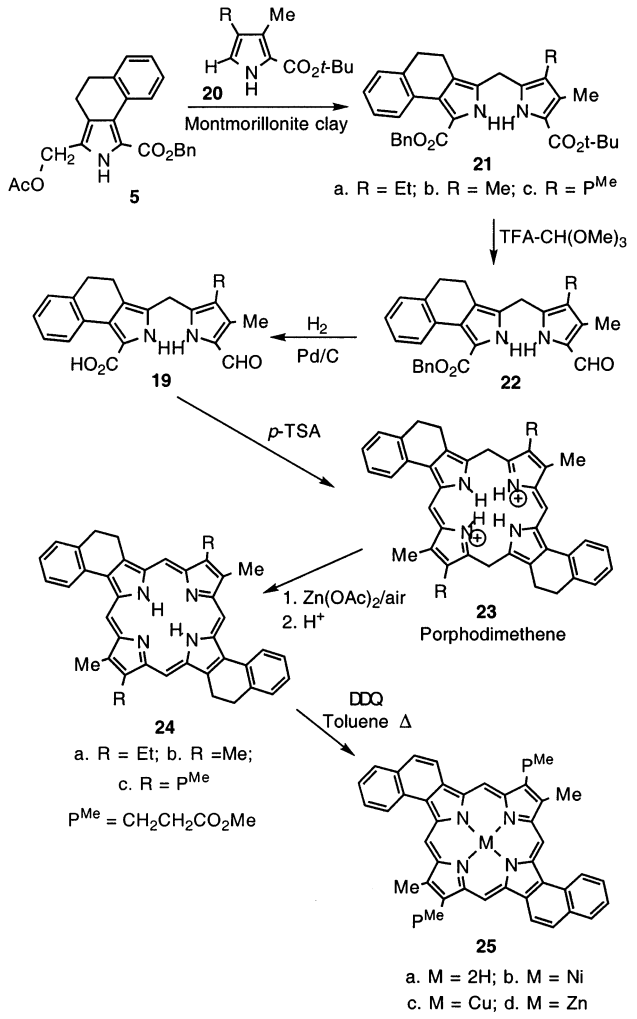
(26) Although the dehydrogenation of tetrahydrobenzoporphyrins to benzoporphyrins, or the related oxidation of dihydronaphthoporphyrins to naphthoporphyrins, using DDQ had not been noted prior to our studies,[8a] dehydrogenation of a tetracyclohexenotetraazaporphyrin to phthalocyanine (and/or intermediary species) with DDQ in *o*-dichlorobenzene had been reported many years earlier. See: Ficken, G. E.; Linstead, R. P.; Stephen, E.; Whalley, M. *J. Chem. Soc.* **1958**, 3879. See also: Ficken, G. E.; Linstead, R. P. *J. Chem. Soc.* **1952**, 4846.

(27) Smith, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 1, pp 119−148.

SCHEME 2



SCHEME 3



could be saponified and decarboxylated with sodium hydroxide in ethylene glycol at 180 °C. The resulting α-unsubstitued pyrrole **12** was immediately treated with trimethyl orthoformate and TFA to generate the corresponding aldehyde **14**. Two equivalents of **14** was reacted with HBr and dipyrrylmethane dicarboxylic acid **15a** to give the *a*,*c*-biladiene **16a**, while reaction of **14** with **15b** afforded the related tetrapyrrole **16b**. Cyclization of *a*,*c*-biladienes **16** with copper(II) chloride in DMF at room temperature,[28,29] followed by demetalation with 15% sulfuric acid in TFA, gave the tetrahydrodinaphthoporphyrins **17** in 34−38% yield. The final step in the synthesis required a dehydrogenation with DDQ in a refluxing solvent such as toluene.[8a] Unfortunately, the poor solubility of **17a** in organic solvents made this transformation difficult to accomplish, and attempts to dehydrogenate diethylporphyrin **17a** gave rise to the formation of inseparable mixtures. However, the dipropionate ester porphyrin **17b** proved to be far more soluble and this was oxidized with DDQ in refluxing toluene to give dinaphthoporphyrin **18a** in 60% yield. The porphyrin was fully characterized and three metallo derivatives were also prepared. Hence, **18a** was reacted with nickel(II), copper(II), and zinc acetate in DMF to give the corresponding metal complexes **18b**−**d**.

Synthesis of Type B Dinaphthoporphyrins. The second targeted dinaphthoporphyrin system could not be synthesized by the foregoing route, but this centrosymmetric structure is accessible via a variation on the MacDonald "2 + 2" condensation[30,31] (Scheme 3). This requires the availability of dipyrrylmethanes **19** that can undergo head-to-tail self-condensations.[31] The previously synthesized acetoxymethylpyrrole **5**[14] was reacted with α-unsubsituted pyrrole *tert*-butyl esters **20** in the pres-

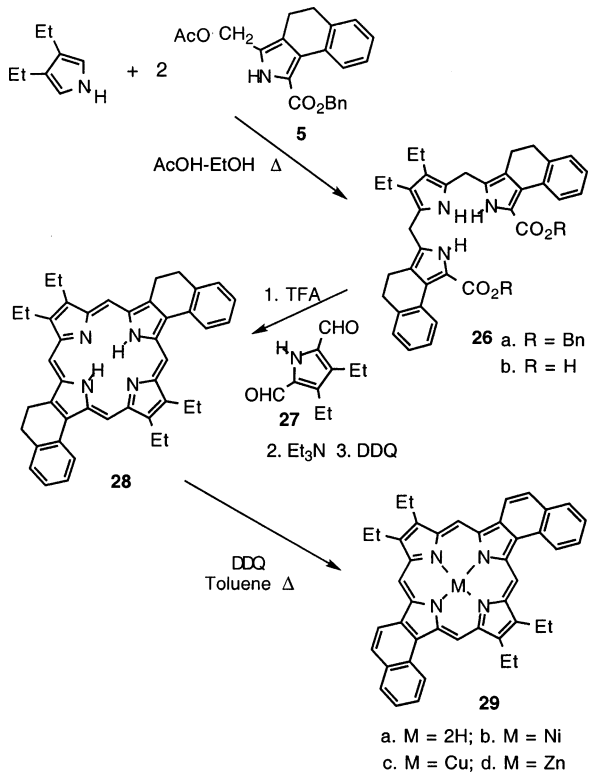
(28) Grigg, R.; Johnson, A. W.; Kenyon, R.; Math, V. B.; Richardson, K. *J. Chem. Soc. C* **1969**, 176.
(29) Smith, K. M.; Minnetian, O. M. *J. Chem. Soc., Perkin Trans. 1* **1986**, 277.
(30) Arsenault, G. P.; Bullock, E.; MacDonald, S. F. *J. Am. Chem. Soc.* **1960**, *82*, 4384.
(31) (a) Jackson, A. H.; Kenner, G. W.; Wass, J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1475. (b) Lash, T. D. *Tetrahedron* **1998**, *54*, 359.

ence of Montmorillonite clay in dichloromethane[32] to afford the corresponding mixed ester dipyrrylmethanes **21**. These were purified by column chromatography but could not be be induced to crystallize. This property is commonly associated with dipyrrylmethanes having mixed terminal *tert*-butyl and benzyl esters.[32] However, these compounds could be taken on in crude form and the *tert*-butyl esters cleaved by treatment with TFA. Further reaction with trimethyl orthoformate−TFA gave the corresponding aldehydes **22** in good yields. The formyl derivatives **22** were easily recrystallized and fully characterized. Cleavage of the benzyl ester protective groups by hydrogenolysis over 10% palladium−charcoal gave the required carboxylic acids **19** in quantitative yields. These underwent self-condensation with *p*-toluenesulfonic acid in methanol−dichloromethane to give the porphodimethene intermediates **23**. Subsequent addition of zinc acetate and air oxidation afforded porphyrins **24** in 27−36% yield. The alkyl substituted porphyrins **24a** and **24b** proved to be too insoluble to take on to the fully conjugated dinaphthoporphyrin system. However, treatment of the dipropionate ester **24c** with 2 equiv of DDQ in refluxing toluene gave the *opp*-dinaphthoporphyrin **25a** in virtually quantitative yield. The related nickel(II), copper(II), and zinc derivatives **25b**−**d** were also prepared and characterized.

Synthesis of Type C Dinaphthoporphyrins. The isomeric *opp*-dinaphthoporphyrin system "type C" has a different symmetry element and cannot be synthesized by the procedures described for the type A or type B systems. However, this system is readily accessible using the "3 + 1" variant on the MacDonald condensation[33−35] (Scheme 4). Two equivalents of acetoxymethylpyrrole **5** was condensed with 3,4-diethylpyrrole under nitrogen in refluxing acetic acid−ethanol[34,36] to give the novel tripyrrane **26a** in 73% yield.

The benzyl ester moieties were cleaved with hydrogen over palladium-charcoal to give the related dicarboxylic acid **26b** (quantitative), and this can be reacted with pyrrole dialdehyde **27** in TFA−dichloromethane and oxidized with DDQ under conventional conditions[34] to give the tetrahydrodinaphthoporphyrin **28** in 51% yield. This convergent route is particularly efficient and could equally well be used in the synthesis of ring fused porphyrin analogue systems.[37] As was the case for the previous *opp*-diannelated system, dehydrogenation of **28** with 2 equiv of DDQ in refluxing toluene occurred smoothly to give a virtually quantitative yield of the *opp*-dinaphthoporphyrin **29a**. Again, the new porphyrin system was metalated with nickel(II), copper(II) or zinc acetate to give the related metalloporphyrins **29b**−**d** (Scheme 4).

SCHEME 4



Synthesis of Type D Dinaphthoporphyrins. The "type D" *adj*-dinaphthoporphyrin system is the least symmetrical of the series and requires the synthesis of an asymmetrical dipyrrylmethane intermediate **30** (Scheme 5). This in turn could be taken on, at least in principle, using the *a*,*c*-biladiene or MacDonald "2 + 2" strategies. Dipyrrylmethane **30** has two naphthalene units (one or both could be in the reduced form), but these have different orientations relative to the pyrrole ester groups and this means that a new naphthopyrrole precursor is required. Although we had avoided the use of fully unsaturated naphtho[1,2-*c*]pyrroles in our initial studies, superior routes to this system were subsequently developed.[38] In addition, it turned out that our qualms about the stability of these compounds were only partly justified. In the Barton−Zard pyrrole synthesis, nitroalkenes react with isocyanoacetate esters in the presence of a non-nucleophilic base to give pyrrole esters.[39,40] This method has been extended to the reaction of nitroaromatic compounds, such as nitrophenanthrene, with isocyanoacetates to give *c*-annelated pyrroles.[41] 1-Nitronaphthalene (**31**) reacted with ethyl isocyanoacetate (**32a**) in

(32) Jackson, A. H.; Pandey, R. K.; Rao, K. R. N.; Roberts, E. *Tetrahedron Lett.* **1985**, *26*, 793.
(33) Lash, T. D. *Chem. Eur. J.* **1996**, *2*, 1197.
(34) (a) Lin, Y.; Lash, T. D. *Tetrahedron Lett.* **1995**, *36*, 9441. (b) Lash, T. D. *J. Porphyrins Phthalocyanines* **1997**, *1*, 29.
(35) (a) Boudif, A.; Momenteau, M. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1235. (b) Sessler, J. L.; Genge, J. W.; Urbach, A.; Sanson, P. *Synlett* **1996**, 187.
(36) Sessler, J. L.; Johnson, M. R.; Lynch, V. *J. Org. Chem.* **1987**, *52*, 4394.
(37) (a) Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533. (b) Lash, T. D.; Chaney, S. T. *Chem. Eur. J.* **1996**, *2*, 944. (c) Lash, T. D.; Hayes, M. J.; Spence, J. D.; Muckey, M. A.; Ferrence, G. M.; Szczepura, L. F. *J. Org. Chem.* **2002**, *67*, 4860.
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(39) (a) Barton, D. H. R.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1985**, 1098. (b) Barton, D. H. R.; Kervagoret, J.; Zard, S. Z. *Tetrahedron* **1990**, *46*, 7587.
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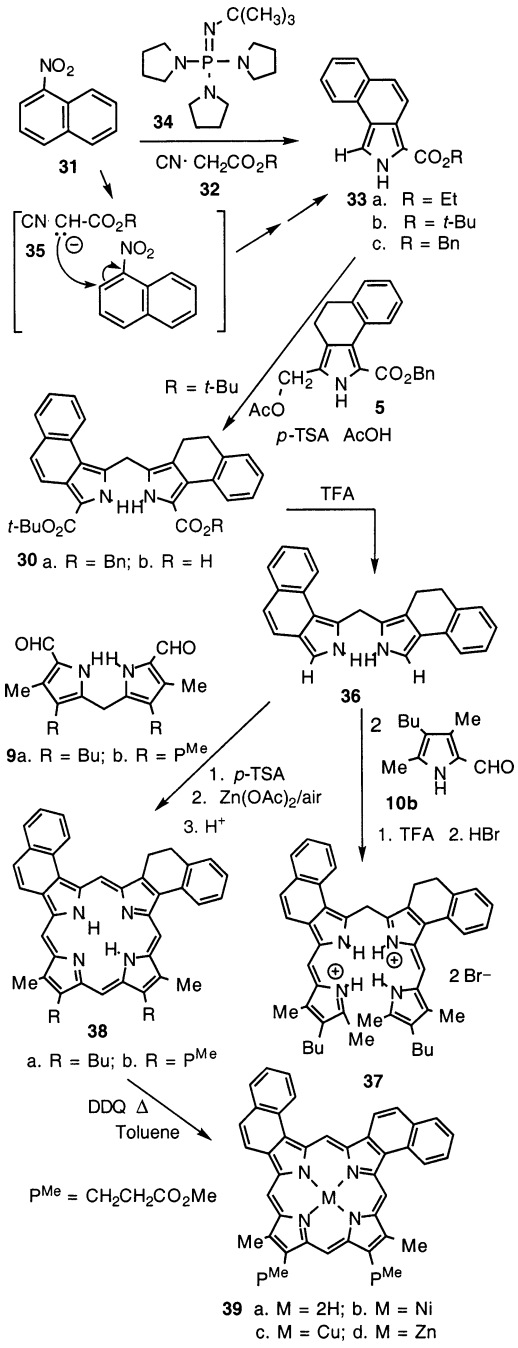
SCHEME 5



the presence of DBU in THF to give low variable yields of naphtho[1,2-*c*]pyrrole **33a**.[38] However, using the phosphazene base **34**,[42] **31** reacted with **32a** to give the required naphthopyrrole **33a** in relatively good yields.[38] In a preliminary investigation, **33a** was obtained in 33% yield[38] but subsequent optimization of this procedure afforded the pyrrolic product in 58% yield. Although phosphazene **34** is a stronger base than DBU, this is probably not directly responsible for the improved yields. The base generates an enolate ion **35** from the isocyanoacetate and the crucial step involves subsequent nucleophilic addition onto the aromatic ring. The more hindered protonated phosphazene is less capable of ion pairing interactions with enolate **35**, and this factor is believed to lead to the enhanced reactivity. A similar argument has been used to rationalize the increased effectiveness of Verkade's superbase in some related chemistry.[43] Condensation of **31** with *tert*-butyl isocyanoacetate (**32b**) similarly afforded the naphthopyrrole *tert*-butyl ester **33b** in 37% yield. However, reaction of **31** with benzyl isocyanoacetate (**32c**) gave poor yields (<10%) of the related naphthopyrrole **33c**, and this result made the use of a benzyl ester protective group at this position impractical for these studies. As the *tert*-butyl ester protective group is also compatible with these investigations, **33b** was reacted with acetoxymethyldihydronaphthopyrrole **5** in acetic acid with a catalytic amount of *p*-toluenesulfonic acid to give the mixed ester dipyrrylmethane **30a** in 58% yield. Hydrogenolysis over 10% Pd/C cleaved the benzyl ester unit to give the corresponding carboxylic acid **30b**. Treatment of **30b** with TFA for 10 min at room temperature cleaves the *tert*-butyl ester group and smoothly decarboxylates the pyrrole carboxylic acid units to give the α-unsubstituted dipyrrylmethane **36**. Initially, this intermediate was taken on via an *a*,*c*-biladiene type route in an attempt to generate the required dinaphthoporphyrin. Reaction of **36** with pyrrole aldehyde **10b** in the presence of HBr, followed by precipitation with anhydrous diethyl ether, gave a crude *a*,*c*-biladiene dihydrobromide salt **37** in 90% yield. Although this material was not pure by NMR spectroscopy, this type of compound is relatively unstable in solution and attempts at purification leads to extensive decomposition. Attempts to cyclize **37** with copper(II) chloride in DMF gave low yields of impure porphyrin products. Slightly better results were obtained using silver iodate and zinc acetate in DMF and this produced impure zinc porphyrins. Demetalation afforded the related porphyrin **34a**, but this appeared to be contaminated with an isomeric species. Oligopyrrolic intermediates can undergo fragmentation−recombination reactions that result in the formation of isomers,[44] but it was unclear whether this problem arose during *a*,*c*-biladiene formation or during the cyclization procedure. As this approach had been unsuccessful, an alternative MacDonald "2 + 2" route was selected. Dipyrrylmethane **30b** was treated with TFA, as before, to give **36** and subsequent acid-catalyzed condensation with diformyldipyrrylmethane **9b** and air oxidation in the presence of zinc acetate gave the required isomerically pure dihydrodinaphthoporphyrin **38a** in 37% yield. Under the same conditions, **36** was reacted with **9c** to give the related porphyrin diester in 36% yield. The dibutyl porphyrin **38a** was poorly soluble and did not give satisfactory results for the dehydrogenation step. However, the diester porphyrin **38b** could be dehydrogenated with DDQ in refluxing toluene to give the dinaphthoporphyrin **39a** in 53% yield. It is notable that the dehydrogenation steps for the two *adj*-dinaphthoporphyrins (type A and D) gave relatively modest results compared to the very high yields obtained for the *opp*-dinaphthoporphyrins series B and

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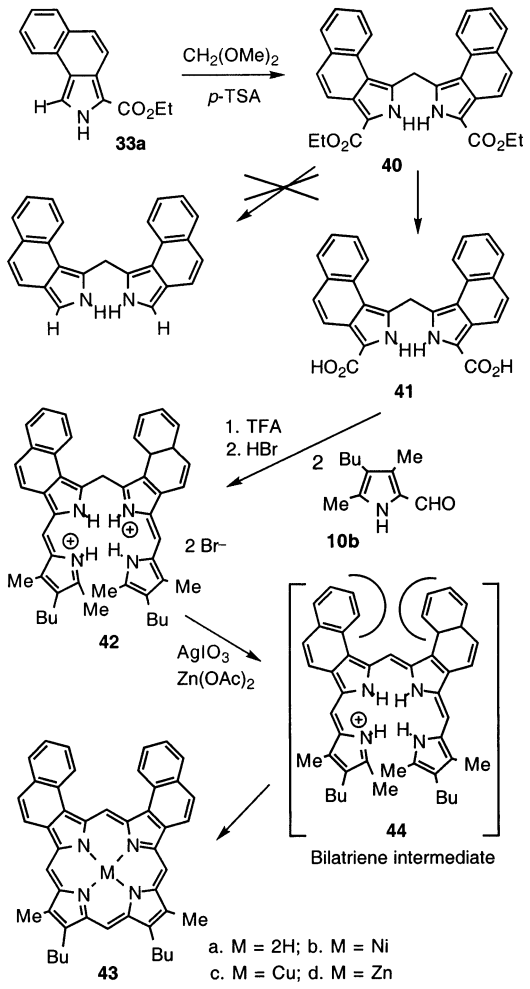
SCHEME 6



C. Nonetheless, these results were satisfactory, and the related metalloderivatives **39b**−**d** could also be generated.

Synthesis of Type E Dinaphthoporphyrins. The synthesis of the final "type E" dinaphthoporphyrin system proved to be the most difficult to accomplish. This work required the availability of a symmetrical dipyrrylmethane **40** (Scheme 6). Naphthopyrrole **33a** was readily available from the Barton−Zard chemistry discussed above. Initially, we favored using the related benzyl ester for these studies but **33c** was obtained in very low yields by reacting 1-nitronaphthalene with benzyl isocyanoacetate. In addition, attempts to transesterify **33a** with benzyl alcohol in the presence of sodium benzyloxide gave rise to extensive decomposition and none of the required benzyl ester could be isolated. Due to these difficulties, the ethyl ester was directly taken on to the dipyrrylmethane. Reaction of **33a** with dimethoxymethane and *p*-toluenesulfonic acid in acetic acid gave dipyrrylmethane **40** in 87% yield. For related dipyrrylmethanes, the ethyl ester units could be saponified with concomitant decarboxylation by treatment with KOH in ethylene glycol under nitrogen at 180 °C. However, these conditions were far too harsh for **40**, and attempts to cleave the ethyl units in this way led to decomposition. The high temperatures allow for clean decarboxylations to occur in many cases to give the corresponding α-unsubstituted pyrroles. However, pyrrolecarboxylic acids decarboxylate at room temperature under acidic conditions, and it was really only necessary to saponify the ester groupings. This was accomplished by refluxing **40** under nitrogen with sodium hydroxide in methanol containing a small amount of hydrazine. Following dilution with water and neutralization with acetic acid, the corresponding dicarboxylic acid **41** was isolated in 81% yield. This compound proved to be somewhat unstable and was used immediately. Attempts to use **41** in MacDonald "2 + 2" condensations failed to give more than a trace amounts of porphyrin products.

However, in contrast to the results for the "type D" system, the *a*,*c*-biladiene route proved to be more successful. The crude diacid was reacted with 2 equiv of formylpyrrole **10b** in the presence of TFA and 30% HBr in acetic acid, and following precipitation with diethyl ether, the *a*,*c*-biladiene dihydrochloride **42** was obtained in 96% yield. Although the NMR spectrum for **42** showed that it was impure, the tetrapyrrole was taken on in crude form. The conventional cyclization procedure using copper(II) chloride in DMF gave no more than trace amounts of porphyrin products. However, treatment of **42** with silver iodate and zinc acetate in DMF[29,45] afforded a zinc complex and following demetalation with TFA, the *adj*-dinaphthoporphyrin **43a** was isolated in 6.8% yield. The low yield may be due in part to a deleterious steric interaction between the two naphthalene units, although the purity of the *a*,*c*-biladiene may also be a factor. In *a*,*c*-biladiene cyclizations, a bilatriene intermediate (i.e., **44**) is formed prior to cyclization,[27] and this would exacerbate the steric problems by changing the hybridization state of bridging carbon atom from sp^3 to sp^2.[46] When the central methylene group is present, the two naphthalenes can easily twist away from one another, but a conjugated center would force these two units into one another. It is less clear why the MacDonald route was unsuccessful, although the instability of dipyrrylmethane **41** is likely to be a factor. Despite the low yields, sufficient quantities of pure porphyrin **43a** were obtained for further study. In addition, the corresponding nickel(II), copper(II) and zinc(II) porphyrins **43b**−**d** were synthesized and spectroscopically characterized.

Spectroscopic Characterization of Dinaphthoporphyrins. Proton and carbon-13 NMR spectroscopy gave spectra for the new porphyrin systems that were consistent with the expected symmetry of the structures and their anticipated aromatic character.[47] The dinaphthoporphyrins were poorly soluble in $CDCl_3$ but gave high quality spectra in TFA−$CDCl_3$. Addition of TFA leads to diprotonation of the porphyrin core to afford the corresponding dications. For instance, porphyrin **29a** (type C, Figure 1) afforded the green dication **29a**H_2^{2+}, and this showed the presence of three upfield resonances at −2.7 (1H), −2.5 (2H), and −1.9 ppm (1H) for the three types of NH protons. The symmetry and aromatic characteristics of **29a**H_2^{2+} is confirmed by the presence of two 2H singlets for the *meso*-protons at 11.1 and 11.5 ppm. The

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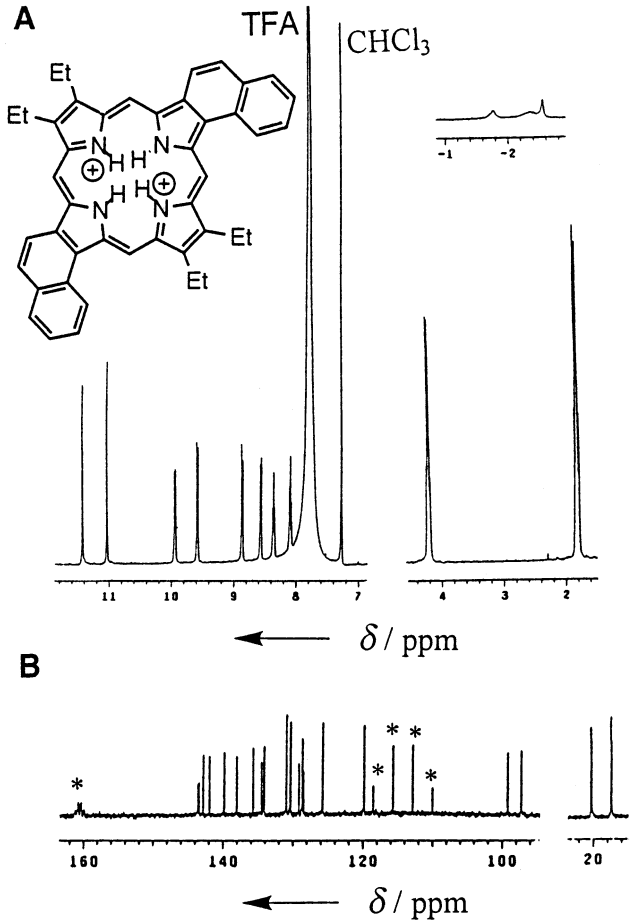

FIGURE 1. (A) 400 MHz proton NMR spectrum of *opp*-dinaphthoporphyrin **29a** in TFA-$CDCl_3$. (B) 100 MHz carbon-13 NMR spectrum of **29a** in TFA−$CDCl_3$. Each of the two peaks near 20 ppm resolve into two resonances at higher scale expansions corresponding to the two slightly different types of ethyl units. Two types of *meso*-carbons can also be seen at 97.3 and 99.2 ppm. The peaks labeled with asterisks correspond to the two quartets from the TFA.

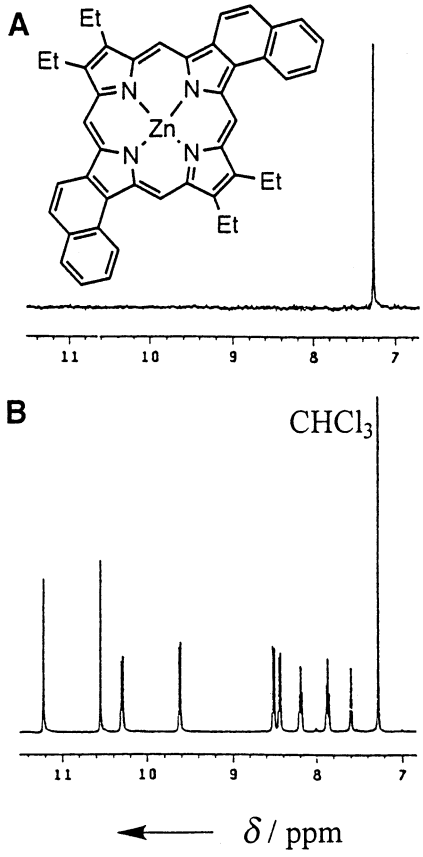

FIGURE 2. Downfield region of the 400 MHz proton NMR spectra for zinc dinaphthoporphyrin **29d** in $CDCl_3$ or pyrrolidine−$CDCl_3$. (A) Proton NMR spectrum of **29d** in $CDCl_3$ showing no sign of the aromatic resonances due to the low solubility of this chelate. (B) This shows the same region after the addition of one drop of pyrrolidine to the NMR tube. The secondary amine coordinates to the zinc porphyrin and greatly increases the solubility producing well-resolved aromatic resonances in the resulting proton NMR spectrum.

naphthalene protons closest to the porphyrin macrocycle are also deshielded giving rise to a 2H doublet at 9.95 ppm (J = 8.4 Hz). The plane of symmetry in **29a**H_2^{2+} leads to an expectation that the 44 carbons will have 18 unique sp^2 environments and 4 sp^3 carbon environments. As expected, the carbon-13 NMR spectrum of **29a** in TFA-$CDCl_3$ shows four resonances between 17 and 21 ppm, two peaks between 97 and 100 ppm, and 16 resonances in the range of 119−144 ppm (Figure 1). The two resonances at 97.3 and 99.2 ppm correspond to the typical values observed for porphyrin *meso*-carbons.[34b,47] The metal complexes of the porphyrins were poorly soluble in organic solvents and gave poor quality NMR spectra due to aggregation. Copper(II) complexes are paramagnetic and no NMR data can be obtained for these species, but the diamagnetic nickel(II) complexes all gave supportive proton NMR spectra. The nickel(II) complex of the type C dinaphthoporphyrin **29b** showed the retention of a strong diatropic ring current, and the *meso*-protons produced two 2H singlets at 10.1 and 10.8 ppm. The naphthalene proton adjacent to the *meso*-position was again deshielded giving a doublet at 9.8 ppm. The zinc complexes are also diamagnetic but aggregation effects led to significantly poorer spectroscopic data. However, addition of a drop of pyrrolidine to the NMR tube allowed solubilization and produced well resolved proton NMR spectra in the aromatic region (Figure 2). This is due to coordination of the secondary amine with the zinc porphyrin which causes deaggregation.[48] In $CDCl_3$, the zinc complex **29d** gave no proton NMR signals but in the presence of pyrrolidine a well-resolved spectrum was obtained. In this case, the *meso*-protons appeared as two 2H protons at 10.5 and 11.2 ppm, while the downfield naphthalene resonance produced a 2H doublet at 10.3 ppm.

Porphyrin free base spectra show a Soret band in the near-UV and a series of four Q-bands in the visible region.[49] For octaethylporphyrin (OEP) in benzene, the Soret band is a strong absorption (log ϵ 5.20) at 400 nm, and this is followed by weaker Q-bands at 498, 532, 568, and 622 nm.[50] Mononaphthoporphyrin **3** in chloroform showed small bathochromic shifts compared to OEP, with

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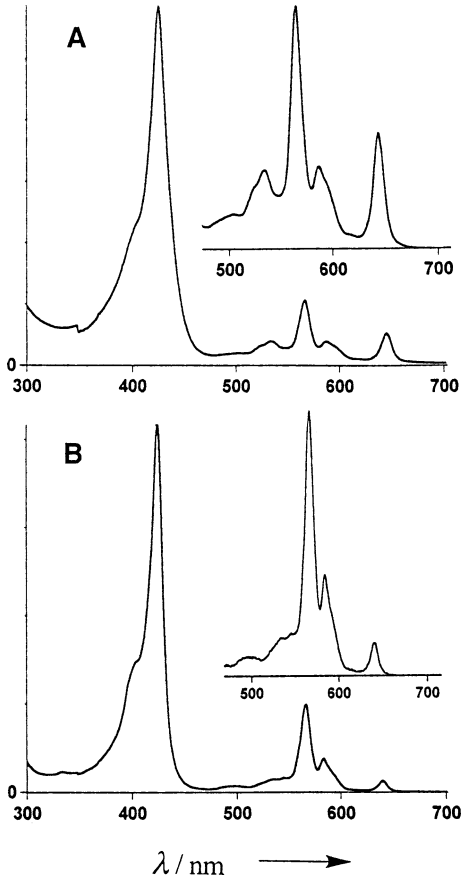
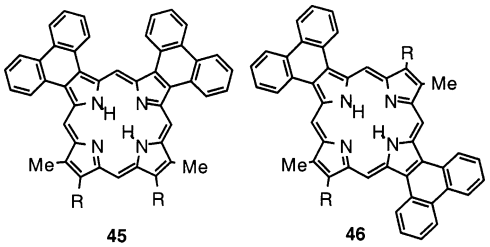


FIGURE 3. UV−vis spectra of free base dinaphthoporphyrins in 1% Et_3N−chloroform: (A) *adj*-dinaphthoporphyrin **39a** (series D); (B) *opp*-dinaphthoporphyrin **29a** (series C).

the Soret band at 415 nm (log ϵ 5.31) and Q-bands at 511, 547, 574, and 630 nm.[14] As anticipated, the free base dinaphthoporphyrins in 1% triethylamine−chloroform showed larger shifts, although the spectra fell into two distinct classes based on the relative positions of ring fusion (Figure 3). The three *adj*-dinaphthoporphyrins gave virtually identical spectra with slightly broadened Soret bands at 426 nm (log ϵ 5.29−5.33) with a shoulder near 400 nm and four defined Q-bands at 535, 567, 587, and 645 nm (all λ_{max} values ±1 nm for series A, D, and E). The ratio of the intensities for the Q-bands, numbered from highest (I) to lowest wavelength (IV),[50] is III > I > II > IV. The *opp*-dinaphthoporphyrins gave UV−vis spectra that differed significantly from the *adj*-series, although minor differences could be seen for porphyrins **25a** and **29a**. Both gave much stronger Soret bands at 425 nm (log ϵ 5.40−5.50) with a more distinct shoulder at 405 nm. The four Q-bands for **25a** were present at λ_{max} values of 529, 565, 585, and 642 nm, while the corresponding bands for **29a** were observed at 531, 567, 584, and 640 nm. In both cases, this region is dominated by Q-band III, while Q-band IV is ill-defined and Q-band I is reduced in intensity compared to the *adj*-series. Overall, the relative intensities are III > II > I > IV. Q-bands II and III are somewhat closer together for the *opp*-systems, but this feature is slightly more pronounced for **29a** ($\Delta\lambda$ 17 nm) compared to **25a** ($\Delta\lambda$ 20 nm). The equivalent Q-band absorptions for *adj*-dinaphthoporphyrins are 25 nm apart. It is noteworthy that these trends

CHART 3. Diphenanthroporphyrins



adj-Diphenanthroporphyrin *opp*-Diphenanthroporphyrin

are further developed for *adj*- and *opp*-diphenanthroporphyrins **45** and **46**, respectively (Chart 3).[15c] Free base **45** gave a Soret band at 433 nm and four Q-bands at 536, 569, 594, and 652 nm (intensities III > I > IV > II). *opp*-Diphenanthroporphyrin **46** showed a Soret band at 429 nm, but Q-band IV could no longer be identified and band I was very weak showing up at λ_{max} 647 nm. In addition, bands II and III for this *opp*-diannelated system appeared at 573 and 591 nm (III ≫ II), values that are again only separated by 18 nm.[15c] Although the *opp*- and *adj*-series of dinaphthoporphyrins have electronic absorption spectra that are quite dissimilar from one another, the individual members of the *adj*-series give virtually identical UV−vis spectra. Series E, in particular, might have been expected to show some differences due to steric interactions, but the data do not show any significance differences for series A, D or E. In 2% TFA−chloroform, the related dications are generated and the UV−vis spectra for these species were also examined. Again, the *adj*-dinaphthoporphyrins gave very similar spectra with a Soret band at 437 nm and two major Q-bands at 580 and 630 nm (Figure 4). However, the dications for *opp*-series B and C were quite different from one another (Figure 4). Porphyrin **25a** (series B) in 2% TFA−chloroform gave a split Soret band with absorptions at 427 and 449 nm and a complex series of Q-bands at 570 (infl), 585, 623, and 636 nm. Porphyrin **29a** (series C) also gave a split Soret band with absorptions at 429 and 446 nm, but the Q-band region was less complicated showing only two major bands at 581 and 626 nm. Hence, the orientation of the naphthalene rings in the *opp*-series does have a significant impact on the UV−vis spectra for the dications. The diphenanthroporphyrins **45** and **46** again show useful comparisons.[15c] As was the case for the *adj*-dinaphthoporphyrins, **45**H_2^{2+} gave a single Soret band, albeit shifted to 448 nm, and two Q-bands at 583 and 632 nm. On the other hand, *opp*-diphenanthroporphyrin **46**H_2^{2+} gave a split Soret band at λ_{max} 438 and 459 nm that was similar to the spectra for **25a**H_2^{2+} and **29a**H_2^{2+} and Q-bands at 583 and 635 nm.[15c] Hence, the trends exhibited for *adj*- vs *opp*-dinaphthoporphyrins clearly apply to systems with larger ring fused units as well. The metallo derivatives of the dinaphthoporphyrins showed further variations, but these results were complicated by aggregation processes. Although the zinc complexes were better dissolved in solutions containing pyrrolidine, coordination from the secondary amine nitrogen can also alter the spectra. As an example, the *opp*-diannealed metalloporphyrins **29b**−**d** (series C) show increasing bathochromic shifts going across the period table from nickel to copper to zinc. This behavior is typical of porphyrins in general[50] and is also demon-

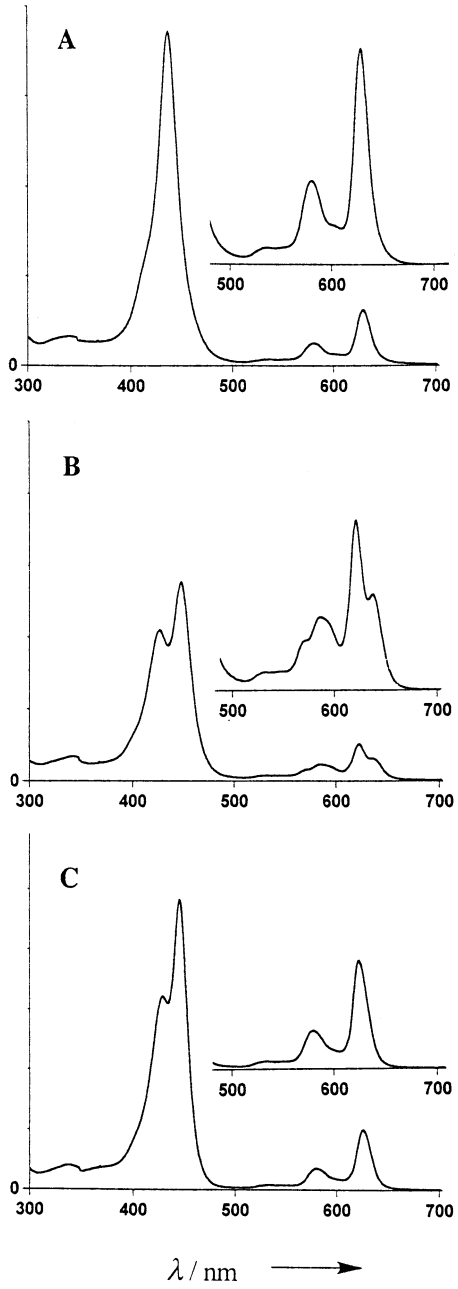


FIGURE 4. UV−vis spectra of dinaphthoporphyrin dications in 2% TFA−chloroform: (A) *adj*-dinaphthoporphyrin **39a**H_2^{2+} (series D); (B) *opp*-dinaphthoporphyrin **25a**H_2^{2+} (series B); (C) *opp*-dinaphthoporphyrin **29a**H_2^{2+} (series C).

strated for the metallo derivatives of the other dinaphthoporphyrin series as well. In chloroform, the nickel(II) complex **29b** is observed at 420 nm with a minor β band at 546 nm and a stronger α band at 591 nm. The equivalent bands were present at 424, 550, and 596 nm for copper(II) complex **29c**, while the zinc chelate **29d** showed these absorptions at 430, 563, and 603 nm. In 2% pyrrolidine−chloroform, the zinc complexes showed sharpened Soret bands and the absorptions were shifted to longer wavelengths (the corresponding bands for **29d** in 2% pyrrolidine-chloroform gave λ_{max} values at 444, 568, and 611 nm, respectively). In general, the absorption bands for the *opp*-dinaphthoporphyrins were shifted to slightly longer wavelengths than the *adj*-dinaphthoporphyrins, although minor differences between all five series can be seen. Full details of these spectra are provided in the Experimental Section and the Supporting Information, and the trends and variations observed for these compounds will be useful in developing an understanding of the conjugation effects in this type of extended porphyrin chromophore. However, a full discussion of the metalloporphyrin electronic absorption spectra goes beyond the scope of this paper.

Conclusions

The synthesis of five isomeric dinaphthoporphyrin systems has been accomplished by making use of several different versions of the MacDonald condensation and *a*,*c*-biladiene cyclizations. In fact, a range of synthetic options were needed to obtain this series of extended porphyrin chromophores due to the symmetry and stability factors that had to be taken into account. In four of the syntheses, one or both of the naphthalene rings were introduced in a reduced form and subsequently dehydrogenated with DDQ in refluxing toluene. This chemistry worked reasonably well in all four cases, but much better results were obtained for the two *opp*-dinaphthoporphyrin systems. Good overall yields were obtained for the type A, B, C, and D porphyrins, but the *a*,*c*-biladiene cyclization leading to the type E dinaphthoporphyrin only occurred in 6.8% yield. Nonetheless, all five structural types were isolated and characterized as the free base and diprotonated forms, and the related nickel(II), copper(II), and zinc(II) complexes. The two *opp*-dinaphthoporphyrins show distinctly different UV−vis spectra from the three *adj*-dinaphthoporphyrins, and more subtle effects could also be seen in the dication and metalloporphyrin spectra due to differences in the relative orientations of the naphthalene rings. This work provides a comprehensive set of matched structures that should allow for a greater understanding of conjugation effects in porphyrin systems.

Experimental Section

Synthesis of Dinaphthoporphyrin Type A. 4,5-Dihydro-3-methylnaphtho[1,2-*c*]pyrrole-1-carbaldehyde (14). Ethyl 4,5-dihydro-3-methylnaphtho[1,2-*c*]pyrrole-1-carboxylate[14] (**4a**; 2.00 g) was refluxed with sodium hydroxide (2.0 g) in ethylene glycol (20 mL). The solution was dispersed between hexane and water and the aqueous solution extracted with hexane. The combined organic solutions were washed with water and dried over sodium sulfate. After the drying agent was filtered off, a yellow oil was obtained by evaporation of the solvent under reduced pressure. The residue was dissolved in trifluoroacetic acid (8 mL) and cooled to 0 °C in a salt/ice bath. Trimethyl orthoformate (2.5 mL) was added dropwise by syringe, maintaining the temperature at 0 °C throughout. The salt/water bath was removed, and the mixture was allowed to stir at room temperature for 5 min. The mixture was poured into ice/water, and after the product had precipitated out, the solid material was filtered off and washed with water. Recrystallization from methanol gave the aldehyde (1.507 g, 91%) as shiny off-white crystals: mp 214−215 °C; IR (Nujol mull) ν 3248 (NH str.), 1633 cm^{-1} (C=O str); ^1H NMR ($CDCl_3$) δ 2.32 (3H, s), 2.58 (2H, q, J = 7 Hz), 2.88 (2H, q, J = 7 Hz), 7.21−7.30 (3H, m), 7.64 (1H, d, J = 7.2 Hz), 9.89 (1H, s), 9.93 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 11.5, 19.6, 30.6, 121.4, 126.4, 126.8, 127.2, 127.7, 129.0, 130.9, 131.7, 132.3, 138.0, 177.4; EI MS (70 eV) *m/z* (rel int) 212 (18), 211 (100, M^+), 210

(38, $[M - H]^+$), 182 (73, $[M - CHO]^+$), 167 (24). Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.32; H, 6.03; N, 6.52.

Ethyl 3-Methylnaphtho[1,2-*c*]pyrrole-1-carboxylate (12). Dihydronaphthopyrrole **4a**[14] (5.00 g) and xylene (250 mL) were placed in a round-bottom reaction flask and purged with nitrogen. Palladium−charcoal (10%; 5.00 g) was carefully added to the flask and washed in with an additional portion of xylene. The mixture was refluxed for 2 h. The catalyst was filtered off and the solvent evaporated on a rotory evaporator using a vacuum pump. Recrystallization from 95% ethanol gave the naphthopyrrole (3.704 g, 75%) as flaky pink crystals: mp 166.5−167 °C (lit.[51] mp 190−191 °C); IR (Nujol mull) ν 3280 (NH str), 1635 cm^{-1} (C=O str); ^1H NMR ($CDCl_3$) δ 1.48 (3H, t, J = 7 Hz), 2.64 (3H, s), 4.48 (2H, q, J = 7 Hz), 7.36 (1H, d, J = 9.2 Hz), 7.46 (1H, d, J = 8.8 Hz), 7.51 (1H, t), 7.58 (1H, t), 7.79 (1H, d, J = 7.6 Hz), 9.77 (1H, d, J = 8.4 Hz), 9.88 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 11.6, 14.9, 60.5, 112.3, 118.7, 122.4, 123.9, 125.6, 126.2, 126.4, 127.9, 128.2, 128.4, 133.3, 160.8; EI MS (70 eV) *m/z* (rel int) 254 (16), 253 (78, M^+), 224 (1.6), 207 (100, $[M - EtOH]^+$), 179 (48, $[M - EtOH - CO]^+$). Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.92; H, 5.87; N, 5.51.

8,12-Diethyl-1,7,13,19-tetramethyl-2^1,2^2,10,18^1,18^2,23-hexahydrodinaphtho[1,2-*b*:2,1-*q*]bilin Dihydrobromide (16a). Dipyrrole **15a**[52] (0.724 g) was dissolved in trifluoroacetic acid (4.35 mL). After the mixture was stirred for 10 min, aldehyde **14** (0.985 g) in methanol (18 mL) was added, followed immediately by 30% HBr−AcOH (3.5 mL). After the mixture was stirred for 30 min, anhydrous ether (110 mL) was added dropwise and the resulting mixture stirred for an additional 2 h. The red/brown precipitate was filtered off and washed well with ether. Upon vacuum-drying overnight, the title compound (1.650 g, 93%) was obtained as a red/brown powder: mp 236 °C dec; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 473 (4.31), 553 nm (5.25); ^1H NMR ($CDCl_3$) δ 0.71 (6H, t, J = 7.4 Hz), 2.27 (6H, s), 2.57−2.64 (8H, m), 2.76 (6H, s), 2.92 (4H, t, J = 7.2 Hz), 5.28 (2H, s), 7.34−7.41 (6H, m), 7.60 (2H, d, J = 7.2 Hz), 7.63 (2H, s), 13.21 (2H, s), 13.60 (2H, s);^{13}C NMR ($CDCl_3$) δ 10.2, 13.1, 14.1. 17.7, 19.2, 26.1, 30.2, 122.7, 124.6, 125.9, 127.2, 127.5, 127.7, 129.3, 129.5, 130.1, 132.9, 139.4, 141.7, 143.0, 150.5, 152.4. Anal. Calcd for $C_{43}H_{46}N_4Br_2$: C, 66.33; H, 5.95; N, 7.19. Found: C, 65.85; H, 5.94; N, 7.13.

8,12-Bis(2-methoxycarbonylethyl)-1,7,13,19-tetramethyl-2^1,2^2,10,18^1,18^2,23-hexahydrodinaphtho[1,2-*b*:2,1-*q*]bilin Dihydrobromide (16b). The *a*,*c*-biladiene was prepared by the previous procedure from dipyrrylmethane **15b**[52] (1.03 g) and pyrrolecarbaldehyde **14** (0.972 g). Following filtration and vacuum-drying, the tetrapyrrole (1.60 g, 75%) was obtained as a red/metallic green powder: mp 187−188 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 471 (4.49), 547 nm (5.26); ^1H NMR ($CDCl_3$) δ 2.09 (4H, t, J = 7.6 Hz), 2.29 (6H, s), 2.62 (4H, t, J = 7.4 Hz), 2.77 (6H, s), 2.86−2.94 (8H, m), 3.46 (6H, s), 5.34 (2H, s), 7.36−7.40 (6H, m), 7.59 (2H, d, J = 6.8 Hz), 7.64 (2H, s), 13.30 (2H, s), 13.68 (2H, s); ^{13}C NMR ($CDCl_3$) δ 10.4, 13.1, 19.2, 19.8, 25.9, 30.2, 34.1, 51.6, 123.3, 125.1, 126.0, 127.0, 127.8, 127.9, 128.9, 129.6, 129.9, 139.4, 142.2, 143.4, 149.5, 153.6, 173.0. Anal. Calcd for $C_{47}H_{50}N_4O_4Br_2 \cdot H_2O$: C, 61.85; H, 5.74; N, 6.14. Found: C, 61.34; H, 5.60; N, 6.12.

13,17-Diethyl-12,18-dimethyl-3^1,3^2,7^1,7^2-tetrahydrodinaphtho[1,2-*b*:2,1-*g*]porphyrin (17a). *a*,*c*-Biladiene **16a** (1.119 g) was added to a stirred solution of copper(II) chloride (2.91 g) in DMF (485 mL). The flask was covered with foil and the solution stirred at room temperature for 2 h. The solution was diluted with dichloromethane (135 mL) and washed with water (3 × 125 mL), and each of the aqueous layers was back-extracted with dichloromethane. The organic layers were combined, dried over sodium sulfate, and filtered, and the solvent was evaporated on a rotary evaporator, first under aspirator pressure and then using a vacuum pump. The residue was taken up in 15% sulfuic acid/trifluoroacetic acid (121 mL) and stirred at room temperature for 45 min. The solution was diluted with dichloromethane and washed with 5% aqueous sodium bicarbonate solution. All of organic layers were combined and dried over sodium sulfate, and the solvent was evaporated under reduced pressure to give a dark purple solid. The residue was chromatographed on a grade 3 alumina column, eluting with dichloromethane. Recrystallization from chloroform−methanol gave the title porphyrin (329 mg, 38%) as a purple solid: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 412 (5.21), 511 (4.18), 548 (4.18), 578 (3.90), 633 nm (3.74); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 410 (5.24), 564 (4.325), 603 nm (4.01); ^1H NMR ($CDCl_3$) δ −3.41 (2H, br s), 1.89 (6H, t, J = 7.6 Hz), 3.61 (4H, t, J = 7 Hz), 3.66 (6H, s), 4.10 (4H, q, J = 7.6 Hz), 4.31 (4H, t, J = 7.2 Hz), 7.52 (2H, t, J = 7.6 Hz), 7.72 (2H, d, J = 7.2 Hz), 7.79 (2H, t, J = 7.4 Hz), 9.02 (2H, d, J = 7.6 Hz), 10.08 (1H, s), 10.20 (1H, s), 10.62 (2H, s); ^1H NMR (TFA−$CDCl_3$) δ −3.40 (2H, br s), −3.04 (2H, br s), 1.73 (6H, t, J = 7.6 Hz), 3.63 (6H, s), 3.88 (4H, t, J = 7.4 Hz), 4.12 (4H, q, J = 7.6 Hz), 4.25 (4H, t, J = 7.6 Hz), 7.63 (2H, t, J = 7.4 Hz), 7.77−7.81 (4H, m), 8.57 (2H, d, J = 7.6 Hz), 10.58 (1H, s), 10.77 (1H, s), 10.99 (2H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.0, 16.5, 20.3, 22.4, 29.7, 97.7, 100.2, 101.1, 128.7, 129.4, 129.9 (2), 130.5, 136.2, 138.3, 138.7, 139.0, 139.2, 142.0, 142.9, 143.3, 144.3; HRMS (FAB) calcd for $C_{42}H_{38}N_4$ + H *m/z* 599.3175, found 599.3177. Anal. Calcd for $C_{42}H_{38}N_4 \cdot {}^1/_{10}$-$CHCl_3$: C, 82.80; H, 6.29; N, 9.17. Found: C, 82.54; H, 6.27; N, 9.15.

13,17-Bis(2-methoxycarbonylethyl)-12,18-dimethyl-3^1,3^2,7^1,7^2-tetrahydrodinaphtho[1,2-*b*:2,1-*g*]porphyrin (17b). The porphyrin was prepared by the previous procedure from *a*,*c*-biladiene **16b** (0.25 g) and copper(II) chloride (0.55 g) in DMF (93 mL). Following demetalation with 15% sulfuric acid/trifluoroacetic acid (23.5 mL) and extraction, the crude product was obtained as a dark purple/metallic green solid. This was chromatographed on grade III alumina, eluting with dichloromethane. Recrystallization from chloroform−methanol gave **17b** (64 mg, 34%) as a purple solid: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 412 (5.26), 512 (4.20), 548 (4.19), 579 (3.91), 635 nm (3.72); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 410 (5.26), 564 (4.33), 604 nm (4.01); ^1H NMR ($CDCl_3$) δ −3.49 (2H, br s), 3.30 (4H, t, J = 7.8 Hz), 3.61 (4H, t, J = 7 Hz), 3.67 (12H, s), 4.29 (4H, t, J = 7 Hz), 4.42 (4H, t, J = 7.6 Hz), 7.53 (2H, t, J = 7.4 Hz), 7.72 (2H, d, J = 7.6 Hz), 7.79 (2H, t, J = 7.2 Hz), 8.99 (2H, d, J = 7.2 Hz), 10.08 (1H, s), 10.17 (1H, s), 10.60 (2H, s); ^1H NMR (TFA-$CDCl_3$) δ −3.62 (2H, br s), −3.16 (2H, br s), 3.14 (4H, t, J = 7.6 Hz), 3.66 (6H, s), 3.69 (6H, s), 3.89 (4H, t, J = 7.6 Hz), 4.26 (4H, t, J = 7.4 Hz), 4.50 (4H, t, J = 7.8 Hz), 7.65 (2H, t, J = 7.4 Hz), 7.77−7.81 (4H, m), 8.55 (2H, d, J = 8 Hz), 10.81 (1H, s), 10.91 (1H, s), 11.03 (2H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.2, 21.8, 22.4, 29.7, 35.6, 52.8, 98.9, 100.5, 101.2, 128.8, 129.5, 129.9, 130.1, 130.3, 136.7, 139.1, 139.3, 139.5, 140.3, 142.3, 142.7, 143.1, 175.1; HRMS (FAB) calcd for $C_{46}H_{42}N_4O_4$ + H *m/z* 715.3284, found 715.3282. Anal. Calcd for $C_{46}H_{42}N_4O_4$: C, 77.29; H, 5.92; N, 7.84. Found: C, 76.86; H, 5.86; N, 7.74.

13,17-Bis(2-methoxycarbonylethyl)-12,18-dimethyldinaphtho[1,2-*b*:2,1-*g*]porphyrin (18a). Porphyrin **17b** (25 mg) was refluxed with DDQ (21. 2 mg) in toluene (10 mL) for 40 min. The solvent was evaporated under reduced pressure and the residue chromatographed on silica eluting initially with dichloromethane and then with chloroform. Recrystallization from chloroform−methanol gave the dinaphthoporphyrin (15 mg, 60%) as a purple solid: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 426 (5.33), 535 (4.11), 567 (4.57), 587 (4.13), 645 nm (4.25); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 437 (5.38), 581 (4.23), 630 nm (4.62); ^1H NMR ($CDCl_3$) δ −5.04 (2H, br s), 3.23 (4H, t, J = 8 Hz), 3.38 (6H, s), 3.71 (6H, s), 4.26 (4H, t, J = 8 Hz), 7.91 (2H, t, J = 7.2 Hz), 8.90 (2H, t, J = 7.2 Hz), 8.25 (2H, d, J = 7.6 Hz), 8.38 (2H, d, J = 8 Hz),

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8.70 (2H, br d), 9.27 (1H, br s), 9.66 (2H, d, J = 7.2 Hz), 9.74 (1H, s), 10.15 (2H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −2.40 (4H, two overlapping broad singlets), 3.14 (4H, t, J = 7.5 Hz), 3.65 (6H, s), 3.74 (6H, s), 4.49 (4H, t, J = 7.5 Hz), 8.11 (2H, t, J = 7.4 Hz), 8.37 (2H, t, J = 7.6 Hz), 8.58 (2H, d, J = 8.4 Hz), 8.91 (2H, d, J = 8.4 Hz), 9.67 (2H, d, J = 8.8 Hz), 9.98 (2H, d, J = 8.4 Hz), 10.95 (1H, s), 11.47 (2H, s), 11.50 (1H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.2, 21.8, 35.7, 53.1, 94.5, 100, 100.7, 119.9, 125.6, 128.9, 129.1, 130.4, 131.0, 134.2, 135.9, 137, 139.8, 140.2, 140.8, 142.7, 175.6; HRMS (FAB) calcd for $C_{46}H_{38}N_4O_4$ + H *m/z* 711.2971, found 711.2969. Anal. Calcd for $C_{42}H_{38}N_4.{}_1/_{10}CHCl_3$: C, 76.61; H, 5.31; N, 7.75. Found: C, 76.87; H, 5.36; N, 7.70.

Nickel(II) Complex 18b. Porphyrin **18a** (7.5 mg) and nickel(II) acetate tetrahydrate (27 mg) were heated for 2 h under reflux in DMF (10 mL). The solution was diluted with chloroform, washed with water, and evaporated to dryness under reduced pressure. Recrystallization from chloroform−methanol gave the nickel(II) complex (6 mg, 80%) as purple crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 419 (5.21), 546 (4.01), 588 nm (4.70); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 422 (4.91), 449 (5.26), 570 (4.22), 592 (4.39), 603 nm (4.42); HRMS (FAB) calcd for $C_{46}H_{36}N_4O_4Ni$ *m/z* 766.2090, found 766.2090.

Copper(II) Complex (18c). Porphyrin **18a** (7 mg) and copper(II) acetate monohydrate (25 mg) were heated for 2 h under reflux in DMF (10 mL). The solution was diluted with chloroform, washed with water, and evaporated to dryness on a rotary evaporator. Recrystallization from chloroform−methanol gave the copper(II) complex (6 mg, 80%) as purple crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 421 (5.26), 552 (3.96), 594 nm (4.52); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 421 (5.17), 442 (sh, 4.79), 555 (3.98), 595 nm (4.50); HRMS (FAB) calcd for $C_{46}H_{36}N_4O_4Cu$ *m/z* 771.2032, found 771.2033.

Zinc Complex (18d). Porphyrin **18a** (7.0 mg) and zinc acetate dihydrate (27 mg) were heated for 2 h under reflux in DMF (10 mL). The solution was diluted with chloroform, washed with water, and evaporated under reduced pressure. Recrystallization from chloroform−methanol gave the zinc chelate (7 mg, 92%) as purple crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (rel int) 407 (infl, 0.216), 433 (1.00), 561 (0.057), 601 (0.170); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 417 (4.73), 441 (5.57), 568 (4.27), 608 nm (4.64); ^{1}H NMR (pyrrolidine−$CDCl_3$; downfield region only) δ 7.83 (2H, t, J = 7.4 Hz), 8.13 (2H, t, J = 7.4 Hz), 8.39 (2H, d, J = 8 Hz), 8.46 (2H, d, J = 8 Hz), 9.54 (2H, d, J = 8 Hz), 10.03 (1H, s), 10.20 (2H, d, J = 8 Hz), 10.78 (1H, br s), 11.06 (2H, s); HRMS (FAB) calcd for $C_{46}H_{36}N_4O_4Zn$ *m/z* 772.2028, found 772.2025.

Synthesis of Dinaphthoporphyrin Type B. Benzyl 3-(3-Ethyl-5-formyl-4-pyrrolylmethyl)-4,5-dihydronaphtho-[1,2-*c*]pyrrole-1-carboxylate (22a). Montmorillonite clay (K10, 5.5 g) was added to a solution of benzyl 2-acetoxymethyl-3,4-dihydronaphtho[2,1-*c*]pyrrole-1-carboxylate[14] (**5**; 1.388 g) and *tert*-butyl 4-ethyl-3-methylpyrrole-2-carboxylate[39] (**20a**; 0.90 g) in dichloromethane (84 mL) and the mixture stirred vigorously overnight. The mixture was filtered, the clay washed with dichloromethane, and the solvent evaporated under reduced pressure. The residual oil was chromatographed on silica, eluting initially with 2% ethyl acetate−toluene and then gradually increasing the polarity to 15% ethyl acetate−toluene. Benzyl 3-(5-*tert*-butyloxycarbonyl-3-ethyl-4-methylpyrrolylmethyl)-3,4-dihydronaphtho[2,1-*c*]pyrrole-1-carboxylate (1.650 g, 85%) was isolated in crude form as a gum that could not be induced to crystallize: IR (Nujol mull) ν 3330 (NH str), 1696, 1643 cm^{-1} (C=O str); ^{1}H NMR ($CDCl_3$) δ 1.01 (3H, t, J = 7.6 Hz), 1.53 (9H, s), 2.25 (3H, s), 2.39 (2H, q, J = 7.6 Hz), 2.55 (2H, t, J = 7 Hz), 2.85 (2H, t, J = 7 Hz), 3.90 (2H, s), 5.30 (2H, s), 7.14−7.40 (8H, m), 8.36−8.39 (1H, m), 8.71 (1H, br s), 8.94 (1H, br s). The *tert*-butyl ester **21a** (2.197 g) was dissolved in trifluoroacetic acid (11.5 mL), stirred at room temperature for 15 min, and then cooled to 0 °C using an ice/salt bath. Trimethyl orthoformate (3.60 mL) was added dropwise keeping the temperature at 0 °C. The mixture was stirred for 5 min at room temperature and then poured into ice/water and allowed to stand for 1−2 h. The precipitate was filtered, washed with water, and recrystallized from 95% ethanol to give the aldehyde (1.051 g, 55%) as off-white crystals: mp 201−202 °C; IR (Nujol mull) ν 3289 (NH str), 1712 (ester C=O str), 1611 cm^{-1} (CH=O str); ^{1}H NMR ($CDCl_3$) δ 1.07 (3H, t, J = 7.5 Hz), 2.18 (3H, s), 2.49 (2H, q, J = 7.5 Hz), 2.71 (2H, t, J = 7 Hz), 2.90 (2H, t, J = 7 Hz), 3.97 (2H, s), 5.27 (2H, s), 7.03 (1H, t, J = 7.4 Hz), 7.11−7.25 (5H, m), 7.28 (2H, d, J = 8 Hz), 8.47 (1H, d, J = 8 Hz), 9.22 (1H, s), 11.04 (1H, br s), 11.56 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 9.1, 15.5, 17.3, 20.5, 22.6, 31.3, 66.0, 116.4, 120.9, 125.4, 126.7, 126.9, 127.5, 127.7, 127.9, 128.0, 128.1, 128.2, 128.5, 128.8, 131.2, 134.2, 136.3, 137.4, 137.6, 160.9, 176.7. Anal. Calcd for $C_{29}H_{28}N_2O_3$: C, 76.97; H, 6.24; N, 6.19. Found: C, 76.83; H, 6.44; N, 6.36.

Benzyl 3-(5-Formyl-3,4-dimethylpyrrolylmethyl)-4,5-dihydronaphtho[2,1-*c*]pyrrole-1-carboxylate (22b). Benzyl 3-(5-*tert*-butyloxycarbonyl-3,4-dimethylpyrrolylmethyl)-3,4-dihydronaphtho[2,1-*c*]pyrrole-1-carboxylate (**21b**) was prepared by the foregoing procedure from **5**[14] (1.343 g) and *tert*-butyl 3,4-methylpyrrole-2-carboxylate[39] (**20b**; 0.87 g). Following chromatography, as described for **22a**, the product **21b** (1.562 g, 86%) was isolated as a yellow gum that could not be induced to crystallize: ^{1}H NMR ($CDCl_3$) δ 1.53 (9H, s), 1.93 (3H, s), 2.22 (3H, s), 2.55 (2H, t, J = 7 Hz), 2.84 (2H, t, J = 7 Hz), 3.89 (2H, s), 5.31 (2H, s), 7.14−7.40 (8H, m), 8.36−8.39 (1H, m), 8.64 (1H, br s), 8.91 (1H, br s). The formyl derivative was prepared by the previous procedure by reacting **21b** (1.917 g) with TFA−$CH(OMe)_3$. Recrystallization from 95% ethanol gave the dipyrrylmethane aldehyde (1.101 g, 67%) as an off-white powder: mp 222.5−223.5 °C; IR (Nujol mull) ν 3288 (NH str), 1691 (ester C=O str), 1620 cm^{-1} (C=O str); ^{1}H NMR ($CDCl_3$) δ 2.02 (3H, s), 2.14 (3H, s), 2.71 (2H, t, J = 7 Hz), 2.89 (2H, t, J = 7 Hz), 3.96 (2H, s), 5.28 (2H, s), 7.07 (1H, t, J = 7.6 Hz), 7.14−7.23 (5H, m), 7.28 (2H, d, J = 7.6 Hz), 8.45 (1H, d, J = 7.2 Hz), 9.21 (1H, s), 10.99 (1H, br s), 11.52 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 8.8, 9.3, 20.6, 22.8, 31.3, 65.9, 116.3, 118.7, 121.0, 126.7, 126.9, 127.5, 127.7, 127.9, 128.0, 128.1, 128.2, 128.5, 128.6, 131.2, 134.8, 136.3, 137.4, 138.0, 160.9, 176.6. Anal. Calcd for $C_{28}H_{26}N_2O_3$: C, 76.69; H, 5.97; N, 6.39. Found: C, 76.53; H, 5.88; N, 6.23.

Benzyl 3-(5-Formyl-3(2-methoxycarbonylethyl)-4-methylpyrrolylmethyl)-4,5-dihydronaphtho[2,1-*c*]pyrrole-1-carboxylate (22c). Benzyl 3-(5-*tert*-butyloxycarbonyl-3(2-methoxycarbonylethyl)-4-methylpyrrolylmethyl)-3,4-dihydronaphtho[2,1-*c*]pyrrole-1-carboxylate (**21c**) was prepared by the foregoing procedure from **5**[14] (3.80 g) and *tert*-butyl 3-(2-methoxycarbonylethyl)-4-methylpyrrole-2-carboxylate[39] (**20c**; 2.85 g). Following chromatography on silica, eluting with 5% ethyl acetate−toluene, the dipyrrylmethane (5.60 g, 95%) was isolated as a reddish gum that could not be induced to crystallize: ^{1}H NMR ($CDCl_3$) δ 1.52 (9H, s), 2.24 (3H, s), 2.47 (2H, t, J = 7.0 Hz), 2.62 (2H, t, J = 7 Hz), 2.73 (2H, t, J = 7.0 Hz), 2.88 (2H, t, J = 7 Hz), 3.53 (3H, s), 3.98 (2H, s), 5.31 (2H, s), 7.16−7.40 (8H, m), 8.38−8.41 (1H, m), 8.59 (1H, br s), 9.46 (1H, br s). The title aldehyde was prepared from **21c** (2.44 g) by the previous procedure. Recrystallization from 95% ethanol gave the product (1.45 g, 68%) as pale brown crystals: mp 181−181.5 °C; IR (Nujol mull) ν 3259 (NH str), 1730 (propionate C=O str), 1694 (pyrrole ester C=O str), 1613 cm^{-1} (CH=O str); ^{1}H NMR ($CDCl_3$) δ 2.19 (3H, s), 2.44 (2H, t, J = 7.6 Hz), 2.68 (2H, t, J = 7 Hz), 2.78 (2H, t, J = 7.6 Hz), 2.88 (2H, t, J = 7 Hz), 3.64 (3H, s), 4.01 (2H, s), 5.27 (2H, s), 7.11 (1H, t, J = 7 Hz), 7.12−7.24 (5H, m), 7.30 (2H, d, J = 7.2 Hz), 8.42 (1H, dd, J = 2.0, 7.2 Hz), 9.29 (1H, s), 10.61 (1H, br s), 10.91 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 9.1, 19.3, 20.5, 22.8, 31.2, 34.7, 51.9, 66.1, 116.5, 121.3, 121.5, 126.7, 127.0, 127.2, 127.7, 127.9, 128.0, 128.2, 128.3, 128.6, 128.9, 131.0, 133.5, 136.3, 137.2, 137.4, 160.9, 173.5, 176.9. Anal. Calcd for $C_{31}H_{30}N_2O_5$: C, 72.92; H, 5.92; N, 5.49. Found: C, 72.62; H, 5.87; N, 5.58.

3-(3-Ethyl-5-formyl-4-methyl-2-pyrrolylmethyl)-4,5-dihydronaphtho[1,2-*c*]pyrrole-1-carboxylic Acid (19a). Benzyl 3-(3-ethyl-5-formyl-4-pyrrolylmethyl)-4,5-dihydronaphtho-[1,2-*c*]pyrrole-1-carboxylate (**22a**; 253 mg), methanol (150 mL), and 6 drops of triethylamine were placed in a hydrogenation vessel and purged with nitrogen. Palladium−charcoal (10%; 100 mg) was added and the mixture shaken under an atmosphere of hydrogen (45 psi) at room temperature overnight. After filtering off the catalyst, the solvent was removed under reduced pressure keeping the water bath below 40 °C. This residue was taken up in 5% aqueous ammonia, transferred to an Erlenmeyer flask, and cooled to 0 °C using an ice/salt bath. The mixture was neutralized to litmus by adding glacial acetic acid dropwise while maintaining the temperature below 5 °C. The solution was stirred for 1 h and the resulting precipitate filtered and washed thoroughly with water to remove all traces of acid. Following vacuum-drying overnight, the carboxylic acid (178 mg, 88%) was obtained as a pink powder: mp 170 °C dec; ^{1}H NMR ($CDCl_3$−DMSO-d_6) δ 0.96 (3H, t, J = 7.6 Hz), 2.17 (3H, s), 2.38 (2H, q, J = 7.6 Hz), 2.56 (2H, t, J = 7 Hz), 2.77 (2H, t, J = 7 Hz), 3.80 (2H, s), 7.03 (1H, t, J = 7.2 Hz), 7.10−7.15 (2H, m), 8.42 (1H, d, J = 7.6 Hz), 9.40 (1H, s), 10.90 (1H, br s), 11.24 (1H, br s). Anal. Calcd for $C_{22}H_{22}N_2O_3$: C, 72.91; H, 6.12; N, 7.73. Found: C, 73.05; H, 6.17; N, 7.56.

3-(5-Formyl-3,4-methyl-2-pyrrolylmethyl)-4,5-dihydronaphtho[1,2-*c*]pyrrole-1-carboxylic Acid (19b). The carboxylic acid was prepared from **22b** (250 mg) as described above. The product (0.178 mg, 90%) was isolated as a pink powder: mp 172 °C dec; ^{1}H NMR (DMSO-d_6) δ 1.97 (3H, s), 2.19 (3H, s), 2.61 (2H, t, J = 7 Hz), 2.81 (2H, t, J = 7 Hz), 3.85 (2H, s), 7.07 (1H, t, J = 7.2 Hz), 7.13−7.18 (2H, m), 8.44 (1H, d, J = 7.2 Hz), 9.47 (1H, s), 11.17 (1H, br s), 11.41 (1H, br s). Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.78; N, 8.04. Found: C, 72.58; H, 6.16; N, 8.22.

3-(5-Formyl-3-(2-methoxycarbonylethyl)-4-methylpyrrolylmethyl)-4,5-dihydronaphtho[2,1-*c*]pyrrole-1-carboxylic Acid (19c). The dipyrrylmethane carboxylic acid was prepared from **22c** (500 mg) by the foregoing procedure. The carboxylic acid (365 mg, 89%) was isolated as an off-white powder: mp 150 °C dec, darkens at 120 °C; ^{1}H NMR (DMSO-d_6) δ 2.16 (3H, s), 2.21 (2H, t, J = 7.8 Hz), 2.44 (2H, t, J = 6.8 Hz), 2.59 (2H, t, J = 7.8 Hz), 2.69 (2H, t, J = 6.8 Hz), 3.53 (3H, s), 3.88 (2H, s), 7.07 (1H, t, J = 7.4 Hz), 7.13−7.19 (2H, m), 8.40 (1H, d, J = 7.6 Hz), 9.47 (1H, s), 11.32 (1H, s), 11.55 (1H, s), 12.39 (1H, v br s). Anal. Calcd for $C_{24}H_{24}N_2O_5$: C, 68.56; H, 5.75; N, 6.66. Found: C, 68.41; H, 5.70; N, 6.43.

7,17-Diethyl-8,18-dimethyl-3^1,3^2,13^1,13^2-tetrahydrodinaphtho[1,2-*b*:1,2-*l*]porphyrin (24a). A solution of *p*-toluenesulfonic acid (125 mg) in methanol (2.2 mL) was added to a solution of dipyrrylmethane monoaldehyde **19a** (176 mg) in dichloromethane (22 mL) and methanol (2.2 mL) and the resulting mixture stirred in the dark at room temperature overnight. A saturated solution of zinc acetate in methanol (2.7 mL) was added and the resulting solution stirred open to the air overnight. The solution was washed with water, 5% hydrochloric acid (2×), 5% aqueous ammonia, and water. The solvent was evaporated under reduced pressure, and the resulting residue was chromatographed on grade 3 alumina, eluting with dichloromethane. Recrystallization from chloroform−methanol gave the porphyrin (52 mg, 36%) as purple crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 397 (infl., 5.00), 413 (5.17), 511 (3.86), 553 (4.12), 590 (4.24), 639 nm (3.47); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 409 (5.18), 563 (4.20), 602 (4.23), 612 nm (4.20); ^{1}H NMR (TFA−$CDCl_3$) δ −3.66 (2H, br s), −3.15 (2H, br s), 1.77 (6H, t, J = 7.8 Hz), 3.65 (6H, s), 3.89 (4H, t, J = 7.5 Hz), 4.13 (4H, q, J = 7.6 Hz), 4.25 (4H, t, J = 7.5 Hz), 7.64 (2H, t, J = 7.4 Hz), 7.76−7.80 (4H, m), 8.54 (2H, d, J = 7.2 Hz), 10.69 (2H, s), 11.01 (2H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.1, 16.5, 20.3, 22.4, 29.7, 99.4, 100.3, 128.7, 129.5, 129.9, 130.0, 130.4, 136.6, 138.2, 138.9, 139.3, 141.9, 142.1, 143.3, 144.7; HRMS (FAB) calcd for $C_{42}H_{38}N_4$ + H *m/z* 599.3175, found 599.3177. Anal. Calcd for $C_{42}H_{38}N_4 \cdot {}^3/_4CHCl_3$: C, 74.60; H, 5.67; N, 8.14. Found: C, 74.64; H, 5.63; N, 8.03.

7,8,17,18-Tetramethyl-3^1,3^2,13^1,13^2-tetrahydrodinaphtho[1,2-*b*:1,2-*l*]porphyrin (24b). The title porphyrin was prepared from **19b** (169 mg) by the previous procedure. Recrystallization from chloroform−methanol gave **24b** (38 mg, 27%) as a purple solid: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 396 (5.03), 405 (infl., 5.01), 510 (3.93), 554 (4.15), 582 (3.91), 640 nm (3.72); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 409 (5.12), 563 (4.15), 602 (4.16), 613 nm (4.18); ^{1}H NMR (TFA−$CDCl_3$) δ −3.59 (2H, br s), −2.96 (2H, br s), 3.63 (6H, s), 3.64 (6H, s), 3.88 (4H, t, J = 7.6 Hz), 4.25 (4H, t, J = 7.6 Hz), 7.63 (2H, t, J = 7.4 Hz), 7.76−7.80 (4H, m), 8.54 (2H, d, J = 7.6 Hz), 10.68 (2H, s), 10.99 (2H, s); ^{13}C NMR (TFA-$CDCl_3$): δ 12.2, 12.3, 22.4, 29.7, 99.6, 100.3, 128.7, 129.5, 129.9, 130.0, 130.4, 136.5, 138.6, 138.9, 139.3, 141.8, 142.9, 143.3; HRMS (FAB) calcd for $C_{40}H_{34}N_4$ + H *m/z* 571.2862, found 571.2864.

7,17-Bis(2-methoxycarbonylethyl)-8,18-dimethyl-3^1,3^2,13^1,13^2-tetrahydrodinaphtho[1,2-*b*:1,2-*l*]porphyrin (24c). Porphyrin **24c** was prepared from **19c** (275 mg) by the previous procedure. Recrystallization from chloroform−methanol gave the porphyrin (72 mg, 31%) as purple crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 398 (5.24), 411 (infl, 5.21), 510 (4.20), 549 (4.30), 580 (3.99), 638 nm (3.95); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 409 (5.35), 564 (4.34), 604 (4.36), 612 nm (infl, 4.21); ^{1}H NMR (TFA−$CDCl_3$) δ −3.52 (2H, br s), −2.94 (2H, br s), 3.18 (4H, t, J = 8 Hz), 3.67 (6H, s), 3.72 (6H, s), 3.89 (4H, t, J = 7.8 Hz), 4.27 (4H, t, J = 7.4 Hz), 4.53 (4H, t, J = 8 Hz), 7.64 (2H, t, J = 7.4 Hz), 7.75−7.81 (4H, m), 8.50 (2H, d, J = 7.6 Hz), 10.82 (2H, s), 11.01 (2H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.2, 21.9, 22.2, 29.6, 35.7, 53.0, 99.9, 100.5, 128.7, 129.6, 129.9, 130.1, 130.3, 136.8, 139.2, 139.4, 139.7, 140.1, 142.0, 142.4, 143.0, 175.1; HRMS (FAB) calcd for $C_{46}H_{42}N_4O_4$ + H 715.3284, found 715.3282. Anal. Calcd for $C_{46}H_{42}N_4O_4 \cdot {}^1/_{10}CHCl_3$: C, 76.18; H, 5.84; N, 7.71. Found: C, 76.08; H, 5.81; N, 7.66.

7,17-Bis(2-methoxycarbonylethyl)-8,18-dimethyldinaphtho[1,2-*b*:1,2-*l*]porphyrin (25a). Porphyrin **24c** (25 mg) was refluxed with DDQ (21. 2 mg) in toluene (10 mL) for 40 min. The solvent was evaporated under reduced pressure and the residue chromatographed on grade 3 alumina, eluting initially with dichloromethane and then with chloroform. Recrystallization from chloroform−methanol gave the dinaphthoporphyrin (25 mg, quantitative) as purple crystals: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 405 (infl, 5.04), 426 (5.40), 529 (3.94), 565 (4.75), 585 (4.26), 642 nm (4.00); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 427 (5.16), 449 (5.28), 570 (infl, 3.97), 585 (4.16), 623 (4.53), 636 nm (4.30); ^{1}H NMR (TFA-$CDCl_3$) δ −2.35 (2H, br s), −2.15 (2H, br s), 3.24 (4H, t, J = 7 Hz), 3.65 (6H, s), 3.76 (6H, s), 4.53 (4H, t, J = 7 Hz), 8.09 (2H, t, J = 7.5 Hz), 8.35 (2H, t, J = 7.6 Hz), 8.57 (2H, d, J = 8 Hz), 8.89 (2H, d, J = 8.5 Hz), 9.69 (2H, d, J = 8.5 Hz), 9.94 (2H, d, J = 8.1 Hz), 11.24 (2H, s), 11.49 (2H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.4, 22.0, 35.8, 52.8, 97.5, 99.9, 120.1, 125.7, 128.5, 128.6, 129.1, 130.2, 130.9, 134.0, 134.6, 135.8, 138.4, 138.8, 139.4, 139.8, 142.2, 142.7, 174.7; HRMS (FAB) calcd for $C_{46}H_{40}N_4O_4$ + H *m/z* 711.2971, found 711.2969. Anal. Calcd for $C_{46}H_{38}N_4O_4$: C, 77.73; H, 5.39; N, 7.88. Found: C, 77.52; H, 5.80; N, 7.36.

Nickel(II) Complex 25b. Porphyrin **25a** (9 mg) and nickel(II) acetate tetrahydrate (29 mg) were heated for 2 h under reflux in DMF (10 mL). The solution was diluted with chloroform, washed with water, and evaporated to dryness under reduced pressure. Recrystallization from chloroform−methanol gave the nickel(II) complex (9 mg, 93%) as purple crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 421 (5.20), 547 (4.02), 590 (4.80); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 420 (4.86), 444 (5.24), 451 (5.29), 567 (4.22), 592 (4.43), 609 nm (4.58); ^{1}H NMR ($CDCl_3$) δ 2.97 (4H, t, J = 7.4 Hz),

3.23 (6H, s), 3.66 (6H, s), 4.05 (4H, t, J = 7.4 Hz), 7.91 (2H, t, J = 7.4 Hz), 8.16 (2H, t, J = 7.4 Hz), 8.38−8.44 (4H, m), 9.17 (2H, d, J = 8 Hz), 9.62 (2H, d, J = 8 Hz), 9.67 (2H, s), 10.12 (2H, s); HRMS (FAB) calcd for $C_{46}H_{36}N_4O_4Ni$ *m/z* 766.2090, found 766.2092.

Copper(II) Complex 25c. Porphyrin **25a** (7.8 mg) and copper(II) acetate monohydrate (27.8 mg) were heated for 2 h under reflux in DMF (10 mL). The solution was diluted with chloroform, washed with water, and evaporated to dryness on a rotary evaporator. Recrystallization from chloroform−methanol gave the copper(II) complex (8.0 mg, 94%) as purple crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 410 (infl, 4.92), 425 (5.04), 553 (3.77), 596 (4.31); HRMS (FAB) calcd for $C_{46}H_{36}N_4O_4Cu$ *m/z* 771.2032, found 771.2030.

Zinc Complex 25d. Porphyrin **25a** (7 mg) and zinc acetate dihydrate (27 mg) were heated for 2 h under reflux in DMF (10 mL). The solution was diluted with chloroform, washed with water, and evaporated in vacuo. Recrystallization from chloroform−methanol gave the zinc chelate (7 mg, 92%) as purple crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 437 (5.36), 567 (3.84), 609 (4.34); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 419 (4.64), 423 (infl, 5.29), 444 (5.48), 568 (4.20), 610 nm (4.71); ^{1}H NMR (pyrrolidine−$CDCl_3$; downfield region only) δ 7.84 (2H, t, J = 7.4 Hz), 8.15 (2H, t, J = 7.6 Hz), 8.41 (2H, d, J = 8 Hz), 8.48 (2H, d, J = 8 Hz), 9.55 (2H, d, J = 8 Hz), 10.22 (2H, d, J = 8 Hz), 10.42 (2H, s), 11.06 (2H, s); HRMS (FAB) calcd for $C_{46}H_{36}N_4O_4Zn$ + H *m/z* 773.2106, found 773.2016.

Synthesis of Dinaphthoporphyrin Type C. Bis-2,5-(3-benzyloxycarbonyl-4,5-dihydro-1-naphtho[1,2-*c*]pyrrolylmethyl)-3,4-diethylpyrrole (26a). 3,4-Diethylpyrrole[53] (0.324 g) and benzyl 3-acetoxymethyl-4,5-dihydronaphtho[1,2-*c*]pyrrole-1-carboxylate (**5**; 1.99 g) were dissolved in ethanol (20 mL) and glacial acetic acid (1.3 mL). The resulting solution was allowed to reflux under a nitrogen atmosphere for 16 h. The mixture was then allowed to cool to room temperature and further cooled with an ice bath to precipitate out the product. The precipitate was collected by suction filtration, washed with cold ethanol, and dried in vacuo overnight to give the tripyrrane dibenzyl ester (1.45 g, 73%) as an off white powder: mp 194 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.04 (6H, t, J = 7.2 Hz), 2.40 (4H, q, J = 7 Hz), 2.54 (4H, br m), 2.74 (4H, t, J = 6.6 Hz), 3.84 (4H, s), 4.53 (4H, br s), 6.73 (2H, br t), 6.87 (4H, br d), 7.07−7.10 (6H, m), 7.16−7.19 (4H, m), 8.07 (2H, d), 8.94 (1H, br s), 11.01 (2H, br s); ^{13}C NMR ($CDCl_3$) δ 16.9, 17.9, 20.5, 22.4, 31.4, 67.3, 115.8, 119.5, 120.9, 122.4, 126.5, 126.7, 127.0, 127.9 (2), 128.2, 128.6, 128.8, 131.3, 131.5, 135.3, 137.3, 162.9. Anal. Calcd for $C_{50}H_{47}N_3O_4$: C, 78.65; H, 6.28; N, 5.57. Found: C, 78.42; H, 6.08; N, 5.65.

7,8,17,18-Tetraethyl-3^1,3^2,12^1,12^2-tetrahydrodinaphtho-[1,2-*b*:2,1-*l*]porphyrin (28). Tripyrrane benzyl ester **26a** (0.500 g) was placed in a hydrogenation vessel along with anhydrous THF (62 mL). Methanol (21 mL) and triethylamine (8 drops) were added to the vessel, and the resulting solution was purged under nitrogen for several minutes. Palladium on activated carbon (10%; 100 mg) was added and the vessel placed on the Parr hydrogenator. The mixture was shaken at 45 psi under a hydrogen atmosphere at room temperature for 16 h. The catalyst was removed by suction filtration and the vessel washed with small portions of ethanol. The filtrate was evaporated under reduced pressure to give a pink residue, which was taken up in a 3% aqueous ammonia solution. The aqueous solution was cooled to 5 °C with an ice/salt bath and neutralized to litmus endpoint with glacial acetic acid, maintaining the temperature between 0 and 5 °C. The resulting mixture was allowed to stand and 0 °C for 1 h and the precipitate collected by suction filtration and washed repeatedly with water to remove all traces of acetic acid. The tripyrrane dicarboxylic acid was dried overnight in vacuo. The crude dicarboxylic acid **26b** (0.375 g, 99%) was obtained as a pink powder and was used without further purification.

The foregoing dicarboxylic acid (0.230 g) was dissolved in trifluoroacetic acid (1.8 mL) under an atmosphere of nitrogen at room temperature for 10 min. The mixture was diluted with dichloromethane (35 mL), followed immediately by the addition of 3,4-diethylpyrrole-2,5-dicarbaldehyde[34b,54] (**27**; 72 mg), and the resulting solution was stirred at room temperature for 2 h under a nitrogen atmosphere. The mixture was neutralized by the dropwise addition of triethylamine, DDQ (193.2 mg; 2.10 equiv) was added, and the mixture was allowed to stir for an additional 1 h at room temperature. The solution was washed with water and the solvent evaporated under reduced pressure to give a dark purple residue. The residue was chromatographed on grade III alumina eluting with dichloromethane. The fractions containing the porphyrin were combined, evaporated under reduced pressure, and recrystallized from chloroform−methanol to give the desired tetrahydrodinaphthoporphyrin (128 mg, 51%) as purple crystals: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 401 (5.26), 512 (4.14), 555 (4.32), 575 (4.02), 640 nm (3.77); UV−vis (2% TFA−($CHCl_3$) λ_{max} (log ϵ) 410 (5.29), 565 (4.31), 615 nm (4.20); ^{1}H NMR (TFA−$CDCl_3$) δ −2.95 (3H, br s), −2.29 (1H, br s), 1.74 (6H, t, J = 7.6 Hz), 1.80 (6H, t, J = 7.6 Hz), 3.90 (4H, t, J = 7.4 Hz), 4.08−4.17 (8H, m), 4.23 (4H, t, J = 7.4 Hz), 7.63 (2H, t, J = 7.4 Hz), 7.78−7.81 (4H, m), 8.55 (2H, d, J = 7.6 Hz), 10.62 (2H, s), 10.96 (2H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 18.6, 18.7, 21.2, 21.3, 23.4, 30.8, 100.2, 100.7, 129.4, 130.3, 130.5, 130.6, 131.4, 136.7, 139.8, 140.0, 140.1, 142.0, 142.8, 143.6, 144.1, 144.3; HRMS (FAB) calcd for $C_{44}H_{42}N_4$ + H *m/z* 627.3487, found 627.3488. Anal. Calcd for $C_{44}H_{42}N_4 \cdot H_2O$: C, 81.95; H, 6.88; N, 8.69. Found: C, 82.31; H, 6.59; N, 8.73.

7,8,17,18-Tetraethyldinaphtho[1,2-*b*:2,1-*l*]porphyrin (29a). Dihydronaphthoporphyrin **28** (71 mg) and DDQ (53.2 mg; 2.0 equiv) were refluxed in toluene (30 mL) for 1 h. The reaction flask was allowed to cool to room temperature and then diluted with chloroform and washed with water. The organic extracts were evaporated under reduced pressure, and the residue was recrystallized from chloroform−methanol to give the fully conjugated dinaphthoporphyrin (68 mg, 97%) as dark purple sheets: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 404 (sh, 4.91), 425 (5.50), 531 (3.83), 567 (4.86), 584 (4.44), 640 nm (3.96); UV−vis (2% TFA−$CHCl_3$) λ_{max} (log ϵ) 429 (sh, 5.27), 446 (5.45), 581 (4.26), 626 nm (4.70); ^{1}H NMR (TFA−$CDCl_3$) δ −2.73 (1H, br s), −2.53 (2H, br s), −1.95 (1H, br s), 1.78 (6H, t, J = 7.8 Hz) 1.83 (6H, t, J = 7.6 Hz), 4.22 (8H, q, J = 7.5 Hz), 8.10 (2H, t, J = 7.4 Hz), 8.36 (2H, t, J = 7.8 Hz), 8.57 (2H, d, J = 8.0 Hz), 8.88 (2H, d, J = 8.4 Hz), 9.60 (2H, d, J = 8.8 Hz), 9.95 (2H, d, J = 8.4 Hz), 11.07 (2H, s), 11.46 (2H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 17.4, 17.5, 20.2, 20.3, 97.3, 99.2, 119.8, 125.7, 128.4, 128.6, 129.1, 130.3, 130.9, 134.1, 134.5, 135.7, 138.0, 139.8, 141.9, 142.8, 143.4, 143.6; HRMS (FAB) calcd for $C_{44}H_{38}N_4$ *m/z* 622.3097, found 622.3096. Anal. Calcd for $C_{44}H_{38}N_4 \cdot {}^1/_2H_2O$: C, 83.64; H, 6.06; N, 8.87. Found: C, 84.13; H, 5.93; N, 8.91.

Nickel(II) Complex 29b. Dinaphthoporphyrin **29a** (10.1 mg) and nickel(II) acetate tetrahydrate (25 mg) were stirred in DMF (10 mL) under reflux conditions for 2 h. The solution was then cooled to room temperature, diluted with chloroform, and washed with three 200 mL portions of water. The organic layers were evaporated under reduced pressure, and the resulting residue was recrystallized from chloroform−methanol to give the nickel complex (10.2 mg, 93%) as deep purple sheets: mp >300 °C. UV−vis ($CHCl_3$) λ_{max} (log ϵ) 420 (5.27), 546 (4.04), 591 (4.87); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 422 (sh, 5.03), 444 (sh, 5.12), 451 (5.14), 554 (4.08), 593 (4.61), 610 nm (sh, 4.51); ^{1}H NMR ($CDCl_3$) δ 1.86 (6H, t, J = 7.6 Hz), 1.92 (6H, t, J = 7.6 Hz), 3.95−4.07 (8H, m), 7.86 (2H, t, J = 7.2 Hz), 8.13 (2H, t, J = 7.6 Hz), 8.38−8.42 (4H, m),

(53) Sessler, J. L.; Mozaffari, A.; Johnson, M. R. *Org. Synth.* **1991**, *70*, 68.

(54) Tardieux, C.; Bolze, F.; Gros, C. P.; Guilard, R. *Synthesis* **1998**, 267.

9.32 (2H, d, J = 8.4 Hz), 9.83 (2H, d, J = 8.4 Hz), 10.12 (2H, s), 10.78 (2H, s); HRMS (EI) calcd for $C_{44}H_{36}N_4Ni$ *m/z* 678.2293, found 678.2293.

Copper(II) Complex 29c. Dinaphthoporphyrin **29a** (10.0 mg) and copper(II) acetate monohydrate (25 mg) were stirred in DMF (10 mL) under reflux conditions for 2 h. The solution was then cooled to room temperature, diluted with chloroform, and washed with water. The organic layer was evaporated under reduced pressure and the resulting residue recrystallized from chloroform−methanol to give the copper complex (8.1 mg, 74%) as deep green sheets: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 397 (sh, 4.53), 424 (5.13), 550 (4.07), 596 nm (4.52); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 397 (sh) (4.50), 424 (5.10), 551 (4.06), 596 (4.50), 633 (sh) (4.03); HRMS (EI) calcd for $C_{44}H_{36}N_4Cu$ *m/z* 683.2236, found 683.2246.

Zinc(II) Complex 29d. Dinaphthoporphyrin **29a** (10.0 mg) and zinc acetate dihydrate (25 mg) were stirred in DMF (10 mL) under reflux conditions for 2 h. The solution was then cooled to room temperature, diluted with chloroform, and washed with water. The organic layer was evaporated under reduced pressure and the resulting residue recrystallized from chloroform−methanol to give the zinc complex (10.2 mg, 93%) as deep green sheets: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (rel int) 430 (1.00), 563 (0.08), 603 nm (0.24); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 419 (4.64), 422 (sh, 5.48), 444 (5.62), 568 (4.34), 611 nm (4.85); ^{1}H NMR (pyrrolidine−$CDCl_3$) δ 2.02 (6H, t, J = 7.6 Hz), 2.09 (6H, t, J = 7.6 Hz), 4.23 (4H, q, J = 7.6 Hz), 4.32 (4H, q, J = 7.6 Hz), 7.87 (2H, t, J = 7.2 Hz), 8.20 (2H, t, J = 7.6 Hz), 8.44 (2H, d, J = 7.6 Hz), 8.51 (2H, d, J = 8.8 Hz), 9.62 (2H, d, J = 8.4 Hz), 10.30 (2H, d, J = 8.4 Hz), 10.55 (2H, s), 11.22 (2H, s); HRMS (EI) calcd for $C_{44}H_{36}N_4Zn$ *m/z* 684.2231, found 684.2213.

Synthesis of Dinaphthoporphyrin Type D. Ethyl Naphtho[1,2-*c*]pyrrole-3-carboxylate (33a). A mixture of 1-nitronaphthalene (2.005 g) and ethyl isocyanoacetate[55] (1.611 g) in anhydrous THF (24.0 mL) was stirred for several minutes, and a phosphazene base, P-*t*-Bu-tris-(tetramethylene) **34** (4.04 g), was then added. The solution was refluxed overnight under anhydrous conditions. The solution was cooled to room temperature, diluted with chloroform, and washed with three portions of water (200 mL). The organic solutions were combined and evaporated under reduced pressure to give a brownish-orange oil. The residue was purified by column chromatography on a silica gel column eluting with dichloromethane. Recrystallization from 95% ethanol gave the desired naphthopyrrole (1.60 g, 58%) as off-white crystals: mp 199−201 °C (lit.[38] mp 200−202 °C); ^{1}H NMR ($CDCl_3$) δ 1.49 (3H, t, J = 7.2 Hz), 4.48 (2H, q, J = 7.2 Hz), 7.47 (1H, t, J = 7.6 Hz), 7.53−7.57 (2H, m), 7.82 (1H, d, J = 7.6 Hz), 7.87 (1H, d, J = 3.2 Hz), 8.03 (1H, d, J = 9.2 Hz), 8.15 (1H, d, J = 7.6 Hz), 9.93 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 14.9, 60.5, 114.4, 114.8, 120.2, 122.8, 122.9, 125.5, 127.0, 127.5, 128.3, 129.0, 130.0, 131.0, 162.0; EI MS (70 eV) *m/z* 239 (57, M^+), 193 (100), 165 (54), 139 (36).

***tert*-Butyl Naphtho[1,2-*c*]pyrrole-3-carboxylate (33b).** A mixture of 1-nitronaphthalene (1.50 g) and *tert*-butyl isocyanoacetate[15c] (1.20 g) in anhydrous THF (18 mL) was stirred until of the all reactants were dissolved. To the yellow solution was added phosphazene base P-*t*-Bu-tris-(tetramethylene) **34** (3.03 g) and the mixture allowed to reflux overnight under anhydrous conditions. The solution was cooled to room temperature and diluted with chloroform. The chloroform solution was then washed with water (3 × 200 mL), and the organic solutions were combined and evaporated to give a brownish-orange oil. The resulting crude product was purified by column chromatography on silica gel, eluting with dichloromethane. Recrystallization with 95% ethanol gave the desired pyrrole (1.23 g, 54%) as off-white crystals: mp 169−171 °C; ^{1}H NMR ($CDCl_3$) δ 1.72 (9H, s), 7.46 (1H, t, J = 7.5 Hz), 7.51−7.56 (3H, m), 7.82 (1H, d, J = 7.9 Hz), 7.84 (1H, d, J = 3.4 Hz), 8.00 (1H, d, J = 9.2 Hz), 8.15 (1H, d, J = 7.9 Hz), 10.2 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 30.0, 82.5, 115.6, 116.2, 121.2, 123.4, 123.7, 125.6, 126.1, 127.7, 127.9, 129.1, 129.7, 131.6, 162.8; EI MS (70 eV) *m/z* 267 (9.5, M^+), 239 (2.1), 211 (55), 193 (100), 167 (91), 139 (59). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 75.98; H, 6.32; N, 5.24.

***tert*-Butyl 1-(1-Benzyloxycarbonyl-4,5-dihydronaphtho[1,2-*c*]pyrrolylmethyl)naphtho[1,2-*c*]pyrrole-3-carboxylate (30a).** Acetoxymethylpyrrole **5**[14] (0.308 g) and *tert*-butyl ester **33b** (0.192 g) were dissolved in acetic acid (5.0 mL) containing *p*-toluenesulfonic acid (10.3 mg). The resulting mixture was stirred at room temperature under a nitrogen atmosphere for 2 h. The solution was then diluted with chloroform and washed successively with water, 10% sodium bicarbonate solution, and water, back-extracting with chloroform at each stage. The combined organic extracts were evaporated under reduced pressure to give a brown residue. Recrystallization from chloroform−hexanes gave the desired dipyrrole (0.244 g, 58%) as off-white needles: mp 230−231 °C; ^{1}H NMR ($CDCl_3$) δ 1.63 (9H, s), 2.62 (2H, t, J = 6.8 Hz), 2.91 (2H, t, J = 6.8 Hz), 4.68 (2H, s), 5.26 (2H, s), 7.19−7.31 (8H, m), 7.44−7.54 (3H, m), 7.84 (1H, d, J = 7.6 Hz), 7.98 (1H, d, J = 9.2 Hz), 8.11 (1H, d, J = 8.0 Hz), 8.42 (1H, d, J = 6 Hz), 8.92 (1H, br s), 9.61 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 20.3, 26.8, 28.8, 31.1, 66.4, 81.5, 113.4, 116.7, 118.3, 120.5, 122.3, 123.0, 125.0, 125.5, 126.8, 127.1, 127.3, 127.6, 128.0, 128.2, 128.4, 128.6, 128.7, 128.8, 129.3, 130.7, 131.4, 136.0, 137.5, 160.6. Anal. Calcd for $C_{38}H_{34}N_2O_4 \cdot {}^1/_2H_2O$: C, 77.14; H, 5.79; N, 4.73. Found: C, 77.10; H, 5.90; N, 4.78.

13,17-Dibutyl-12,18-dimethyl-3^1,3^2-dihydrodinaphtho[1,2-*b*:1,2-*g*]porphyrin (38a). Dipyrrylmethane **30a** (0.310 g) was placed in a hydrogenation vessel and dissolved in anhydrous THF (50 mL). The solution was then diluted with methanol (17 mL), and triethylamine (7 drops) was added. The solution was purged with nitrogen for several minutes, and 10% palladium on activated carbon (100 mg) was added. The resulting mixture was shaken under a hydrogen atmosphere at 40 psi for 16 h at room temperature on a Parr hydrogenator. The palladium catalyst was then removed by suction filtration and the solvent evaporated under reduced pressure giving a light blue residue. The residue was taken up in 3% aqueous ammonia solution and cooled to 0 °C using an ice/salt bath. The solution was then neutralized to a litmus endpoint with glacial acetic acid, maintaining the temperature below 5 °C. The mixture was allowed to stand at 0 °C for 1 h. The precipitate was filtered under suction, washed with copious amounts of water, and dried overnight in vacuo to give the carboxylic acid **30b** as a pink powder (0.249 g, 95%): ^{1}H NMR ($CDCl_3$) 1.54 (9H, s), 2.74 (2H, br t), 2.90 (2H, br t, J = 6 Hz), 2.98−3.06 (4H, m), 4.75 (2H, s), 7.12 (1H, t, J = 7.2 Hz), 7.17−7.22 (2H, m), 7.43 (1H, t, J = 7.4 Hz), 7.48 (1H, d, J = 9 Hz), 7.54 (1H, t, J = 7.4 Hz), 7.80 (1H, d, J = 7.6 Hz), 7.95 (1H, d, J = 9 Hz), 8.36 (1H, d, J = 8 Hz), 8.57 (1H, d, J = 7.6 Hz), 10.94 (2H, 2 broad overlapping singlets). Dipyrrylmethane **30b** (0.200 g) was treated with trifluoroacetic acid (2 mL) under a nitrogen atmosphere for 10 min and then diluted with chloroform and washed successively with water, 10% sodium bicarbonate solution, and water. The organic phase was dried over sodium sulfate and evaporated to dryness under reduced pressure to give a dark purple residue. The residue and dialdehyde **9b**[31b] (0.145 g) were dissolved in a mixture of dichloromethane (45 mL) and methanol (5 mL), and the resulting solution was placed in a 100 mL pressure equalized addition funnel. The solution was then added dropwise over a 2 h period to a 100 mL round-bottom flask containing a stirred mixture of *p*-toluenesulfonic acid (260 mg), methanol (5 mL) and dichloromethane (45 mL) under a nitrogen atmosphere. The deep purple solution was allowed to stir at room temperature for 16 h under nitrogen. A saturated solution of $Zn(OAc)_2$ in methanol (10 mL) was then added and the mixture stirred for an additional 2 days open to the air. The organic solution was monitored every 8 h using a UV−vis spectrophotometer

(55) Hartman, G. D.; Weinstock, L. M. *Org. Synth.* **1979**, *59*, 183.

to detect the emergence of a Soret band at 424 nm. The organic mixture was then diluted further with dichloromethane and washed successively with water, aqueous sodium bicarbonate solution, and water, back-extracting with chloroform at each step. The organic layers were combined and evaporated down under reduced pressure to give a dark purple residue. The residue was columned on grade III alumina eluting with dichloromethane to remove tarry impurities. A second column was performed on grade III alumina, eluting with dichloromethane, and the fractions containing pure porphyrin by TLC were combined, evaporated under reduced pressure, and recrystallized from chloroform−methanol to give the desired dinaphthoporphyrin (110 mg, 41%) as reddish purple fibers: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 424 (5.34), 517 (4.16), 552 (4.45), 583 (3.99), 640 nm (4.13); UV−vis (2% TFA−$CHCl_3$) λ_{max} (log ϵ) 431 (5.33), 561 (sh, 4.10), 572 (4.29), 611 (4.18), 624 nm (4.26); ^{1}H NMR ($CDCl_3$) δ −3.96 (2H, br s), 1.11−1.18 (6H, 2 overlapping triplets), 1.70−1.85 (4H, m), 2.20−2.29 (4H, m), 3.50 (3H, s), 3.55 (3H, s), 3.61 (2H, t, J = 7.2 Hz), 3.92 (2H, t, J = 7.6 Hz), 4.01 (2H, t, J = 7.8 Hz), 4.23 (2H, t, J = 7.2 Hz), 7.59 (1H, t, J = 7.2 Hz), 7.76 (1H, d, J = 7.6 Hz), 7.80−7.87 (2H, m), 8.07 (1H, t, J = 7.6 Hz), 8.34 (2H, d, J = 7 Hz), 9.03 (1H, d, J = 7.6 Hz), 9.18 (1H, d, J = 8.0 Hz), 9.84−9.85 (2H, overlapping singlet and doublet), 10.04 (1H, s), 10.44 (1H, s), 10.69 (1H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −2.97 (1H, br s), −2.81 (1H, br s), −2.62 (2H, br s), 1.05−1.12 (6H, 2 overlapping triplets), 1.60−1.73 (4H, m), 2.04−2.18 (4H, m), 3.64 (3H, s), 3.70 (3H, s), 3.97 (2H, t, J = 7.2 Hz), 4.07−4.15 (4H, m), 4.32 (2H, t, J = 7.4 Hz), 7.64 (1H, t, J = 7.2 Hz), 7.77−7.82 (2H, m), 8.10 (1H, t, J = 7.2 Hz), 8.37 (1H, t, J = 7.6 Hz), 8.56 (2H, t, J = 7.4 Hz), 8.88 (1H, d, J = 8.8 Hz), 9.61 (1H, d, J = 8.8 Hz), 10.03 (1H, d, J = 8.4 Hz), 10.58 (1H, s), 11.02 (1H, s), 11.04 (1H, s), 11.55 (1H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.1, 12.2, 14.0 (2), 22.5, 23.2 (2), 26.7, 26.8, 29.8, 34.4, 34.5, 96.1, 99.1, 100.3, 101.3, 119.9, 125.7, 128.7, 128.9, 129.1, 129.6, 129.9 (2), 130.2, 130.5, 130.9, 134.0, 134.6, 135.8, 136.3, 137.7, 138.2, 138.3, 139.3 (2), 139.8, 139.9, 140.8, 142.0, 142.1, 142.2, 142.7, 143.8, 144.0; HRMS (FAB) calcd for $C_{46}H_{44}N_4$ + H *m/z* 653.3644, found 653.3645. Anal. Calcd for $C_{46}H_{44}N_4 \cdot {}^1/_2H_2O$: C, 83.47; H, 6.70; N, 8.46. Found: C, 83.58; H, 6.61; N, 8.48.

13,17-Bis(2-methoxycarbonylethyl)-12,18-dimethyl-3^1,3^2-dihydrodinaphtho[1,2-*b*:1,2-*g*]porphyrin (38b). Dipyrrylmethane **54** (0.300 g) was treated with trifluoroacetic acid (2 mL) for 10 min under a nitrogen atmosphere. The acidic solution was then diluted with chloroform and washed successively with water, 10% sodium carbonate solution, and water. The organic solutions were combined, dried over sodium sulfate, and evaporated to dryness under reduced pressure to give a brown residue. The residue was then combined in a solution of dichloromethane (63 mL) and methanol (6 mL) with dialdehyde **9c**[56] (0.247 g) and the resulting mixture placed in a 100 mL pressure-equalized addition funnel. The solution was then added dropwise under a nitrogen atmosphere over a 2 h period to a stirred solution of *p*-toluenesulfonic acid (390 mg) in methanol (6 mL) and dichloromethane (63 mL). The resulting solution was allowed to stir at room temperature for 16 h under nitrogen. A saturated solution of zinc acetate in methanol (10 mL) was then added and the mixture stirred for an additional 2 days open to the air. The solution was then diluted with dichloromethane and washed successively with water, sodium bicarbonate, and water. The organic layer was evaporated under reduced pressure to give a dark purple residue. The residue was dissolved in 5% sulfuric acid/methanol (30 mL) and allowed to stir for 24 h. The resulting mixture was partitioned between chloroform and water, and the chloroform layer was carried through a sequence of washes with water, 5% sodium bicarbonate solution, and water, back-extracting with chloroform at each step. The organic solutions were combined and evaporated under reduced pressure to give a brown residue. The residue was chromatographed twice on grade 3 alumina eluting with dichloromethane. The fractions containing the porphyrin were combined, evaporated under reduced pressure, and recrystallized from chloroform−methanol to give the desired dinaphthoporphyrin (166 mg, 38%) as reddish purple fibers: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 424 (5.34), 513 (4.18), 552 (4.46), 584 (3.98), 641 nm (4.12); UV−vis (2% TFA−$CHCl_3$) λ_{max} (log ϵ) 430 (5.33), 559 (sh, 4.10), 573 (4.30), 611 (4.19), 624 nm (4.21); ^{1}H NMR ($CDCl_3$) δ -3.92 (2H, br s), 3.25−3.31 (4H, 2 overlapping triplets), 3.54 (3H, s), 3.64 (5H, overlapping singlet and triplet), 3.67 (3H, s), 3.71 (3H, s), 4.25−4.34 (4H, 2 overlapping triplets), 4.44 (2H, t, J = 7.8 Hz), 7.60 (1H, t, J = 7.4 Hz), 7.77 (1H, d, J = 7.2 Hz), 7.83−7.88 (2H, m), 8.11 (1H, t, J = 7.2 Hz), 8.40 (2H, t, J = 8.6 Hz), 9.03 (1H, d, J = 7.2 Hz), 9.25 (1H, d, J = 8.4 Hz), 9.89 (1H, d, J = 8.8 Hz), 9.95 (1H, s), 10.15 (1H, s), 10.49 (1H, s), 10.76 (1H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −2.84 (1H, br s), −2.68 (1H, br s), −2.59 (2H, br s), 3.13 (2H, t, J = 7.6 Hz), 3.19 (2H, t, J = 7.6 Hz), 3.65 (6H, s), 3.67 (3H, s), 3.73 (3H, s), 3.97 (2H, t, J = 7.4 Hz), 4.32 (2H, t, J = 7.6 Hz), 4.45−4.53 (4H, 2 overlapping triplets), 7.65 (1H, t, J = 7.6 Hz), 7.78 (2H, m), 8.11 (1H, t, J = 7.6 Hz), 8.38 (1H, t, J = 7.6 Hz), 8.54 (1H, d, J = 7.6 Hz), 8.58 (1H, d, J = 7.6 Hz), 8.90 (1H, d, J = 9.2 Hz), 9.61 (1H, d, J = 8.8 Hz), 10.02 (1H, d, J = 8.8 Hz), 10.93 (1H, s), 11.03 (1H, s), 11.04 (1H, s), 11.55 (1H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.0, 12.1, 21.6, 21.7, 22.4, 29.6, 35.6, 35.7, 53.2, 96.4, 99.6, 100.5, 101.6, 119.8, 125.6, 128.8, 129.0 (2), 129.1, 129.6, 130.0, 130.1, 130.4, 130.5, 131.0, 134.6, 134.9, 136.0, 137.2, 138.3, 138.9, 139.3 (2), 139.6, 139.8, 140.4, 140.5, 141.0, 141.3, 141.4, 141.9, 143.6, 176.1; HRMS (FAB) calcd for $C_{46}H_{40}N_4O_4$ + H *m/z* 713.3128, found 713.3131. Anal. Calcd for $C_{46}H_{40}N_4O_4$: C, 77.51; H, 5.66; N, 7.89. Found: C, 77.03; H, 5.64; N, 7.78.

13,17-Bis(2-methoxycarbonylethyl)-12,18-dimethyldinaphtho[1,2-*b*:1,2-*g*]porphyrin (39a). Dihydrodinaphthoporphyrin **38a** (50.0 mg) was refluxed with DDQ (17.0 mg, 1 equiv) in toluene (19 mL) for 15 min. The solvent was evaporated under reduced pressure and the residue washed with copious amounts of methanol. The residue was then purified by chromatography on a silica gel column eluting with dichloromethane. The fractions containing pure porphyrin were combined and recrystallized from chloroform−methanol to give **39a** (26.7 mg, 53%) as dark purple crystals: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 402 (sh, 4.91), 426 (5.32), 535 (4.07), 567 (4.55), 587 (4.07), 645 nm (4.23); UV−vis (2% TFA−$CHCl_3$) λ_{max} (log ϵ) 438 (5.43), 581 (4.22), 630 nm (4.64); ^{1}H NMR (TFA−$CDCl_3$) δ -2.72 (1H, br s), -2.35 (1H, br s), −2.25 (1H, v br), −1.84 (1H, v br), 3.11−3.18 (4H, 2 overlapping triplets), 3.65 (3H, s), 3.66 (3H, s), 3.72 (3H, s), 3.74 (3H, s), 4.48−4.52 (4H, m), 8.09−8.14 (2H, m), 8.35−8.43 (2H, m), 8.59 (2H, d, J = 8.6 Hz), 8.92 (2H, d, J = 9.2 Hz), 9.61 (1H, d, J = 8.8 Hz), 9.68 (1H, d, J = 8.8 Hz), 9.98 (1H, d, J = 8.4 Hz), 10.08 (1H, d, J = 8.4 Hz), 10.93 (1H, s), 11.06 (1H, s), 11.48 (1H, s), 11.91 (1H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.1, 12.3, 21.8, 35.7 (2), 52.8, 96.9, 97.5, 99.7, 100.8, 119.8, 119.9, 125.7, 125.8, 128.1, 128.6, 128.8, 128.9, 129.1, 129.2, 130.4 (2), 131.0, 134.1, 134.2, 134.5, 135.0, 135.8, 135.9, 137.7, 137.8, 138.3, 140.3, 140.4 (2), 140.7, 141.6, 142.4, 143.0, 175.1; HRMS (EI) calcd for $C_{46}H_{38}N_4O_4$ *m/z* 711.2971, found 711.2972. Anal. Calcd for $C_{46}H_{38}N_4O_4 \cdot {}^1/_2H_2O$: C, 76.75; H, 5.32; N, 7.78. Found: C, 76.34; H, 5.35; N, 7.69.

Nickel(II) Complex 39b. Dinaphthoporphyrin **39a** (7.3 mg) and nickel(II) acetate tetrahydrate (33.4 mg) were stirred in DMF (10 mL) under reflux conditions for 2 h. The solution was then cooled to room temperature, diluted with chloroform, and washed with three 200 mL portions of water. The organic layers were evaporated under reduced pressure, and the resulting residue was recrystallized from chloroform−methanol to give the nickel complex (6.4 mg, 81%) as purple sheets: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 419 (5.21), 546 (4.02), 588 nm (4.77); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 423 (4.84), 449 (5.32), 569 (4.23), 590 (sh, 4.39), 604 nm (4.48); ^{1}H

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NMR ($CDCl_3$) δ 2.98−3.05 (4H, m), 3.06 (3H, s), 3.13 (3H, s), 3.70 (3H, s), 3.71 (3H, s), 3.93−3.99 (4H, m), 7.81−7.86 (2H, m), 7.95−8.00 (2H, m), 8.06 (1H, d, J = 8.4 Hz), 8.21 (1H, d, J = 8.0 Hz), 8.29 (1H, d, J = 8 Hz), 8.33 (1H, d, J = 8 Hz), 8.42 (1H, d, J = 8 Hz), 8.77 (1H, d, J = 8.0 Hz), 9.07 (1H, d, J = 8.0 Hz), 9.16−9.20 (3H, m), 9.61 (1H, s), 9.66 (1H, s); HRMS (FAB) calcd for $C_{46}H_{36}N_4O_4Ni$ *m/z* 766.2089, found 766.2090.

Copper(II) Complex 39c. Dinaphthoporphyrin **39a** (6.0 mg) and copper(II) acetate monohydrate (33.2 mg) were stirred in DMF (10 mL) under reflux conditions for 2 h. The solution was then cooled to room temperature, diluted with chloroform, and washed with water. The organic layers were evaporated under reduced pressure, and the resulting residue was recrystallized from chloroform−methanol to give the copper complex (5.6 mg, 86%) as dark green sheets: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 422 (5.39), 553 (4.00), 594 nm (4.68); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 422 (5.37), 553 (4.02), 594 nm (4.67); HRMS (FAB) calcd for $C_{46}H_{36}N_4O_4Cu$ *m/z* 771.2030, found 771.2032.

Zinc(II) Complex 39d. Dinaphthoporphyrin **39a** (7.2 mg) and zinc(II) acetate dihydrate (33.7 mg) were stirred in DMF (10 mL) under reflux conditions for 2 h. The solution was then cooled to room temperature, diluted with chloroform, and washed with water. The organic solution was evaporated under reduced pressure and the resulting residue recrystallized from chloroform−methanol to give the zinc complex (6.4 mg, 82%) as deep green sheets: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 411 (sh, 4.82), 433 (5.38), 562 (4.11), 602 nm (4.66); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 417 (sh, 4.68), 442 (5.57), 568 (4.24), 608 nm (4.67); ^{1}H NMR (pyrrolidine−$CDCl_3$, downfield region only) δ 7.85−7.90 (2H, m), 8.15−8.24 (2H, m), 8.41−8.45 (2H, m), 8.50 (2H, t, J = 9.4 Hz), 9.55 (1H, d, J = 8.8 Hz), 9.64 (1H, d, J = 8.4 Hz), 10.04 (1H, s), 10.24 (1H, d, J = 8.8 Hz), 10.35 (1H, d, J = 8.8 Hz), 10.46 (1H, s), 11.10 (1H, s), 11.46 (1H, s); HR (FAB) calcd for $C_{46}H_{36}N_4O_4Zn$ *m/z* 772.2030, found 772.2028.

Synthesis of Dinaphthoporphyrin Type E. Diethyl Bis(1-naphtho[1,2-*c*]pyrrolylmethane)-3,3′-dicarboxylate (40). A mixture of naphthopyrrole ethyl ester **33a** (0.500 g), dimethoxymethane (0.159 g), *p*-toluenesulfonic acid monohydrate (62 mg), and glacial acetic acid (31 mL) was allowed to stir at room temperature under a nitrogen atmosphere for 3 days. The resulting greenish-blue, colloidal suspension was poured into ice−water (250 mL) and was allowed to stand for 2 h at room temperature. The resulting precipitate was suction filtered and washed with copious amounts of water. The crude pale blue solid was heated with ethanol on a warm water bath to dissolve any impurities and then suction filtered and dried overnight in vacuo to give the desired dipyrrole (0.472 g, 92%) as a pale blue powder: mp 240 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.93 (6H, t, J = 7.2 Hz), 3.39 (4H, br q), 5.44 (2H, s), 7.46−7.56 (4H, m), 7.58 (2H, d, J = 9 Hz), 7.82 (2H, d, J = 8.8 Hz), 7.90 (2H, d, J = 7.2 Hz), 8.28 (2H, d, J = 8.0 Hz), 11.32 (2H, br s); ^{13}C NMR ($CDCl_3$) δ 14.1, 29.8, 60.5, 112.8, 119.1, 120.9, 123.2, 125.0, 126.4, 126.6, 127.1, 127.4, 129.0, 129.3, 131.7, 162.4. Anal. Calcd for $C_{31}H_{26}N_2O_4$: C, 75.90; H, 5.34; N, 5.71. Found: C, 75.52; H, 5.33; N, 5.65.

13,17-Dibutyl-12,18-dimethyldinaphtho[2,1-*b*:1,2-*g*]porphyrin (43a). Sodium hydroxide (1.10 g) in water (5 mL) was added to dipyrrole **40** (250 mg) in methanol (13 mL) and hydrazine (25 drops) and the resulting mixture refluxed under a nitrogen atmosphere for 24 h. The mixture was cooled to room temperature and diluted with water (60 mL). The resulting cloudy solution was then cooled to 0 °C with the aid of an ice−salt bath and the aqueous mixture neutralized to litmus endpoint with glacial acetic acid, maintaining the temperature between 0 and 5 °C. The resulting precipitate was then suction filtered, washed with copious amounts of water, and dried overnight in vacuo to yield dicarboxylic acid **41** (189 mg, 85%) as a light purple powder. Crude **41** proved to be rather unstable when exposed to air and was used immediately in the following reaction. Dicarboxylic acid **41** (220 mg) was dissolved in trifluoroacetic acid (1.0 mL) in a pear-shaped flask and stirred under a nitrogen atmosphere for 10 min. A solution of monoaldehyde **9b**[57,58] (182 mg) in methanol (4 mL) was added, followed immediately by the addition of 30% HBr−AcOH (0.784 mL). The resulting mixture was allowed to stir at room temperature under nitrogen for 30 min. Anhydrous diethyl ether (20 mL) was then added dropwise to give a dark red solution, which was allowed to stir under nitrogen for an additional 2 h. The reaction mixture was stirred in an ice−water bath for the second hour to further induce precipitation. After this time, the precipitate was suction filtered, washed with cold anhydrous diethyl ether, and dried in vacuo overnight. The crude *a*,*c*-biladiene dihydrobromide salt **42** (402 mg, 96%), which was obtained as dark green crystals (mp >300 °C), was taken on without further purification. ^{1}H NMR ($CDCl_3$, downfield region only) δ 5.61 (2H, s), 7.27−7.35 (4H, m), 7.57 (2H, s), 7.65−7.83 (6H, m), 8.16 (2H, d, J = 8 Hz), 13.52 (2H, s), 14.40 (2H, s). Biladiene **42** (524 mg) was added to DMF (153 mL) containing zinc acetate (2.03 g) and silver iodate (2.60 g) and the mixture heated with stirring at 160 °C for 40 min under a nitrogen atmosphere. The mixture was then cooled to room temperature, diluted with dichloromethane (250 mL), and suction filtered through Celite. The filtrate was washed with water (2 × 300 mL) and dried over anhydrous sodium sulfate. The organic solution was then evaporated under reduced pressure to yield a green residue, which was dissolved in trifluoroacetic acid (3.0 mL) and stirred under nitrogen for 10 min. The acidic solution was then diluted with dichloromethane (150 mL), washed successively with water, 5% sodium bicarbonate, and water, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the purple residue chromatographed on grade III alumina eluting with dichloromethane to remove tarry byproducts. A second column was then performed on grade III alumina eluting with 5% hexanes in dichloromethane. The fractions containing pure porphyrin were combined, evaporated under reduced pressure, and recrystallized from chloroform−methanol. The title porphyrin (28 mg, 6.8%) was obtained as purple crystals: mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 400 (sh, 4.92), 427 (5.29), 535 (4.16), 568 (4.62), 588 (4.15), 646 nm (4.31); UV−vis (2% TFA−$CHCl_3$) λ_{max} (log ϵ) 436 (5.45), 579 (4.26), 629 nm (4.61); ^{1}H NMR ($CDCl_3$) δ −3.51 (2H, br s), 1.15 (6H, t, J = 7.4 Hz), 1.76−1.84 (4H, m), 2.26−2.32 (4H, m), 3.65 (6H, s) 4.04 (4H, t, J = 7.6 Hz), 7.94 (2H, t, J = 7.4 Hz), 8.25 (2H, t, J = 7.4 Hz), 8.47 (2H, d, J = 8.0 Hz), 8.54 (2H, d, J = 8.4 Hz), 9.49 (2H, d, J = 8.4 Hz), 10.00 (1H, s), 10.22 (2H, d, J = 8.8 Hz), 10.41 (2H, s), 11.91 (1H, s); ^{1}H NMR (TFA−$CDCl_3$) δ -2.98 (2H, br s), −2.0 (2H, v br), 1.08 (6H, t, J = 7.2 Hz), 1.61−1.70 (4H, m), 2.06−2.15 (4H, m), 3.70 (6H, s), 4.12 (4H, t, J = 7.8 Hz), 8.13 (2H, t, J = 7.6 Hz), 8.39 (2H, t, J = 7.6 Hz), 8.62 (2H, d, J = 8.4 Hz), 8.95 (2H, d, J = 8.4 Hz), 9.65 (2H, d, J = 8.4 Hz), 10.04 (2H, d, J = 8.0 Hz), 10.70 (1H, s), 11.17 (2H, s), 12.49 (1H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.1, 13.9, 23.2, 26.7, 34.5, 97.4, 99.2, 100.3, 119.9, 125.6, 128.0, 128.6, 129.1, 130.6, 131.1, 134.6, 135.0, 135.9, 137.4, 138.5, 140.7, 141.5, 142.8, 143.9; HRMS (FAB) calcd for $C_{46}H_{42}N_4$ + H *m/z* 651.3489, found 651.3488. Anal. Calcd for $C_{46}H_{42}N_4 \cdot {}^1/_2H_2O$: C, 83.73; H, 6.42; N, 8.42. Found: C, 83.24; H, 6.24; N, 8.47.

Nickel(II) Complex 43b. Dinaphthoporphyrin **43a** (6.4 mg) and nickel(II) tetrahydrate (33 mg) were stirred in DMF (10 mL) under reflux conditions overnight. The solution was then cooled to room temperature, diluted with chloroform, and washed with three 200 mL portions of water. The organic layers were evaporated under reduced pressure, and the resulting residue was recrystallized from chloroform−methanol to give the nickel complex (5.1 mg, 73%) as dark purple sheets: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 418 (5.14),

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547 (3.96), 590 nm (4.67); UV−vis (2% pyrroldine−$CHCl_3$) λ_{max} (log ϵ) 419 (5.02), 448 (4.82), 548 (sh, 3.90), 591 nm (4.55); ^{1}H NMR ($CDCl_3$) δ 1.10 (6H, t, J = 7.4 Hz), 1.64−1.72 (4H, br m), 2.02−2.10 (4H, br m), 3.25 (6H, s), 3.60−3.66 (4H, br m), 7.85 (2H, t, J = 7.0 Hz), 8.06 (2H, t, J = 7.2 Hz), 8.25 (2H, d, J = 8.4 Hz), 8.34 (2H, d, J = 8 Hz), 8.95 (2H, br), 9.20 (1H, br s), 9.52 (4H, br m), 10.91 (1H, br s); HRMS (FAB) calcd for $C_{46}H_{40}N_4Ni$ *m/z* 706.2606, found 706.2606.

Copper(II) Complex 43c. Dinaphthoporphyrin **43a** (6.1 mg) and copper(II) acetate monohydrate (32 mg) were stirred in DMF (10 mL) under reflux conditions overnight. The solution was then cooled to room temperature, diluted with chloroform, and washed with water. The organic solution was evaporated under reduced pressure and the residue recrystallized from chloroform−methanol to give the copper complex (5.4 mg, 81%) as dark green sheets: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 398 (sh, 4.67), 422 (5.30), 553 (3.97), 597 nm (4.56); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 397 (sh, 4.65), 422 (5.28), 554 (3.97), 597 nm (4.57); HRMS (FAB) calcd for $C_{46}H_{40}N_4Cu$ *m/z* 711.2549, found 711.2549.

Zinc(II) Complex 43d. Dinaphthoporphyrin **43a** (8.3 mg) and zinc(II) acetate dihydrate (32 mg) were stirred in DMF (10 mL) under reflux conditions for 2.5 h. The solution was then cooled to room temperature, diluted with chloroform, and washed with water. The organic solution was evaporated under reduced pressure and the residue recrystallized from chloroform-methanol to give the zinc complex (7.2 mg, 79%) as greenish-blue sheets: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} 440, 567, 603, 610 nm (sh); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 417 (sh, 4.74), 442 (5.56), 568 (4.30), 603 (4.63), 612 nm (sh, 4.68); ^{1}H NMR (pyrrolidine−$CDCl_3$, downfield region only) δ 7.91 (2H, t, J = 7.6 Hz), 8.28 (2H, t, J = 7.4 Hz), 8.47 (2H, d, J = 7.6 Hz), 8.53 (2H, d, J = 8.0 Hz), 9.64 (2H, d, J = 8.4 Hz), 10.08 (1H, s), 10.54 (4H, d), 10.55 (2H, s), 12.33 (1H, s); HRMS (EI) calcd for $C_{46}H_{40}N_4Zn$ *m/z* 712.2541, found 712.2544.

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Supporting Information Available: UV−vis, ^{1}H NMR, ^{13}C NMR, and mass spectra for selected compounds are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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