Porphyrins with Exocyclic Rings. 13.[1] Synthesis and Spectroscopic Characterization of Highly Modified Porphyrin Chromophores with Fused Acenaphthylene and Benzothiadiazole Rings

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As part of a survey on the influence of fused aromatic rings on the porphyrin chromophore, a series of novel structures with fused acenaphthylene or benzothiadiazole rings have been synthesized. Base-catalyzed condensation of 1-nitroacenaphthylene or 4-nitrobenzothiadiazole with esters of isocyanoacetic acid afforded good yields of the annelated pyrroles **5** and **28**. Cleavage of the ester moieties with KOH in refluxing ethylene glycol gave the unsubstituted heterocycles, and subsequent condensation with 2 equiv of acetoxymethylpyrroles **9** in acetic acid/ethanol produced the modified tripyrranes **12** and **31**. Tripyrranes with terminal *tert*-butyl ester units were treated with TFA and condensed with 3,4-diethyl-2,5-pyrroledicarboxaldehyde **13** in dichloromethane to give, following oxidation with DDQ, the corresponding π-extended porphyrins **14** and **32**. Acenaphthoporphyrins **14** showed unique UV−vis spectra with a triply split Soret band region and a relatively strong band near 660 nm. Strongly red-shifted absorptions were also noted for the dications and the nickel(II), copper(II), and zinc chelates for this system. Thiadiazoloporphyrins **32** gave two broadened Soret bands, but the Q-band region was unexceptional. However, the nickel(II), copper-(II), and zinc complexes all showed abnormally strong absorptions between 600 and 612 nm. Porphyrins with two antipodal fused aromatic rings were easily prepared by condensing *c*-annelated pyrroledialdehydes **17** with tripyrranes **12** and **31**, and the spectroscopic properties of the resulting porphyrins showed that the observed ring-fusion effects were essentially additive. Porphyrins with two adjacent acenaphthylene rings were also prepared by the MacDonald "2 + 2" condensation, although this chemistrry gave poor results in the synthesis of a porphyrin with two fused benzothiadiazole rings. The spectroscopic properties of these new highly conjugated porphyrin structures show that ring fusion can profoundly modify the porphyrin chromophore.

Introduction

Porphyrinoid chromophores with strong absorptions in the far-visible/near-IR region have attracted considerable attention in recent years due to their intrinsic value in the development of novel optical materials with potential applications in optical recording technology.[2] In addition, some porphyrins show a high affinity for tumor cells and can act as photosensitizers for singlet oxygen formation in photodynamic therapy (PDT).[3] However, light is strongly absorbed by bodily tissues over much of the visible region, and this limits clinical applications. Light penetration is greatest at higher wavelengths (>700 nm), and for this reason, there has been a great deal of effort directed at the development of more effective photosensitizers for PDT that absorb between 700 and 800 nm.[3] Increased conjugation usually induces a red shift for a given chromophore, and one might naively expect that aromatic subunits fused to the porphyrin nucleus (see Chart 1) would have the desired effect on the chromophores electronic spectra. However, in many cases, the influence of benzenoid ring fusion on porphyrin UV−vis absorption spectra is minimal. Solutions of 2,3,7,8,-12,13,17,18-octaethylporphyrin (OEP) in organic solvents such as chloroform or benzene show a strong Soret band at 400 nm, together with a series of Q-bands between 490 and 625 nm (Table 1).[4] The longest wavelength

Chart 1. Porphyrins with Fused Aromatic Subunits

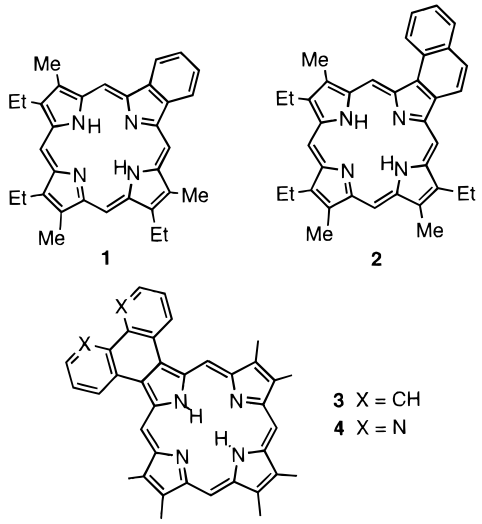

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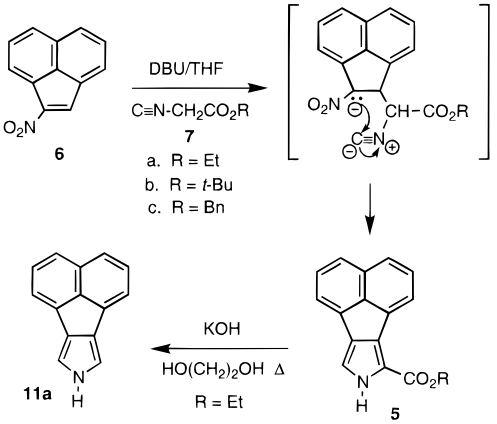
Table 1. Electronic Spectra of OEP and Selected Porphyrins with One Fused Aromatic Ring

porphyrin (solvent)	λ_{max} (nm) ($\log_{10}\epsilon$)	Soret bands		Q bands IV	III	II	I
OEP[4]		400		498	532	568	622
(Benzene)		(5.20)		(4.16)	(4.03)	(3.83)	(3.76)
1[5]		403		503	541	573	628
($CHCl_3$)		(5.47)		(4.07)	(4.40)	(3.89)	(4.16)
2[7]		415		511	547	574	630
(CH_2Cl_2)		(5.31)		(3.99)	(4.46)	(4.03)	(3.76)
3[8]		417		516	553	577	634
(CH_2Cl_2)		(5.23)		(4.02)	(4.47)	(4.11)	(3.58)
14a	387	431	454	529	571	598	658
($CHCl_3$)	(4.79)	(4.95)	(4.84)	(4.16)	(4.19)	(4.03)	(4.34)
14b	387	431	456	530	569	597	657
($CHCl_3$)	(4.86)	(5.01)	(5.02)	(4.27)	(4.03)	(3.98)	(4.42)
32a	380	436		528	566	588	
($CHCl_3$)	(4.85)	(5.06)		(3.86)	(4.45)	(4.41)	

Q-band, which by convention is assigned as band I, appears at 622 nm for OEP and has a molar absorptivity of 5800.[4] Monobenzoporphyrins (**1**) were first prepared over 20 years ago[5] and are minor constituents of organic-rich sediments such as oil shales and petroleum.[5,6] The Soret band for **1** is slightly shifted to 403 nm, while Q-band I is significantly enhanced with a molar extinction coefficient of 14 500 and a λ_{max} value of 628 nm. Further extension of the π-system in naphthoporphyrin **2**[7] leads to a Soret band at 415 nm and Q-band I at 630 ($\epsilon = 5750$) nm. In phenanthroporphyrin **3**,[8] these values are 417 and 634 nm ($\epsilon = 3800$), respectively, while the related phenanthroline structure **4**[9] gave a Soret band at 424 nm and a very weak Q-band I at 636 nm. While some small shifts are apparent, and these are somewhat enhanced by the addition of two or more fused aromatic ring systems,[8,10−12] the overall effects are minimal, suggesting that benzenoid ring fusion does not significantly alter the porphyrin chromophore. Furthermore, there is a trend toward diminished molar absorptivities for band I as the size of the annelated ring system increases. On the other hand, these extended structures do hold promise in the development of nanomolecular systems,[13] and phenanthrolinoporphyrins **4** might act as "molecular aligator clips".[14] However, the ability to more profoundly alter the porphyrin chromophore remains an important goal. In this paper, we report the effects of fused acenaphthylene and benzothiadiazole rings on the spectroscopic properties of annelated porphyrins. Following on from the lackluster results for **1**−**4**, these new systems show remarkably large effects, which for the first time allow the electronic structure of the porphyrin macrocycle to be radically changed by ring fusion.

Scheme 1



Results and Discussion

Acenaphtho[1,2-*b*]porphyrins.[15,16] The synthesis of *b*-annelated porphyrins such as **1**−**4** generally relies on the availability of suitable pyrrolic precursors with fused aromatic rings. Nitroalkenes have been shown to condense with isocyanoacetates in the presence of a nonnucleophilic base such as DBU to give pyrrole-2-carboxylates,[17] and this methodology has been extended to reactions with nitroaromatic compounds that have a certain degree of nitroalkene character.[8,9,18,19] This approach can be applied to the preparation of acenaphtho[1,2-*c*]pyrroles **5** from 1-nitroacenaphthylene **6** (Scheme 1). Hence, condensation of **6** with esters of isocyanoacetic acid (**7a**−**c**) in the presence of 1 equiv of DBU in THF gave the required acenaphthopyrroles **6** as stable crystalline compounds. The yields for the ethyl and *tert*-butyl

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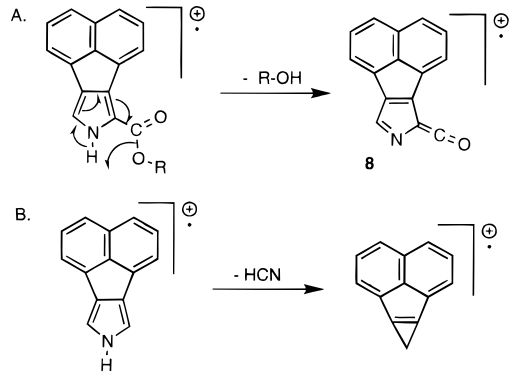
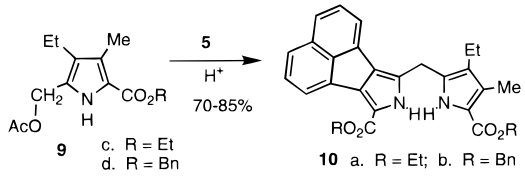
Scheme 2



Scheme 3

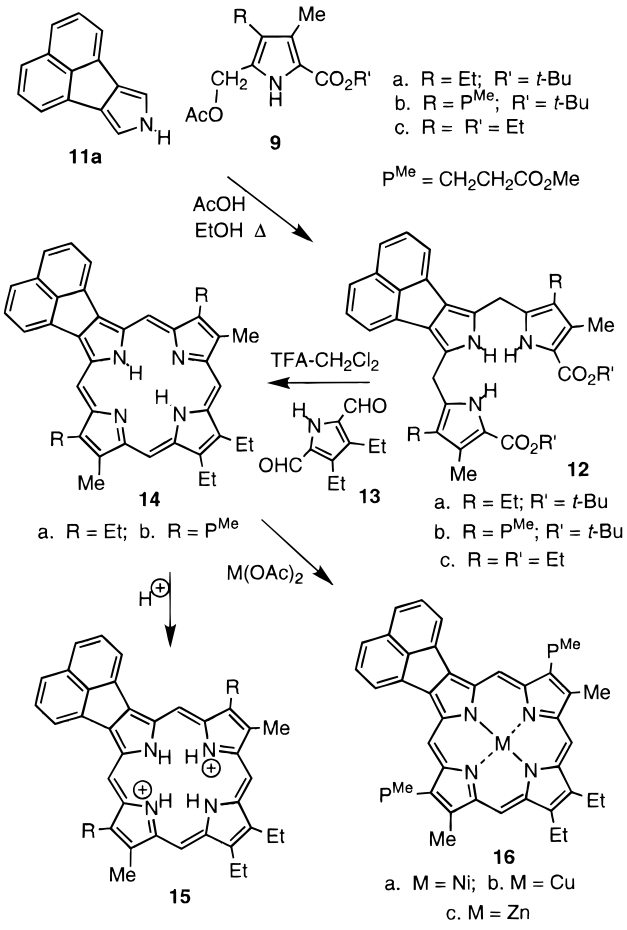


esters were in the range of 44−47%, although the benzyl ester was obtained in somewhat lower yield. In the proton NMR spectra, the acenaphthylene protons resonated in the region from 7.5 to 7.8 ppm, with the exception of the proton closest to the ester moiety, which was further deshielded and appeared at 8.1 ppm. The latter shift is much smaller than that observed in the related phenanthro[9,10-*c*]pyrroles[8] because the proximal acenaphthylene proton is held further away from the carbonyl unit. In the EI MS for **5a**−**c**, the major fragmentation pathway involves loss of ROH, and this presumably results in the formation of the ketene radical cation **8** (Scheme 2A).

Our previous syntheses of b-annelated porphyrins such as naphthoporphyrins **2**[7] and phenanthroporphyrins **3**[8] had made effective use of MacDonald's "2 + 2" condensation[20] to construct the porphyrin macrocycle, and this necessitated the preparation of suitably substituted dipyrrylmethane intermediates. Condensation of acetoxymethylpyrroles **9** with acenaphthopyrroles **5b** or **5c** in the presence of *p*-toluenesulfonic acid in acetic acid or Montmorillonite clay in dichloromethane[21] gave the required dipyrrylmethanes in excellent yields (Scheme 3). Deprotection of the ester moieties, followed by acid-catalyzed condensation with dipyrrylmethanedialdehydes under standard conditions,[20] afforded low yields of porphyrin products. Although UV−vis spectra for these crude products indicated that the acenaphthylene ring system had a pronounced effect on the porphyrin chromophore, these early studies were not sufficiently successful to allow the isolation of pure acenaphthoporphyrins.

In other studies, our group[9,22−24] and others[25] have found that a "3 + 1" variant on the MacDonald condensation provides an excellent alternative route to novel

Scheme 4



porphyrinoid structures, and these successes prompted us to explore this approach in the synthesis of acenaphtho[1,2-*b*]porphyrins. Treatment of ethyl ester **5a** with potassium hydroxide in refluxing ethylene glycol afforded the unsubstituted acenaphtho[1,2-*c*]pyrrole **11a** in good yield (Scheme 1). This compound was a stable solid that could be stored indefinitely. Proton and carbon-13 NMR spectroscopy demonstrated the symmetry of the structure and the absence of a carboxylate unit (also confirmed by IR). EI MS showed the anticipated strong molecular ion at *m*/*z* 191 with fragmentation primarily occurring with loss of HCN (Scheme 2B); this mode of fragmentation was also noted for the corresponding phenanthro[9,10-*c*]-pyrrole **11b** (vide supra).

Acenaphthopyrrole **11a** was condensed with 2 equiv of acetoxymethylpyrroles **9a**, **9b**, or **9c** in refluxing acetic acid/ethanol under nitrogen (Scheme 4). Precipitation by pouring the reaction mixture into ice−water afforded the related tripyrranes **12a**−**c** in crude form. Tripyrrane **12c** was recrystallized from chloroform and fully characterized. However, *tert*-butyl esters **12a** and **12b** could not

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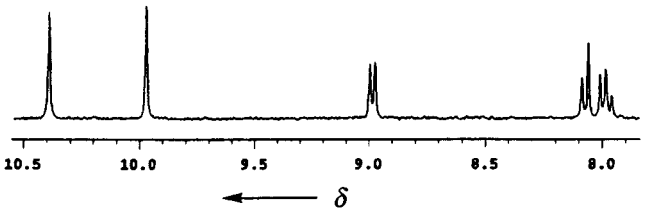


Figure 1. Partial 300 MHz proton NMR spectrum of acenaphthoporphyrin **14a** in deuteriochloroform.

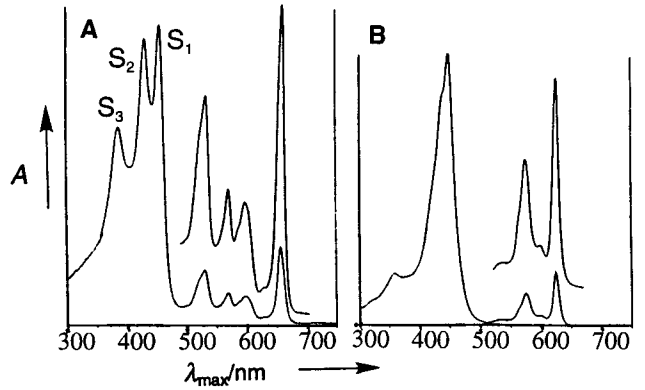
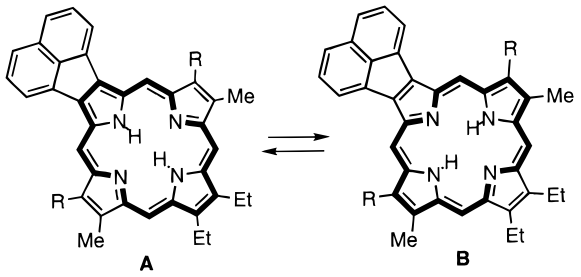


Figure 2. UV−vis spectra of acenaphthoporphyrin **14b**: (A) free base in chloroform. (B) Dication in 1% TFA/chloroform.

be recrystallized and were insufficiently stable in solution to allow column chromatography to be performed. For this reason, these critical intermediates were used in crude form for porphyrin synthesis. The *tert*-butyl ester protected tripyrranes were treated with TFA under nitrogen for 10 min, diluted with dichloromethane, and further reacted with the pyrroledialdehyde **13**.[23] Following neutralization with triethylamine and oxidation with 1 equiv of DDQ, the products were purified by column chromatography. The major porphyrin fractions were recrystallized from chloroform/methanol to give the pure acenaphthoporphyrins **14a** and **14b** in 33−36% yield.

The proton and carbon-13 NMR spectra for **14a** and **14b** confirmed the isomeric purity of the products and demonstrated the presence of a plane of symmetry. The aromatic ring current of the porphyrin macrocycle was not significantly perturbed by the presence of the acenaphthylene subunit, and the proton NMR spectra (Figure 1) showed the external *meso* protons at 10.0 and 10.4 ppm (the latter being slightly deshielded by the adjacent acenaphthylene ring), while the NHs were observed upfield at −3.2 ppm. Similarly, the acenaphthylene protons showed no indication of this moiety taking part in an expanded delocalization pathway. Only the protons nearest to the porphyrin were significantly deshielded, appearing as a 2H doublet at 8.9 ppm, and this can be attributed to the expected anisotropy for this positioning relative to the aromatic macrocycle. While the NMR spectra were unexceptional, the electronic spectra for porphyrins **14a** and **14b** were truly unique (Figure 2). The Soret band region was split into three strong bands at 387, 431, and 454 nm in the case of **14a**, followed by a series of four Q-bands. The longest wavelength Q-band appeared near 660 nm, compared to the comparitively weak absorption at 634 nm in phenanthroporphyrin **3**, and perhaps more significantly, this band showed a molar absorptivity of greater than 20 000. Clearly, the acenaphthylene unit interacts far more strongly with the porphyrin chromophore than does the larger phenanthrene system, and this indicates that the UV−vis spectra for annelated porphyrins can be modified to a far greater extent than had been previously recognized. Interestingly, the relative intensities for the three Soret bands in chloroform solutions of **14b** consistently gave somewhat different results than for **14a**. In particular, the longer wavelength Soret band (S_1) for **14b** (Figure 2) was more intense (ϵ = 106 000) and the middle band (S_2) weaker (ϵ = 102 000), whereas S_1 was considerably weaker than S_2 for **14a**. At first glance, these differences seem inexplicable as the chromophores would appear to be the same for both structures. However, the acenaphthoporphyrins are likely to exist in solution as nonequivalent tautomers **A** and **B** (Scheme 5), although additional tautomers with adjacent NHs are also possible. The chromophore for **A** may be distinctly different from that for **B** (in **A** the acenaphthylene system is an integral part of the 18π electron delocalization pathway, shown in bold, whereas it is peripheral in tautomer **B**), and as the observed UV−vis spectra for **14a** and **14b** must consist of a superimposition of the absorbances for the various tautomers in solution, any perturbation of the relative populations for these species is likely to alter the relative intensities of the various bands, particularly those that are unique for a particular tautomer. The presence of ester side chains on **14b** presumably affects the equilibrium, possibly via hydrogen-bonding interactions. The intensity of S_1 was slightly diminished in spectra that were run in acetone, although this band remained more intense for **14b** than for **14a**. Addition of 1% TFA afforded the dications **15**, which show a single strong Soret band at 445 nm and a moderately intense band at 625 nm. Again, these absorptions were strongly red-shifted compared to the dications for phenanthroporphyrins **3**.[8] Acenaphthoporphyrin dications **15a** and **15b** gave similar spectra, which is to be expected as NH tautomerization is no longer a possibility.

Scheme 5



Porphyrin **14b** was reacted with nickel(II), copper(II), and zinc acetates under standard conditions to give the corresponding metalloporphyrins **16** (Scheme 4), and these also showed bathochromically shifted absorptions in their UV−vis spectra (Figure 3). As is the case for OEP[4] and phenanthroporphyrins,[8] the absorptions shift to higher wavelength with increasing atomic number across the periodic table. The nickel(II) complex showed a Soret band at 434 nm, together with a strong Q-band at 602 nm (compared to 412 and 578 nm, repectively, for the nickel chelates of phenanthroporphyrins **3**), whereas these appear at 436 and 610 nm for the copper(II) complex **16b** and at 446 and 616 nm for the zinc chelate **16c** (these values are 418 and 590 nm for the corresponding zinc phenanthroporphyrin). Clearly, the unprecedented modifying influence of the acenaphthylene

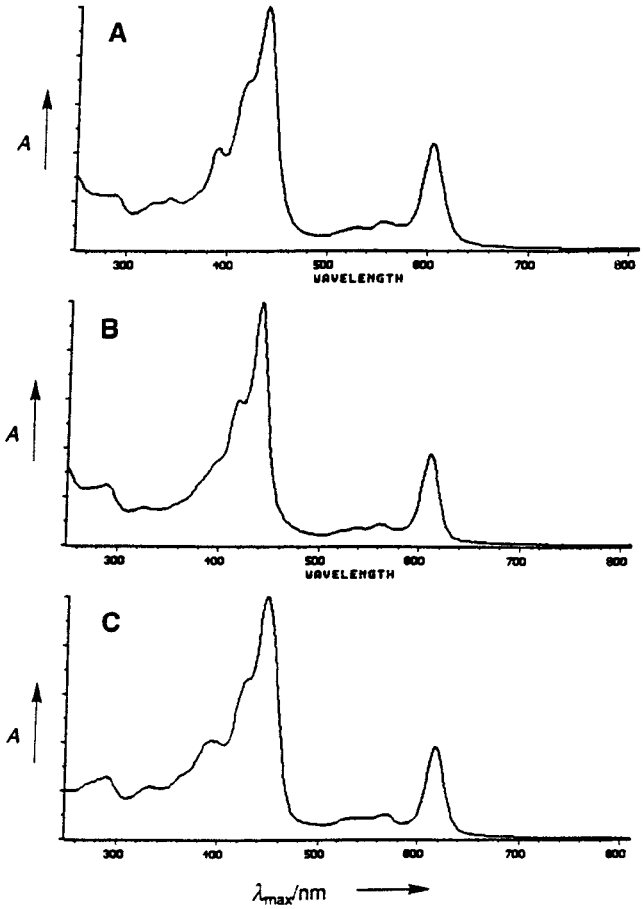


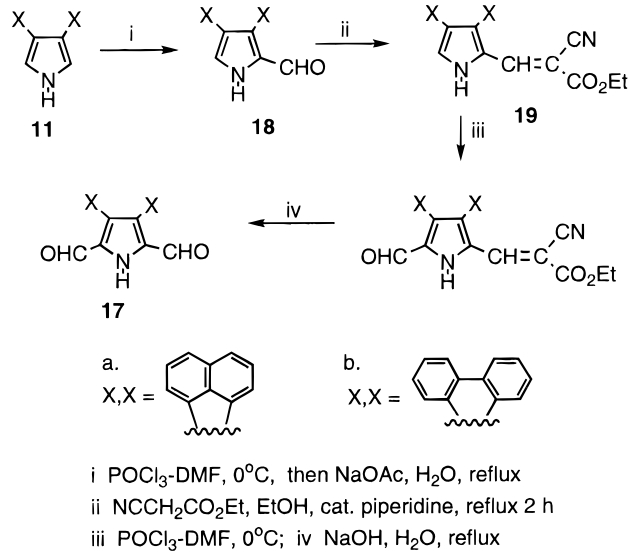
Figure 3. UV−vis spectra of acenaphthoporphyrin metal chelates **16** in chloroform: (A) nickel(II) complex; (B) copper-(II) complex; (C) zinc complex. Note that the UV−vis absorptions shift to longer wavelengths from nickel to zinc across the periodic table.

ring system applies equally well for the free bases, dications, and transition metal chelates of these annelated porphyrin structures.

The magnitude of the effects induced by the presence of a single acenaphthylene ring encouraged us to consider the synthesis of diacenaphthoporphyrins. The "3 + 1" method served as an ideal route for the synthesis of the oppositely annealed diacenaphthylene system. To accomplish this synthesis, the diformylacenaphthopyrrole **17a** was required, and this was obtained in excellent overall yield (>80%) from the unsubstituted tetracycle **11a** (Scheme 6). Vilsmeier formylation of **11a** afforded the monoaldehyde **18a**, but this species proved to be insufficiently reactive to allow further substitution. The aldehyde was protected by reaction of ethyl cyanoacetate with catalytic piperidine in refluxing ethanol to give cyanovinylpyrrole **19a** as bright-yellow crystals. Subsequent formylation and deprotection with refluxing aqueous sodium hydroxide gave the required dialdehyde **17a**. This strategy has been used to prepare pyrroledialdehydes for many years,[26] but for simpler pyrrolic structures, the final step often gives modest yields due to extensive decomposition that is caused by the harsh conditions utilized in the deprotection of the cyanovinyl

(26) Dolphin, D.; Paine, J. B. III; Woodward, R. B. *J. Org. Chem.* **1976**, *41*, 2830. For an alternative one-step synthesis of pyrrole-2,5-dicarboxaldehydes, see: Tardieux, C.; Bolze, F.; Gros, C. P.; Guilard, R. *Synthesis* **1998**, 267.

Scheme 6



i $POCl_3$-DMF, 0°C, then NaOAc, H_2O, reflux
ii $NCCH_2CO_2Et$, EtOH, cat. piperidine, reflux 2 h
iii $POCl_3$-DMF, 0°C; iv NaOH, H_2O, reflux

unit. In this series, the deprotection occurs in virtually quantitative yield, most likely due to the very low solubility of the product, which is thereby protected from further reaction/degradation. The related diformylphenanthropyrrole **17b** was prepared in a similar fashion (Scheme 6). Phenanthropyrrole **11b** was prepared from the corresponding ethyl ester[8] by treatment with KOH in refluxing ethylene glycol. Subsequent formylation afforded the monoaldehyde **18b**, and following protection as the cyanovinyl derivative, reformylation, and deprotection, the required dialdehyde was obtained in excellent overall yield.

The availability of the dialdehydes **17** facilitated the synthesis of both the *opp*-diacenaphthoporphyrin **20** and the mixed acenaphthophenanthroporphyrin system **21** (Scheme 7). The bispropionate substituted tripyrrane **12b** was selected in this study because it was anticipated that the longer side chains would increase the solubility of the resulting porphyrin products. Condensation of **12b** with **17a** under the "3 + 1" conditions afforded the *opp*-diacenaphthylene annelated porphyrin **20** in 50% yield. Similarly, condensation of **12b** with **17b** gave the mixed fused acenaphthylene/phenanthrene system **21** in 42% yield. It is noteworthy that this mix and match approach allows access to many novel arrangements of fused aromatic ring systems around the periphery of the porphyrin macrocycle and hence provides the opportunity to fully probe the influence of fused aromatic rings on the porphyrin chromophore. The diacenaphtho[1,2-*b*:1,2-*l*]porphyrin **20** showed further bathochromic shifts to its major UV−vis absorptions and demonstrated that the presence of a second acenaphthylene unit had a cumulative affect (Figure 4). Porphyrin **20** exhibited a split Soret band a 443 and 470 nm, while Q-band I gave a strong absorption at 692 nm. By contrast, the mixed system **21** showed a single Soret band at 436 nm and a far weaker Q-band I at 675 nm (Figure 4), further underlining the minimal influence of fused phenanthrene subunits on the electronic spectra of porphyrins. The same trends were evident for the dications and the metal chelates for these systems. The dication for **20** shows a Soret band at 472 nm, compared to 466 nm for **21** and 448 nm in the case of monoacenaphthoporphyrin **15b**. For the Ni(II), Cu(II), and Zn chelates of **20**, the Soret bands were apparent at 440, 446, and 458 nm, respec-

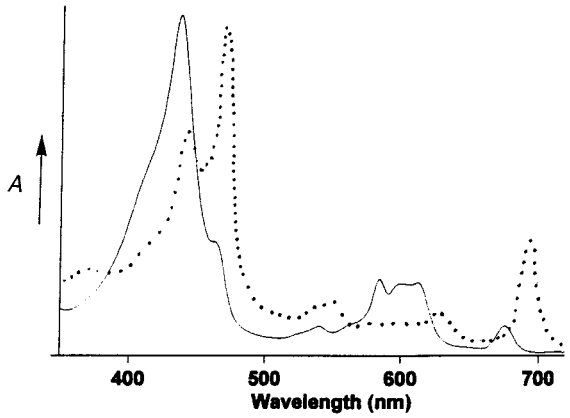
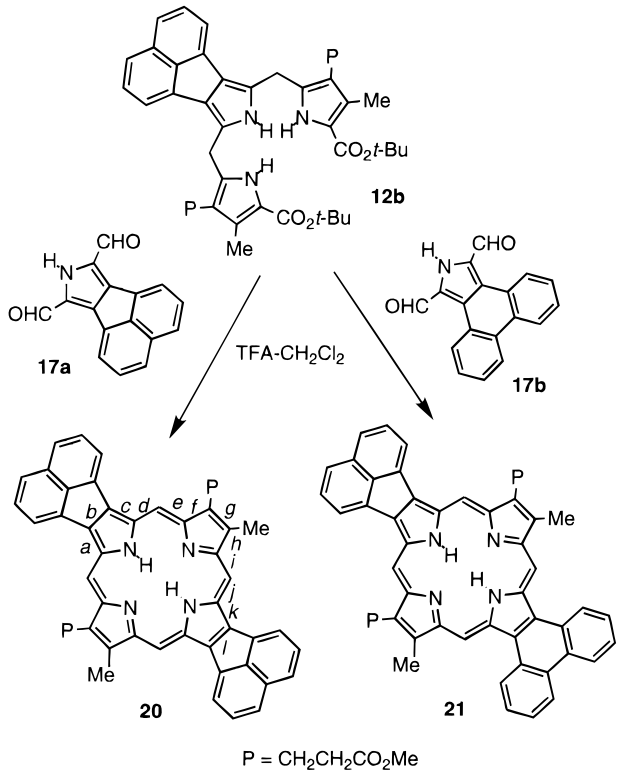


Figure 4. UV−vis spectra of *opp*-diacenaphthoporphyrin **20** (dotted line) and mixed diannelated porphyrin **21** (solid line) in chloroform.

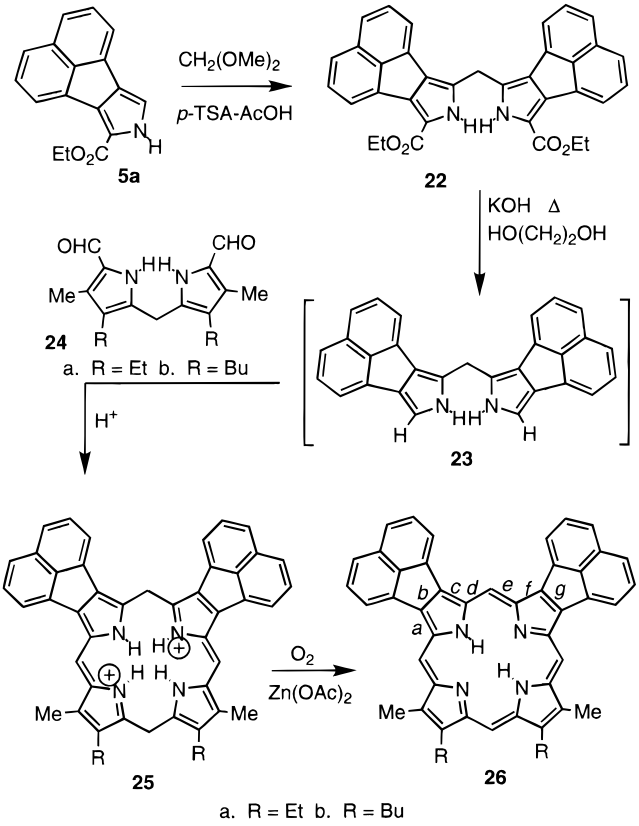
Scheme 7



tively, while the longest wavelength bands (strong) were at 642, 650, and 656 nm. By contrast, these values were 434, 436, and 450 nm (Soret bands) and 618, 624, and 632 nm for the longer wavelength absorptions in the corresponding chelates for porphyrin **21**. The trend toward longer wavelength absorptions from Ni(II) to Cu(II) to Zn complexes clearly also holds for these structures, but the "acenaphthylene effect" remains a strong factor in the recorded UV−vis absorption maxima.

The synthesis of a porphyrin with adjacent fused acenaphthylene rings could not be achieved by the "3 + 1" methodology, and this forced us to reconsider the MacDonald "2 + 2" approach (Scheme 8). Condensation of ethyl ester **5a** with dimethoxymethane in acetic acid containing catalytic *p*-toluenesulfonic acid at room temperature for 3 days afforded the symmetrical dipyrrylmethane **22** in 92% yield. The bridging methylene for dipyrrylmethane **22** resonated at 4.6 ppm in the proton

Scheme 8

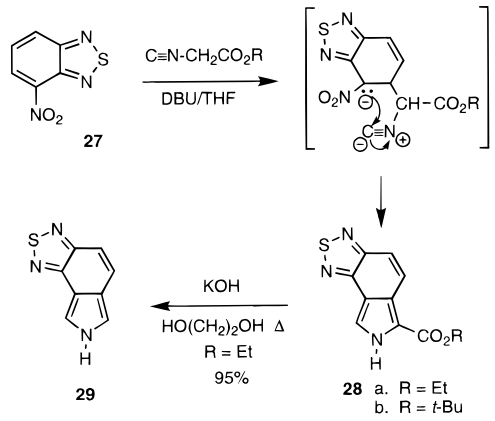


NMR spectra, compared to 4.2 ppm in the monoacenaphthodipyrrylmethanes **10** and 3.8 ppm for analogous dipyrrylmethanes without the fused aromatic subunits, again demonstrating the modest deshielding influence due to the fused acenaphthylene ring system. Saponification and decarboxylation was accomplished by treating **22** with KOH in refluxing ethylene glycol with strict exclusion of oxygen. Initial attempts to condense the crude intermediate **23** with dialdehydes **24** failed to give more than trace amounts of the required porphyrin, perhaps not surprisingly given the lack of success that we had previously using this chemistry in the synthesis of monoacenaphthoporphyrins. However, when the dipyrrylmethane precursors **23** and **24** were added dropwise over a period of 2 h to a stirred solution of the acid catalyst (this essentially mimics high-dilution conditions[27]) and the porphodimethene intermediate **25** was allowed to air oxidize in the presence of zinc acetate, the required diacenaphtho[1,2-*b*:1,2-*g*]porphyrins **26** could be isolated in 20−23% yield. While high-dilution conditions are often favored in the formation of larger ring structures, these are usually eschewed in porphyrin synthesis due to the risk of the intermediates undergoing fragmentation/recombination reactions under the acid cyclization conditions that can lead to isomer formation.[28] In this case, the NMR data showed that these porphyrins were single isomers, although this need not necessarily always be the case (vide supra). The triethyl-substituted porphyrin **26a** was highly insoluble in organic solvents and was not further investigated. However, the sparingly soluble dibutylporphyrin **26b** proved to be more ame-

(27) Burns, D. H.; Caldwell, T. M.; Burden, M. W. *Tetrahedron Lett.* **1993**, *34*, 2883.

(28) Jackson, A. H.; Lertwanawatana, W.; Pandey, R. K.; Rao, K. R. N. *J. Chem. Soc., Perkin Trans. 1* **1989**, 374.

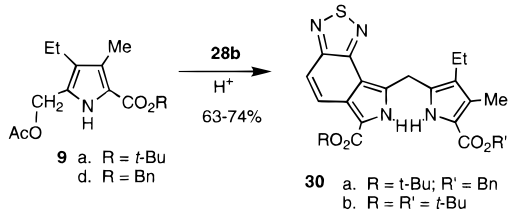
Scheme 9



nable for study. Proton and carbon-13 NMR spectroscopy in TFA/$CDCl_3$ confirmed the symmetry of the porphyrin structure, and the former technique showed three resonances for the meso protons at 10.6 (1H), 11.1 (2H), and 11.6 (1H) ppm. The downfield signal corresponds to the meso proton between the two acenaphthylene rings; the corresponding value for an *adj*-diphenanthroporphyrin was 12.3 ppm,[8] again demonstrating the greater deshielding influence of the phenanthrene ring system. The bathochromic shifts observed in the UV−vis spectra for *adj*-diacenaphthoporphyrin **26b** were less pronounced than those observed for *opp*-diacenaphthoporphyrin **20**, and the principal Soret band appeared at 476 nm, while Q-band I gave a moderately strong absorption maximum at 672 nm. The UV−vis spectra for the dication and the nickel(II) and zinc chelates (the copper complex could not be formed under conventional conditions, probably due to the low solubility of **26b**) showed the same intermediary bathochromic shifts. Interestingly, dinaphtho- and diphenanthroporphyrins[8] showed the opposite trend, where longer wavelength absorptions were noted for the adjacent ring fused structures compared to the corresponding *opp*-diannealed compounds. In a separate study, the influence of four fused acenaphthylene rings[29] was shown to have an even more pronounced effect on the porphyrin chromophore, and this further confirms the cumulative nature of the acenaphthylene ring-fusion factor.

Thiadiazolobenzoporphyrins.[30] Nitroaromatic compounds are valuable precursors to c-annelated pyrroles, although they vary considerably in reactivity (nitroalkene character) and availability.[8,9,18,19] 4-Nitro-2,1,3-benzothiadiazole (**27**) reacts smoothly with isocyanoacetates **7** in the presence of DBU in THF at high dilution to give the thiadiazolobenzopyrroles **28** in good yields (Scheme 9),[18b,19] and this chemistry allows the influence of this heterocyclic system on the porphyrin chromophore to be assessed. High-dilution conditions were not helpful in the synthesis of acenaphthopyrroles or phenanthropyrroles,[18] and the origin of this effect was not clear, although much lower yields of **28** were obtained under conventional conditions. Two examples of **28** were prepared, the ethyl

Scheme 10



and *tert*-butyl esters, and the former was shown to cleanly saponify and decarboxylate with KOH in ethylene glycol at 180−190 °C to give the unsubstituted tricycle **29**. As was the case for the acenaphthoporphyrins (vide infra), the synthesis of porphyrins with fused benzothiadiazole rings was attempted using the MacDonald condensation. Condensation of **28b** with acetoxymethylpyrroles **9a** or **9d** in the presence of Montmorillonite clay in dichloromethane afforded the dipyrrylmethanes **30** in good yields (Scheme 10). In the proton NMR spectra, the bridge CH_2 was more deshielded than was the case for acenaphthylene analogues **10**, appearing as a 2H resonance near 4.6 ppm. These compounds were reasonably stable, although they quickly discolored on exposure to air, but initial attempts to utilize them in the "2 + 2" synthesis of thiadiazolobenzoporphyrins were unsuccessful. However, the "3 + 1" methodology again proved to be an excellent alternative. Condensation of **29** with 2 equiv of acetoxymethylpyrroles **9a**−**c** in refluxing acetic acid/ethanol afforded the tripyrranes **31a**−**c** in good to excellent yields. The diethyl ester **31c** crystallized from the reaction mixture and could be fully characterized, but as was the case for the acenaphthylene series, the *tert*-butyl esters **31a** and **31b** could not be recrystallized and were used in crude form.

Treatment of **31a** or **31b** with TFA, followed by dilution with dichloromethane, addition of dialdehyde **13**, and oxidation with DDQ, gave the novel thiadiazolobenzoporphyrins **32** in 31−42% yield. The availability of dialdehydes **17a** and **17b** also allowed the convenient synthesis of the mixed systems **33a** and **33b**, again in excellent yields, from tripyrrane **31b** (47−55%) (Scheme 11). The proton NMR spectra for **32** showed the expected porphyrin ring-current effects, although the meso protons were further deshielded in TFA/$CDCl_3$ due to protonation on both the internal pyrrolenic nitrogens and the external heterocycle. The meso proton adjacent to the thiadiazole moiety was shifted slightly downfield for the free bases, appearing near 10.2 ppm, but protonation shifted this resonance to 12 ppm. Similar shifts were also noted for the mixed diannelated porphyrins **33a** and **33b**. The monoannelated porphyrins **32** gave very unusual UV−vis spectra with broadened split Soret bands at 380 and 436 nm, although no strongly red-shifted Q-bands were evident (Figure 5A). However, the presence of propionate ester side chains did not significantly influence these electronic spectra, in contrast to the results for acenaphthoporphyrins **14**, although the shorter wavelength Soret band for **33a** was slightly more intense than was the case for porphyrin **33b**. The spectra in 1% TFA/$CHCl_3$ also showed a split Soret at 422 and 434 nm, although these absorptions were somewhat sharper and more intense. However, the most remarkabe spectra were obtained for the metal chelates derived from **32a**. The nickel(II) complex showed two Soret bands of diminished intensity at 386 and 428 nm, but more significantly, a strong Q-band was evident at 600 nm. These values were 388,

(29) Lash, T. D.; Chandrasekar, P. *J. Am. Chem. Soc.* **1996**, *118*, 8767. See also ref 19b.

(30) Results presented, in part, at the 211th National Meeting of the American Chemical Society, New Orleans, Louisiana, March 28, 1996 (Osuma, A. T.; Lash, T. D. *Book of Abstracts*, ORGN 478) and the 29th Great Lakes Regional American Chemical Society Meeting, Normal, Illinois, May 1996 (Osuma, A. T.; Lash, T. D. *Program and Abstracts*, Abstract 132).

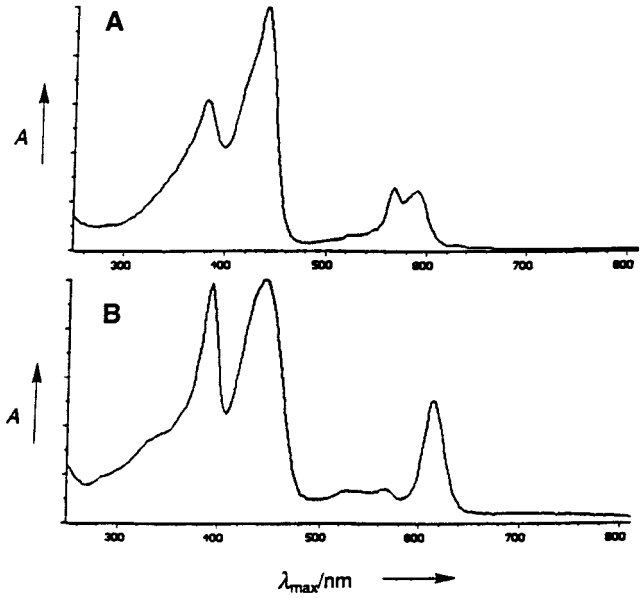
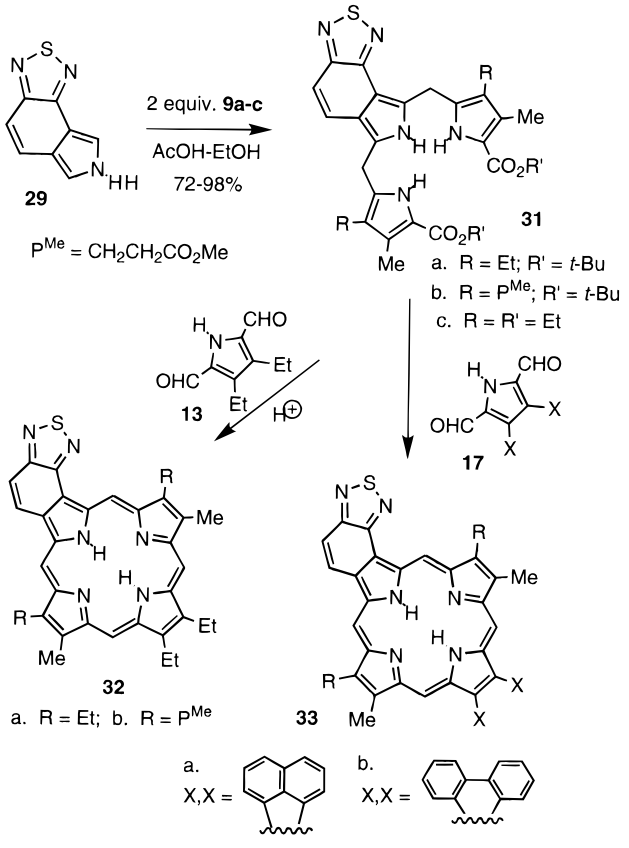


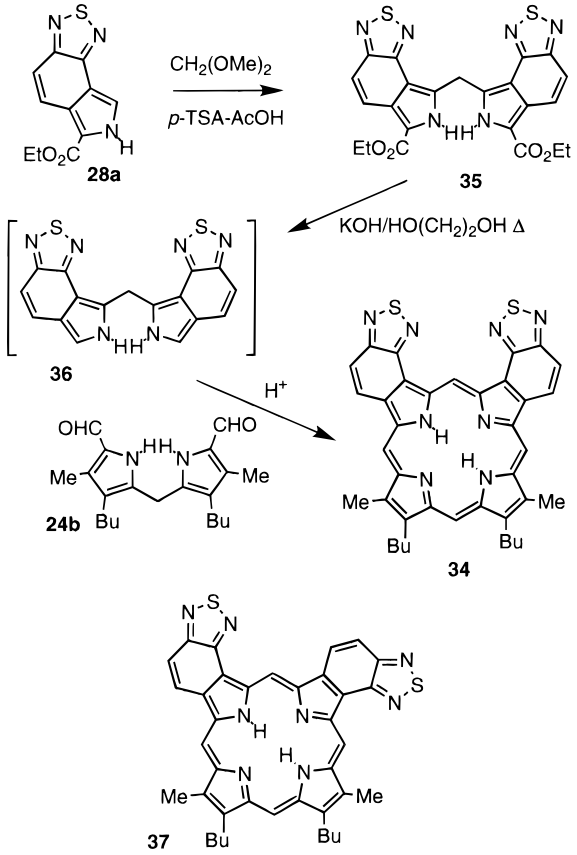
Figure 5. Electronic spectra of (A) thiadiazolobenzoporphyrin **32a** in chloroform and (B) zinc chelate of **32a** in chloroform.

Scheme 11



434, and 606 nm in the copper(II) chelate and 390, 442, and 612 nm in the case of the zinc complex (Figure 5B). Clearly, the same trends apply for these transition metal chelates, but the appearance of a strong band at greater than 600 nm was an unexpected bonus. The mixed systems also provided insightful data. The acenaphtho structure **33a** gave a Soret band at 442 nm and a weak Q-band I at 686 nm, whereas phenanthroporphyrin **33b** showed a Soret band at 440 nm and no significant bands above 604 nm. The metal chelates again showed the most profound effects, with weak split Soret bands and relatively strong bands above 600 nm. In the acenaphthylene series, the long-wavelength bands appeared at 636, 644, and 650 nm for the nickel(II), copper(II), and zinc complexes, respectively, whereas these value were 618, 624, and 632 nm for the phenanthroporphyrin chelates. The zinc complex of the mixed acenaphthylene/thiadiazolobenzoporphyrin **33a** not only showed the greatest red shift, as would be expected, but more significantly, the molar absorptivity for the band at 650 nm was greater than 80 000.

Scheme 12



We were also interested in the synthesis of porphyrins with two fused benzothiadiazole rings, but in this case, the "3 + 1" route could not be easily applied due to the lack of symmetry in the pyrrolic precursors (in the "3 + 1" method, one of the condensing fragments, tripyrrane or dialdehyde, must be symmetrical or two isomeric porphyrins will be formed). However, the MacDonald condensation provided a possible route to the *adj*-diannelated porphyrin **34** (Scheme 12). Acid-catalyzed condensation of **28a** with dimethoxymethane afforded the symmetrical dipyrrole **35** in quantitative yield. As would be expected, the linking methylene unit afforded a highly deshielded singlet at 5.3 ppm, indicating that the two proximate benzothiadiazole rings induce a downfield shift of 1.5 ppm. Cleavage of the ester moieties of **35** was accomplished with KOH in refluxing ethylene glycol, and the resulting unstable intermediate **36** was condensed with diformyldipyrrylmethane **24b** under modified MacDonald condensation conditions. Virtually no porphyrin product was produced in the initial studies, and we turned to the slow addition protocol to overcome these problems. This procedure increased the yield of product to 7%, but the proton NMR spectrum showed additional

peaks that suggested an isomeric species **37** was present (approximately 15%). The two benzothiadiazole units in **34** are orientated toward one another such that the lone pair electrons on two of the nitrogen atoms point toward one another, and this unfavorable interaction may hinder the cyclization reaction. This would allow the intermediates a greater opportunity to undergo acidolysis reactions and hence form isomeric species. This result provides a clear warning that dilution techniques must be used with great caution in porphyrin synthesis. Careful flash chromatography allowed a small sample of pure **34** to be isolated. The 300 MHz proton NMR spectrum in TFA/$CDCl_3$ confirmed the symmetry of the dithiadiazoloporphyrin and displayed the usually strong ring current with the meso protons producing singlets at 10.7 (1H), 11.3 (2H), and 13.3 ppm (1H). The singlet at 13.3 ppm, which is due to the meso proton that is sandwiched between the two benzothiadiazole units, is unique to isomer **34**, as highly deshielded resonances of this type could not arise in related structures (e.g., **37**) where the two heterocyclic units have different relative orientations. On the other hand, the UV−vis spectra were unexceptional showing a Soret band at 465 nm and Q-band I at 662 nm. For this reason, no further attempts were made to optimize the chemistry leading to **34**.

Conclusions

The "3 + 1" methodology provides a convenient and high-yielding approach to the synthesis of novel porphyrin chromophores with fused aromatic subunits. Pyrroles with fused acenaphthylene and benzothiadiazole rings are easily synthesized from nitroaromatic precursors and can be converted into tripyrranes in two additional steps. Further acid-catalyzed condensation with pyrrole dialdehydes affords the novel acenaphtho- and thiadiazolobenzoporphyrins **14** and **33**. By selecting diformylpyrroles with fused aromatic rings, it is possible to mix and match two different aromatic subunits on the antipodal positions, and four examples are provided. Furthermore, the more conventional MacDonald "2 + 2" condensation allows access to porphyrins with two adjacent fused subunits as well. The UV−vis spectra for these porphyrins and their metal chelates show that the porphyrin chromophore has been profoundly altered, and this suggests that the electronic spectra can be fine-tuned by the addition of fused aromatic rings.

Experimental Section

Acenaphthylene (75% pure) was nitrated with nitryl chloride in carbon tetrachloride as described by Iida et al.[31] Ethyl, *tert*-butyl, and benzyl isocyanoacetate were also prepared by published methods.[32,33,8b] Acenaphthylene (75%), 4-nitro-2,1,3-benzothiadiazole, DBU, piperidine, and ethyl cyanoacetate were purchased from Aldrich Chemical Co. and were used without further purification. Chromatography was performed using grade 3 neutral alumina or 70−230 mesh silica gel. Metalloporphyrins were prepared under standard conditions by reacting the free-base porphyrin with nickel(II), copper(II), or zinc acetate in methanol/chloroform[34] or DMF.[35] Melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus or a Mel-Temp apparatus and are uncorrected. EI and FAB mass spectral determinations were made at the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, supported in part by a grant from the National Institute of General Medical Sciences (GM 27029). Elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

Ethyl Acenaphtho[1,2-*c*]pyrrole-1-carboxylate (5a). DBU (4.582 g) was added dropwise to a solution of ethyl isocyanoacetate (**7a**) (3.42 g) and 1-nitroacenaphthylene (6.00 g) in THF (300 mL), and the resulting mixture was stirred at room temperature overnight. The solution was diluted with chloroform, washed with water, dried over sodium sulfate, and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (3 cm i.d. × 14.5 cm) eluting with dichloromethane. A small amount of unreacted 1-nitroacenaphthylene was collected in the early fractions, followed by a red band corresponding to the acenaphthopyrrole. Recrystallization from carbon tetrachloride afforded the title pyrrole (3.48 g, 44%) as pale-yellow needles, mp 182 °C. IR (Nujol mull): ν 3305 (NH stretch), 1674 cm^{-1} (C=O stretch). ^1H NMR ($CDCl_3$): δ 1.54 (3H, t, J = 7.2 Hz, 4.51 (2H, q, J = 7.2 Hz, 7.17 (1H, d, J = 2.7 Hz), 7.49−7.65 (3H, m), 7.71 (1H, d, J = 8.1 Hz), 7.76 (1H, d, J = 7.8 Hz), 8.11 (1H, d, J = 6.9 Hz), 9.07 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 14.82, 60.97, 115.04, 115.99, 119.75, 123.14, 125.18, 126.41, 127.80, 128.17, 130.56, 130.95, 132.59, 132.89, 133.45, 137.45, 161.67. MS (EI, 70 eV) *m*/*z* (%): 263 (75) [M^+], 217 (100) [M^+ − EtOH], 189 (49), 163 (40). Anal. Calcd for $C_{17}H_{13}NO_2 \cdot {}^1/_5H_2O$: C, 76.50; H, 5.06; N, 5.25. Found: C, 76.61; H, 4.83; N, 5.19.

***tert*-Butyl Acenaphtho[1,2-*c*]pyrrole-1-carboxylate (5b).** 1-Nitroacenaphthylene (0.500 g) was reacted with *tert*-butyl isocyanoacetate (0.354 g) in the presence of DBU (0.764 g) using the previous procedure. Recrystallization with chloroform/hexanes afforded the title pyrrole (0.35 g, 47%) as bright-yellow crystals, mp 198−199 °C. IR (Nujol mull): ν 3289 (NH stretch), 1665 cm^{-1} (C=O stretch). ^1H NMR ($CDCl_3$): δ 1.74 (9H, s), 7.15 (1H, d, J = 2.7 Hz), 7.51−7.76 (5H, m), 8.14 (1H, d, J = 6.6 Hz), 9.11 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 28.83, 82.07, 114.48, 117.46, 119.60, 123.03, 125.05, 126.20, 127.77, 128.07, 130.48, 130.92, 132.57, 132.84, 132.99, 137.59, 161.26. MS (EI, 70 eV) *m*/*z* (%): 291 (41) [M^+], 235 (100) [M^+ − $(CH_3)_2C{=}CH_2$], 217 (92) [M^+ − *t*-BuOH], 189 (34), 163 (32). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 77.90; H, 5.85; N, 4.74.

Benzyl Acenaphtho[1,2-*c*]pyrrole-1-carboxylate (5c). The previous procedure was adopted using benzyl isocyanoacetate (2.40 g), 1-nitroacenaphthylene (2.40 g), and DBU (2.24 g). The crude product was chromatographed on a silica column eluting with toluene and recrystallized from carbon tetrachloride to give the benzyl ester (0.55 g, 14%) as fluffy yellow needles, mp 182−184 °C. IR (Nujol mull): ν 3303 (NH stretch), 1679 cm^{-1} (C=O stretch). ^1H NMR ($CDCl_3$): δ 5.18 (2H, s), 7.18 (1H, d, J = 3.3 Hz), 7.38−7.50 (5H, m), 7.53 (2H, m), 7.63 (1H, d, J = 6.6 Hz), 7.71 (2H, m), 7.95 (1H, d, J = 6.6 Hz), 9.01 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 66.84, 115.25, 115.61, 119.81, 123.41, 125.24, 126.45, 127.77, 128.18, 128.78, 128.92, 129.02, 130.66, 130.91, 132.39, 132.77, 134.04, 136.41, 137.56, 161.29. MS (EI, 70 eV) *m*/*z* (%): 325 (100) [M^+], 217 (26) [M^+ − $PhCH_2OH$], 189 (6.5), 163 (22). Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30. Found: C, 81.36; H, 4.52; N, 4.30.

Ethyl Thiadiazolobenzo[3,4-*c*]pyrrole-1-carboxylate (28a). Ethyl isocyanoacetate (2.50 g) and DBU (3.36 g) were dissolved in THF (1100 mL) in a 2000 mL round-bottom flask. A solution of 4-nitro-2,1,3-benzothiadiazole in 800 mL of THF

(31) Iida, H.; Kajiyama, I.; Yamada, K. *Nippon Kagaku Kaishi* **1972**, 137; *Chem. Abstr.* **1972**, *76*, 99395m.
(32) Hartman, G. D.; Weinstock, L. M. *Org. Synth.* **1979**, *59*, 183.
(33) Lash, T. D.; Bellettini, J. R.; Bastian, J. A.; Couch, K. B. *Synthesis* **1994**, 170. See also: Burns, D. H.; Jabara, C. S.; Burden, M. W. *Synth. Commun.* **1995**, *25*, 379.
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was added, and the resulting dark mixture was allowed to stir under reflux overnight. The solution was diluted with chloroform, washed with water, dried over sodium sulfate, and evaporated under reduced pressure. A residue was chromatographed on silica gel eluting with chloroform. A reddish-brown fraction was collected and recrystallized from methanol to afford the title pyrrole (2.50 g 46%) as a pale-brown powder, mp 173−174 °C. IR (Nujol mull): ν 3300 (NH stretch), 1691 cm^{-1} (C═O stretch). ^1H NMR ($CDCl_3$): δ 1.48 (3H, t, J = 7.2 Hz), 4.49 (2H, q, J = 7.1 Hz), 7.61 (1H, d, J = 9.9 Hz), 7.96 (1H, d, J = 2.7 Hz), 8.19 (1H, d, J = 9.6 Hz), 10.09 (1H, br s). ^{13}C NMR (d_6-DMSO): δ 14.32, 60.20, 115.34, 115.69, 118.32, 119.18, 125.11, 125.57, 150.56, 154.09, 160.62. MS (EI, 70 eV) m/z (%): 247 (90) [M^+], 219 (8.5) [$M^+ - CH_2{=}CH_2$], 201 (100) [M^+ − EtOH], 173 (33), 147 (14), 115 (7). Anal. Calcd for $C_{11}H_9N_3O_2S$: C, 53.43; H, 3.67; N, 16.99. Found: C, 53.30; H, 3.67; N, 16.68.

***tert*-Butyl Thiadiazolobenzo[3,4-*c*]pyrrole-1-carboxylate (28b).** 4-Nitro-2,1,3-benzothiadiazole (0.500 g) was reacted with 0.389 g of *tert*-butyl isocyanoacetate in the presence of DBU (0.420 g) using the previous procedure. Recrystallization from methanol afforded the title pyrrole (0.374 g, 49%) as yellow needles, mp 200−201 °C. IR (Nujol mull): ν 3295 (NH stretch), 1680 cm^{-1} (C═O stretch). ^1H NMR ($CDCl_3$): δ 1.70 (9H, s), 7.60 (1H, d, J = 9.6 Hz), 7.93 (1H, d, J = 2.7 Hz), 8.14 (1H, d, J = 9.6 Hz), 10.41 (1H, br s). ^{13}C NMR (d_6-DMSO): δ 28.05, 81.02, 115.59, 116.63, 118.13, 118.72, 124.55, 125.75, 150.65, 154.11, 160.12. MS (EI, 70 eV) m/z (%): 275 (23) [M^+], 219 (100) [$M^+ - (CH_3)_2C{=}CH_2$], 201 (97) [M^+ − *t*-BuOH], 173 (18), 147 (10). Anal. Calcd for $C_{13}H_{13}N_3O_2S$: C, 56.71; H, 4.76; N, 15.29. Found: C, 56.74; H, 4.80; N, 14.68.

Acenaphtho[1,2-*c*]pyrrole (11a). Nitrogen gas was bubbled through a mixture of **5a** (0.91 g) and potassium hydroxide (2.00 g) in ethylene glycol (30 mL) for 10 min, and the resulting solution was refluxed on a preheated oil bath at 195 °C under an atmosphere of nitrogen for an additional 30 min. The mixture was poured into ice−water, and the resulting precipitate was collected by suction filtration, washed well with water, and dried under vacuum overnight. The precipitate was recrystallized from chloroform/methanol to give the acenaphthopyrrole (0.54 g, 83%) as a pale-brown powder, mp 128 °C. IR (KBr): ν 3355 cm^{-1} (NH). ^1H NMR ($CDCl_3$): δ 7.01 (2H, d, J = 2.4 Hz), 7.48 (2H, m), 7.57 (2H, d, J = 6.6 Hz), 7.61 (2H, d, J = 8.4 Hz), 8.13 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 110.94, 118.85, 124.38, 127.96, 129.23, 131.37, 134.21, 138.26. MS (EI, 70 eV) m/z (%): 191 (100) [M^+], 164 (33) [M^+ − HCN]. Anal. Calcd for $C_{14}H_9N$: C, 87.93; H, 4.74; N 7.32. Found: C, 87.43; H, 4.59; N, 7.28.

Phenanthro[9,10-*c*]pyrrole (11b). Nitrogen gas was bubbled through a mixture of ethyl phenanthro[9,10-*c*]pyrrole-1-carboxylate[8] (0.50 g) and potassium hydroxide (1.00 g) in ethylene glycol (15 mL) for 10 min, and the resulting solution was refluxed on a preheated oil bath at 195 °C under an atmosphere of nitrogen for an additional 30 min. The mixture was poured into ice−water, and the resulting precipitate was collected by suction filtration, washed well with water, and dried under vacuum overnight to give **11b** (0.37 g, 99%) as an off-white powder, mp 150−151 °C. IR (KBr): ν 3415 (NH stretch), 750 cm^{-1} (aromatic oop bending). ^1H NMR ($CDCl_3$): δ 7.47 (4H, m), 7.57 (2H, d, J = 2.7 Hz), 8.06 (2H, d, J = 6.9 Hz), 8.47 (2H, d, J = 8.1 Hz), 8.89 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 110.58, 120.09, 123.57, 123.87, 125.39, 127.23, 128.97, 129.13. MS (EI, 70 eV) m/z (%): 217 (100) [M^+], 189 (23) [M^+ − HCN]. Anal. Calcd for $C_{16}H_{11}N{\cdot}^1/_{10}H_2O$: C, 87.72; H, 5.15; N 6.39. Found: C, 87.60; H, 5.05; N, 6.48.

Thiadiazolobenzo[3,4-*c*]pyrrole (29). Nitrogen was bubbled through a mixture of ethyl thiadiazolobenzo[3,4-*c*]-pyrrole-1-carboxylate (1.00 g) and potassium hydroxide (2.35 g) in ethylene glycol (47 mL) for 10 min, and the resulting solution was refluxed under nitrogen for 30 min. The mixture was poured into ice−water, extracted with chloroform, dried over sodium sulfate, and evaporated under reduced pressure. The resulting dark residue was recrystallized from chloroform/petroleum ether to give the α-free pyrrole (671 mg, 95%) as long brown needles, mp 143 °C, dec. IR (Nujol mull): ν 3376 cm^{-1} (NH). ^1H NMR ($CDCl_3$): δ 7.27 (1H, s), 7.46 (1H, d, J = 9.3 Hz), 7.62 (1H, d, J = 9.3 Hz), 7.79 (1H, s), 9.21 (1H, br s). ^{13}C NMR (d_6-DMSO): δ 114.02, 114.21, 114.27, 114.38, 121.54, 127.20, 151.58, 154.99. MS (EI, 70 eV) m/z (%): 175 (100) [M^+], 148 (22) [M^+ − HCN]. Anal. Calcd for $C_8H_5N_3S$: C, 54.84; H, 2.88; N, 23.98. Found: C, 54.99; H, 2.91; N, 23.88.

1-(2-Cyano-2-ethoxycarbonylvinyl)acenaphtho[1,2-*c*]-pyrrole (19a). DMF (1.10 g) was cooled in an ice bath, and the internal temperature was maintained at 10−20 °C while $POCl_3$ (2.30 g) was added dropwise. An exothermic reaction occurred with the formation of the Vilsmeier complex. The ice bath was removed, and the mixture was stirred at room temperature for 15 min. Dichloromethane (6 mL) was added to the mixture, and the reaction temperature was lowered to 0−2 °C with the aid of a salt−ice bath. A solution of acenaphthopyrrole **11a** (0.90 g) in dichloromethane (4 mL) was added to the stirred mixture over a period of 15 min. After the addition was completed, the ice bath was replaced with a hot water bath and the mixture was refluxed for 15 min. The mixture was then cooled to 25−30 °C, a solution of sodium acetate trihydrate (10.13 g) in water (14 mL) was added dropwise, and the reaction mixture refluxed for an additional 15 min. The two layers were separated, and the aqueous portion of the mixture was extracted with chloroform. The combined organic layers were washed with saturated sodium carbonate solution and dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue (crude monoaldehyde) was treated with ethyl cyanoacetate (0.923 g) and piperidine (7 drops) in absolute ethanol (34 mL), and the resulting dark solution was refluxed for 3 h. The solution was cooled to room temperature, and the resulting yellow suspension was collected by suction filtration to give the cyanovinyl derivative (1.34 g, 93%) as saffron-colored crystals, mp 198−199 °C. An analytical sample was obtained by recrystallization from dichloromethane/hexanes as small, bright-yellow, fluffy needles, mp 199−200 °C. IR (Nujol mull): ν 3403 (NH stretch), 2211 (CN stretch), 1700 cm^{-1} (C═O stretch). ^1H NMR ($CDCl_3$): δ 1.42 (3H, t, J = 7.2 Hz), 4.38 (2H, q, J = 7.2 Hz), 7.37 (1H, d, J = 3.0 Hz), 7.52−7.85 (6H, m), 8.34 (1H, s), 9.76 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 14.40, 62.37, 92.03, 119.36, 120.32, 120.60, 120.84, 122.04, 125.96, 127.66, 128.14, 128.24, 130.90, 131.00, 131.62, 131.71, 137.16, 140.25, 141.11, 163.74. Anal. Calcd for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.09; H, 4.32; N, 8.54.

Acenaphtho[1,2-*c*]pyrrole-1-carboxaldehyde (18a). Recrystallization of the crude product from chloroform/methanol prior to protection with ethyl cyanoacetate afforded the monoaldehyde **18a** as greenish-yellow crystals, mp 215 °C, dec. IR (Nujol mull): ν 3241 (NH stretch), 1645 cm^{-1} (C═O stretch). ^1H NMR ($CDCl_3$): δ 7.33 (1H, d, J = 2.4 Hz), 7.53−7.63 (2H, m), 7.67 (1H, d, J = 6.6 Hz), 7.74 (1H, d, 8.1 Hz), 7.82 (1H, d, J = 8.4 Hz), 7.92 (1H, d, J = 6.3 Hz), 9.31 (1H, br s), 10.06 (1H, s). ^1H NMR (d_6-DMSO/$CDCl_3$): δ 7.09 (1H, d, J = 3.0 Hz), 7.28−7.39 (2H, m), 7.43 (1H, d, J = 6.9 Hz), 7.48 (1H, d, 8.4 Hz), 7.56 (1H, d, J = 8.4 Hz), 7.92 (1H, br d), 9.80 (1H, s), 11.31 (1H, br s). ^{13}C NMR (d_6-DMSO/$CDCl_3$): δ 118.23, 119.60, 121.80, 124.62, 125.40, 126.27, 127.44, 129.74, 130.18, 131.62, 132.27, 136.34, 177.74. Anal. Calcd for $C_{15}H_9NO{\cdot}^1/_{10}H_2O$: C, 81.50; H, 4.19; N, 6.33. Found: C, 81.44; H, 4.06; N, 6.33.

1-(2-Cyano-2-ethoxycarbonylvinyl)phenanthro[9,10-*c*]-pyrrole (19b). Following the procedure described for **19a**, phenanthropyrrole **11b** (0.500 g) afforded the title cyanovinyl product (714 mg, 90%) as yellowish-brown crystals, mp 208−209 °C. An analytical sample was obtained by recrystallization from chloroform/ethanol as saffron-colored crystals, mp 210−210.5 °C. IR (Nujol mull): ν 3312 (NH stretch), 2214 (CN stretch), 1707 cm^{-1} (C═O stretch). ^1H NMR ($CDCl_3$): δ 1.43 (3H, t, J = 7 Hz), 4.41 (2H, q, J = 7 Hz), 7.57−7.65 (4H, m), 8.05 (1H, d, J = 3.3 Hz), 8.09 (1H, m), 8.38 (1H, m), 8.53 (1H, m), 8.62 (1H, m), 8.99 (1H, s), 10.76 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 14.45, 62.34, 90.20, 121.84, 122.47, 123.25, 123.49, 123.88, 124.55, 125.60, 126.96, 127.40, 127.86, 128.05, 128.15,

129.15, 131.99, 141.23, 164.40. Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.45; H, 4.38; N, 8.03.

Phenanthro[9,10-*c*]pyrrole-1-carboxaldehyde (18b). Recrystallization of the crude monoaldehyde from carbon tetrachloride afforded **18b** as light-brown crystals, mp 262 °C, dec. IR (Nujol mull): ν 3223 (NH stretch), 1626 cm^{-1} (C=O stretch). ^{1}H NMR (d_6-DMSO/$CDCl_3$): δ 6.84−6.96 (4H, m), 7.51 (1H, d, J = 3 Hz), 7.53 (1H, m), 7.88−7.97 (2H, m), 8.43 (1H, br m), 9.61 (1H, s), 12.38 (1H, br s). ^{13}C NMR (d_6-DMSO): δ 119.37, 119.42, 121.19, 122.10, 122.21, 122.38, 123.03, 124.68, 125.87, 126.04, 126.19, 126.30, 126.95, 129.17, 177.17. Anal. Calcd for $C_{17}H_{11}NO\cdot{}^3/_5H_2O$: C, 79.41; H, 4.80; N, 5.47. Found: C, 79.70; H, 4.50; N, 5.70.

Acenaphtho[1,2-*c*]pyrrole-1,3-dicarboxaldehyde (17a). The protected formyl pyrrole **19a** (1.34 g) was reformylated by the procedure detailed above with the exception of using more solvent (approximately 60 mL of dichloromethane). The resulting crude 1-(2-cyano-2-ethoxycarbonylvinyl)-3-formylacenaphtho[1,2-*c*]pyrrole, which was not purified, was refluxed in 3 M aqueous sodium hydroxide (44 mL) for 30 min. The solution was cooled to room temperature and neutralized with dilute sulfuric acid. The resulting greenish-brown precipitate was collected by suction filtration, washed several times with water, and dried in vacuo. The crude material (1.03 g, 89%; mp >300 °C) was very sparingly soluble in many solvents and hence was used in subsequent reactions without recrystallization. An analytical sample was obtained by dissolving the crude material in DMSO and diluting the solution with chloroform as a dark-green powder. IR (Nujol mull): ν 3237 (NH stretch), 1659 cm^{-1} (C=O stretch). ^{1}H NMR (d_6-DMSO): δ 7.69 (2H, t, J = 7.2 Hz), 7.95 (2H, d, J = 7.8 Hz), 8.20 (2H, d, J = 6.6 Hz), 10.11 (2H, s). ^{13}C NMR (d_6-DMSO): δ 123.58, 127.28, 128.22, 128.44, 130.09, 130.71, 181.97. Anal. Calcd for $C_{16}H_9NO_2\cdot{}^1/_5\,H_2O$: C, 76.62; H, 3.75; N, 5.59. Found: C, 76.65; H, 3.74; N, 5.58.

Phenanthro[9,10-*c*]pyrrole-1,3-dicarboxaldehyde (17b). Cyanovinylphenanthropyrrole **19b** (600 mg) was formylated and deprotected using the conditions described above for **17a**. The dialdehyde was obtained as a brown powder (480 mg, quantitative; mp >300 °C, dec) and was very sparingly soluble in many solvents. Thus, succeeding reactions were carried out using the crude material. An analytical sample was obtained by dissolving the crude material in DMSO and diluting the solution with chloroform as a brown powder, mp >300 °C. IR (Nujol mull): ν 3241 (NH stretch), 1689, 1626 cm^{-1} (C=O stretch). ^{1}H NMR (d_6-DMSO): δ 7.60 (4H, m), 8.75 (2H, m), 9.72 (2H, m), 10.20 (2H, s). ^{13}C NMR (d_6-DMSO): δ 123.78, 124.40, 126.43, 127.37, 127.64, 127.74, 129.81, 130.45, 182.24. Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.12. Found: C, 79.41; H, 4.45; N, 5.47.

Ethyl 3-(5-Ethoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)acenaphtho[1,2-*c*]pyrrole-1-carboxylate (10a). *p*-Toluenesulfonic acid (0.535 g) was added to a stirred mixture of **5a** (1.00 g) and **9c**[36,37] (0.85 g) in glacial acetic acid (135 mL). The mixture was stirred at room temperature for 2 h, and the solution was then poured into 250 mL of ice−water and allowed to stand for an additional 2 h. The mixture was extracted with chloroform, washed with 50 mL of 5% sodium bicarbonate solution then with 50 mL of water, and dried over sodium sulfate. The solution was evaporated under reduced pressure, and the solid residue was recrystallized from chloroform to give the dipyrrylmethane (1.218 g, 70%) as a pale-yellow powder, mp 234−235 °C. IR (Nujol mull): ν 3345, 3288 (NH stretch), 1692 (C=O stretch), 1645 cm^{-1} (C=O stretch). ^{1}H NMR ($CDCl_3$): δ 1.07 (3H, t, J = 7.2 Hz), 1.17 (3H, br t), 1.28 (3H, br t), 2.30 (3H, s), 2.48 (2H, q, J = 7.5 Hz), 4.09−4.21 (4H, m), 4.26 (2H, s), 7.31 (1H, d, J = 7.5 Hz), 7.48 (1H, t, J = 7.5 Hz), 7.56 (1H, t, J = 7.5 Hz), 7.67 (1H, d, J = 7.8 Hz), 7.75 (1H, d, J = 8.1 Hz), 7.93 (1H, d, J = 6.6 Hz), 9.33 (1H, br s), 9.42 (1H, br s). ^{13}C NMR (d_6-DMSO): δ 10.02, 14.36, 14.47, 15.14, 16.56, 23.46, 58.88, 59.99, 114.03, 116.80, 119.41, 122.19, 123.62, 124.08, 125.79, 127.68, 127.80, 129.41, 129.80, 130.11, 131.95, 132.61, 136.25, 160.58, 161.12. Anal. Calcd for $C_{28}H_{28}N_2O_4$: C, 73.68; H, 6.14; N, 6.14. Found: C, 73.44; H, 6.26; N, 5.97.

Benzyl 3-(5-Benzyloxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)acenaphtho[1,2-*c*]pyrrole-1-carboxylate (10b). Montmorillonite clay (K10) (0.55 g) was added to a mixture of acenaphthopyrrole **5c** (100 mg) and benzyl 5-acetoxymethyl-4-ethyl-3-methylpyrrole-2-carboxylate (**9d**)[23,39] (95 mg) in 10 mL of dichloromethane, and the mixture was vigorously stirred overnight at room temperature. The mixture was then suction filtered, the clay washed several times with hot chloroform, and the solvent removed on a rotary evaporator. The residue was recrystallized from chloroform to give the dipyrrole (144 mg, 82%) as a pink powder, mp 246 °C, dec. IR (Nujol mull): ν 3343, 3287 (NH stretch), 1688 (C=O stretch), 1640 cm^{-1} (C=O stretch). ^{1}H NMR (d_6-DMSO/$CDCl_3$): δ 0.90 (3H, t, J = 7.3 Hz), 2.22 (3H, s), 2.49 (2H, q, J = 7.3 Hz), 4.16 (2H, s), 5.30 (2H, s), 5.45 (2H, s), 7.29−7.44 (10H, m), 7.47−7.53 (2H, m), 7.60−7.68 (2H, m), 7.83 (2H, m), 11.14 (1H, br s), 11.53 (1H, br s). ^{13}C NMR (d_6-DMSO/$CDCl_3$): δ 9.37, 14.62, 16.08, 22.61, 63.79, 64.85, 113.22, 116.13, 117.96, 121.59, 122.84, 123.16, 124.74, 125.06, 125.32, 126.57, 126.79, 126.88, 127.31, 127.47, 127.62, 128.13, 129.17, 129.33, 131.21, 131.87, 135.40, 135.71, 135.92, 159.77, 160.35. Anal. Calcd for $C_{38}H_{32}N_2O_4$: C, 78.60; H, 5.55; N, 4.82. Found: C, 78.36; H, 5.52; N, 4.74.

***tert*-Butyl 3-(5-*tert*-Butoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)thiadiazolobenzo[3,4-*c*]pyrrole-1-carboxylate (30a).** Montmorillonite clay (K10) (2.58 g) was added to a mixture of *tert*-butyl thiadiazolobenzo[3,4-*c*]pyrrole-1-carboxylate (**28**) (0.50 g) and *tert*-butyl 5-acetoxymethyl-4-ethyl-3-methylpyrrole-2-carboxylate (**9a**)[38] (0.51 g) in 38 mL of dichloromethane, and the mixture was vigorously stirred overnight at room temperature. The mixture was then suction filtered, and the clay was washed with dichloromethane. The solvent was evaporated to yield a reddish oily residue, which was recrystallized from petroleum ether to give the title dipyrrylmethane (0.665 g, 74%) as a bright-yellow powder, mp 118−120 °C. IR (Nujol mull): ν 3523, 3232 (NH stretch), 1694 (C=O stretch), 1679 cm^{-1} (C=O stretch). ^{1}H NMR ($CDCl_3$): δ 1.00 (3H, t, J = 7.5 Hz), 1.51 (9H, s) 1.62 (9H, s), 2.23 (3H, s), 2.47 (2H, q, J = 7.3 Hz), 4.59 (2H, s), 7.53 (1H, d, J = 9.6 Hz), 8.05 (1H, d, J = 9.6 Hz), 9.76 (1H, br s), 10.05 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 10.51, 15.87, 17.36, 24.28, 28.61, 80.55, 82.31, 113.86, 115.51, 119.43, 119.69, 124.50, 125.23, 125.97, 126.37, 127.47, 130.89, 151.52, 154.95, 161.34, 161.54. Anal. Calcd for $C_{26}H_{32}N_4O_4S$: C, 62.88; H, 6.49; N, 11.28. Found: C, 62.76; H, 6.54; N, 10.89.

***tert*-Butyl 3-(5-Benzyloxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)thiadiazolobenzo[3,4-*c*]pyrrole-1-carboxylate (30b).** *tert*-Butyl thiadiazolobenzo[3,4-*c*]pyrrole-1-carboxylate (**28b**) (0.40 g) and benzyl 5-acetoxymethyl-4-ethyl-3-methylpyrrole-2-carboxylate (**9d**)[39] (0.49 g) were reacted with 2.06 g of Montmorillonite clay in 30 mL of dichloromethane by the procedure described above. The resulting product was recrystallized from 95% ethanol to give the title dipyrrylmethane (0.488 g, 63%) as a white powder, mp 163−165 °C. IR (Nujol mull): ν 3336, 3264 (NH stretch), 1681 (C=O stretch), 1631 cm^{-1} (C=O stretch). ^{1}H NMR ($CDCl_3$): δ 0.97 (3H, t, J = 7.7 Hz), 1.60 (9H, s), 2.28 (3H, s), 2.50 (2H, q, J = 7.5 Hz), 4.59 (2H, s), 5.23 (2H, s), 7.25−7.35 (5H, m), 7.53 (1H, d, J = 9.6 Hz), 8.06 (1H, d, J = 9.6 Hz), 10.18 (1H, br s), 10.44 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.68, 15.81, 17.25, 24.08, 24.55, 65.98, 82.21, 113.79, 115.58, 117.92, 119.33, 124.97, 125.37, 125.93, 127.93, 128.12, 128.69, 128.79, 129.56, 130.71, 136.46, 151.39, 154.89, 161.26, 162.35. Anal. Calcd for $C_{29}H_{30}N_4O_4S$: C, 65.64; H, 5.70; N, 10.56. Found: C, 66.08; H, 5.95; N, 9.71.

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Bis-(3-Ethoxycarbonyl-1-acenaphtho[1,2-*c*]pyrrolyl)-methane (22). A mixture of ethyl acenaphtho[1,2-*c*]pyrrole-1-carboxylate (**5a**, 0.455 g), dimethoxymethane (0.132 g), and *p*-toluenesulfonic acid (50 mg) in 30 mL of glacial acetic acid was allowed to stir under a nitrogen atmosphere at room temperature for 3 days. The resulting cloudy mixture was poured into 250 mL of ice−water and allowed to stand for 2 h. The resulting precipitate was filtered and vacuum dried. The pale-yellow powder was recrystallized with THF/hexanes to give the diacenaphthodipyrrylmethane (0.428 g, 92%) as yellow crystals, mp 285 °C, dec. IR (Nujol mull): ν 3163 (NH stretch), 1681 cm^{-1} (C═O stretch). ^{1}H NMR (d_6-DMSO): δ 1.45 (6H, t, J = 7 Hz), 4.43 (4H, q, J = 7 Hz), 4.56 (2H, s), 7.08 (2H, d, J = 6.9 Hz), 7.29 (2H, d, J = 7.2 Hz), 7.49−7.65 (2H, m), 7.54−7.58 (2H, m), 7.71 (2H, d, J = 8.1 Hz), 8.01 (2H, d, J = 6.9 Hz), 12.04 (2H, br s). ^{13}C NMR (d_6-DMSO): δ 14.47, 24.99, 60.03, 114.07, 119.23, 122.28, 124.09, 125.80, 126.47, 127.62, 127.83, 128.24, 130.05, 131.94, 132.51, 132.92, 136.13, 160.57. Anal. Calcd for $C_{35}H_{26}N_2O_4$: C, 78.07; H, 4.83; N, 5.20. Found: C, 77.86; H, 4.97; N, 5.14.

Bis-(3-Ethoxycarbonyl-1-thiadiazolobenzo[3,4-*c*]pyrrolyl)methane (35). A mixture of ethyl thiadiazolobenzo[3,4-*c*]pyrrole-1-carboxylate (**28a**) (0.50 g) was condensed with dimethoxymethane (0.154 g) and *p*-toluenesulfonic acid (60 mg) in glacial acetic acid (30 mL) under the conditions described above. Recrystallization from chloroform/petroleum ether (60−80°) gave the title dipyrrylmethane (0.53 g, quantitative) as a pale-yellow powder, mp 225−227 °C. IR (Nujol mull): ν 3144 (NH stretch), 1659 cm^{-1} (C═O stretch). ^{1}H NMR ($CDCl_3$): δ 1.29 (6H, t, J = 7.2 Hz), 4.05 (4H, q, J = 7.1 Hz), 5.28 (2H, s), 7.51 (2H, d, J = 9 Hz), 8.00 (2H, d, J = 9 Hz), 11.50 (2H, br s). ^{13}C NMR ($CDCl_3$): δ 14.37, 25.28, 60.97, 114.26, 114.48, 119.43, 125.88, 130.22, 151.23, 154.97, 161.66. Anal. Calcd for $C_{23}H_{18}N_6O_4S_2$: C, 54.53; H, 3.58; N, 16.59. Found: C, 54.54; H, 3.66; N, 16.48.

Bis-1,3-(5-ethoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)acenaphtho[1,2-*c*]pyrrole (12c). Acenaphthopyrrole **11a** (0.500 g) and acetoxymethylpyrrole **9c**[36,37] (1.387 g) were taken up in a mixture of ethanol (30 mL) and acetic acid (2 mL) and heated under reflux while stirring under a nitrogen atmosphere overnight. The solution was poured into 100 mL of ice−water and allowed to stand for 3 h. The solution was filtered and recrystallized from chloroform to give the tripyrrane **12c** (1.17 g, 77.5%) as a pale-yellow amorphous powder, mp 258−260 °C. IR (Nujol mull): ν 3314 (NH stretch) 1672 cm^{-1} (C═O stretch). ^{1}H NMR (d_6-DMSO): δ 0.91 (6H, t, J = 7 Hz), 1.33 (6H, t, J = 6.8 Hz), 2.24 (6H, s), 2.42 (4H, q, J = 7 Hz), 4.09 (4H, s), 4.25 (4H, q, J = 6.8 Hz), 7.10 (2H, d, J = 6.6 Hz), 7.36 (2H, t), 7.45 (2H, d, J = 8.1 Hz), 10.10 (1H, br s), 10.73 (2H, br s). ^{13}C NMR (d_6-DMSO/$CDCl_3$): δ 9.30, 13.51, 14.37, 16.03, 22.93, 58.03, 116.17, 116.55, 121.73, 122.72, 123.15, 125.05, 126.58, 129.62, 129.77, 133.38, 136.54, 160.66. Anal. Calcd for $C_{36}H_{39}N_3O_4$: C, 74.87; H, 6.76; N, 7.28. Found: C, 74.90; H, 6.87; N, 7.18.

Bis-1,3-(5-*tert*-Butoxycarbonyl-3-(2-methoxycarbonylethyl)-4-ethyl-2-pyrrolylmethyl)acenaphtho[1,2-*c*]pyrrole (12b). Following the previous procedure, acenaphthopyrrole **11a** (0.30 g) was reacted with **9b**[40] (0.98 g). The crude tripyrrane (1.00 g; 76.5%) was obtained as a brown precipitate but could not be recrystallized and hence was used without further purification. Mp 104 °C, dec. IR (Nujol mull) ν 3317 (NH stretch), 1679 cm^{-1} (C═O stretch). ^{1}H NMR ($CDCl_3$): δ 1.44 (18H, s), 2.26 (6H, s), 2.47 (4H, t, J = 7.0 Hz), 2.78 (4H, t, J = 7.0 Hz), 3.53 (6H, s), 4.14 (4H, s), 7.26 (2H, m), 7.42 (2H, t, J = 7.5 Hz), 7.57 (2H, d, J = 8.7 Hz), 8.70 (3H, br s).

Bis-1,3-(5-*tert*-Butoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)acenaphtho[1,2-*c*]pyrrole (12a). The previous procedure was utilized for the preparation of **12b** using **11a** (0.36 g) and **9a**[38] (1.11 g). The resulting tripyrrane could not be recrystallized and hence was used in crude form. Yield: 1.15 g, 72%. Mp 106 °C, dec. IR (Nujol mull): ν 3315 (NH stretch), 1656 cm^{-1} (C═O). ^{1}H NMR ($CDCl_3$): δ 1.01 (6H, t, J = 7.2 Hz), 1.47 (18H, s), 2.28 (6H, s), 2.42 (4H, q, J = 7.2 Hz), 4.10 (4H, s), 7.17 (2H, d, J = 7.2 Hz), 7.42 (2H, t, J = 7.8 Hz), 7.56 (2H, d, J = 8.1 Hz), 7.75 (1H, br s), 8.80 (2H, br s).

1,3-Bis-(5-ethoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)thiadiazolobenzo[3,4-*c*]pyrrole (31c). Thiadiazolobenzopyrrole **29** (0.10 g) and ethyl 5-acetoxymethyl-4-ethyl-3-methylpyrrole-2-carboxylate (**9c**)[36,37] (0.289 g) were taken up in ethanol (6.5 mL) and acetic acid (0.5 mL), and the mixture was stirred while heating under reflux overnight under a nitrogen atmosphere. The solution was poured into ice−water (80 mL) and allowed to stand for 3 h. The precipitate was filtered and washed with cold ethanol to give the tripyrrane **31c** (0.23 g, 72%) as a pale-brown powder, mp 242−245 °C. IR (Nujol mull): ν 3290 (NH stretch), 1667 (C═O stretch), 1639 cm^{-1} (C═O stretch). ^{1}H NMR ($CDCl_3$): δ 0.83 (6H, br t), 0.95 (3H, t), 1.03 (3H, t), 2.19 (6H, s), 2.48 (4H, m), 3.11 (4H, br), 4.16 (2H, s), 4.60 (2H, br s), 7.24 (1H, d, J = 9.3 Hz), 7.62 (1H, d, J = 9.3 Hz), 10.55 (1H, br s), 11.45 (1H, br s), 11.52 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 10.83, 10.88, 14.06, 15.88, 15.94, 17.17, 17.32, 22.25, 23.64, 60.14, 60.26, 111.01, 114.42, 117.87, 118.18, 122.74, 123.73, 124.60, 125.32, 125.96, 126.78, 126.87, 130.84, 131.85, 152.80, 155.94, 163.95. Anal. Calcd for $C_{30}H_{35}N_5O_4S$: C, 64.15; H, 6.28; N, 12.47. Found: C, 64.00; H, 6.44; N, 12.47.

1,3-Bis-(5-*tert*-butoxycarbonyl-3-(2-methoxycarbonylethyl)-4-ethyl-2-pyrrolylmethyl)thiadiazolobenzo[3,4-*c*]-pyrrole (31b). Prepared by the previous procedure using thiadiazolobenzopyrrole **29** (200 mg) and acetoxymethylpyrrole **9b**[40] (780 mg) in ethanol (15 mL)/acetic acid (1 mL). The crude tripyrrane was obtained as a mustard-yellow powder (769 mg, 92%), but this could not be recrystallized and hence was used without further purification. ^{1}H NMR ($CDCl_3$): δ 1.48 (9H, s), 1.54 (9H, s), 2.22 (3H, s), 2.24 (3H, s), 2.45 (4H, m), 2.78 (4H, m), 3.63 (3H, s), 3.65 (3H, s), 4.17 (2H, s), 4.44 (2H, s), 7.19 (1H, d, J = 9.3 Hz), 7.42 (1H, d, J = 9.3 Hz), 8.77 (1H, br s), 9.95 (1H, br s), 10.44 (1H, br s).

Bis-1,3-(5-*tert*-butoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)-thiadiazolobenzo[3,4-*c*]pyrrole (31a). The previous procedure was used for the preparation of **31c** using **29** (0.666 g) and **9a**[38] (2.14 g) in ethanol (43 mL)/acetic acid (3 mL). The resulting tripyrrane (2.30 g, 98%) could not be recrystallized and was used without further purification. Mp 186−195 °C. IR (Nujol mull): ν 3346, 3304 (NH stretch), 1667 cm^{-1} (C═O stretch). ^{1}H NMR ($CDCl_3$): δ 0.99 (6H, m), 1.49 (18H, s), 2.21 (3H, s), 2.23 (3H, s), 2.40 (4H, m), 4.17 (2H, s), 4.42 (2H, s), 7.21 (1H, d, J = 9.3 Hz), 7.41 (1H, d, J = 9.3 Hz), 8.68 (1H, br), 9.00 (1H, br), 9.64 (1H, br).

8,12,13,17-Tetraethyl-7,18-dimethylacenaphtho[1,2-*b*]-porphyrin (14a). Tripyrrane **12a** (100 mg) was dissolved in TFA (2 mL) and stirred at room temperature for 10 min under nitrogen. The mixture was diluted with dichloromethane (38 mL), followed immediately by the addition of dialdehyde **13**[23] (32 mg). The mixture was stirred under nitrogen for an additional further 2 h. Then, the mixture was neutralized by the dropwise addition of triethylamine (3.6 mL), DDQ (36 mg) was added, and the solution was stirred for another 1 h. The solution was then diluted with chloroform was washed with water, and the solvent evaporated under reduced pressure. The residue was recrystallized twice with chloroform/methanol to give the porphyrin (32 mg, 36%) as dark-blue crystals, mp >300 °C. When the reaction was carried out with 7 mL of TFA and 280 mL of CH_2Cl_2, a yield of 30 mg (33%) was obtained. UV−vis ($CHCl_3$): λ_{max} (log ϵ) 387 (4.79), 431 (4.95), 454 (4.84), 529 (4.16), 571 (4.19), 598 (4.03), 658 nm (4.34). UV−vis (1% TFA/$CHCl_3$): λ_{max} (log ϵ) 356 (4.48), 445 (5.30), 574 (4.23), 627 nm (4.58). ^{1}H NMR ($CDCl_3$): δ −3.25 (2H, br s), 1.89−1.96 (12H, 2 overlapping triplets), 3.60 (6H, s), 4.05−4.15 (8H, m), 7.94 (2H, t), 8.04 (2H, d, J = 8.4 Hz), 8.89 (2H, d, J = 6.6 Hz), 9.98 (2H, s), 10.41 (2H, s). ^{1}H NMR (TFA/$CDCl_3$): δ −3.3 (4H, br s), 1.76 (6H, t, J = 7.3 Hz), 1.84 (6H, t, J = 7.3 Hz), 3.69 (6H, s), 4.15 (4H, q, J = 7.5 Hz), 4.23 (4H, q, J = 7.5 Hz), 8.13 (2H, t, J = 7.5 Hz), 8.32 (2H, d, J = 8.1 Hz), 9.14 (2H, d, J = 6.9 Hz), 10.62 (2H, s), 11.10 (2H, s). ^{13}C NMR (TFA-$CDCl_3$): δ 11.88, 16.50, 17.32, 20.05, 20.34, 98.89, 100.66, 127.18, 129.45, 131.18, 131.31, 131.52, 135.62, 136.93,

(40) Clezy, P. S.; Liepa, A. J. *Aust. J. Chem.* **1970**, *23*, 2443.

138.51, 141.98, 142.57, 143.39, 144.26, 144.68, 145.41. HRMS (EI): calcd for $C_{40}H_{38}N_4$, 574.309 65; found, 574.309 73. Anal. Calcd for $C_{40}H_{38}N_4 \cdot {}^1/_2H_2O$: C, 82.30; H, 6.73; N, 9.34. Found: C, 82.58; H, 6.70; N, 9.34.

2,3-Diethyl-8,17-bis-(2-methoxycarbonylethyl)-7,18-dimethylacenaphtho[1,2-*b*]porphyrin (14b). The procedure for **14a** was adopted using **12b** (100 mg), **13**[23] (24 mg), DDQ (33 mg), TFA (2 mL), and CH_2Cl_2 (38 mL). Recrystallization from chloroform/methanol afforded the acenaphthoporphyrin (31 mg, 34%) as dark-blue crystals, mp >300 °C. UV−vis ($CHCl_3$): λ_{max} (log ϵ) 387 (4.86), 431 (5.01), 456 (5.02), 530 (4.27), 569 (4.03), 597 (3.98), 657 nm (4.42). UV−vis (1% TFA/$CHCl_3$): λ_{max} (log ϵ) 358 (4.52), 447 (5.31), 575 (4.31), 625 nm (4.54). ^{1}H NMR ($CDCl_3$): δ −3.31 (2H, br s), 1.92 (6H, t, J = 7.5 Hz), 3.30 (4H, t, J = 7.5 Hz), 3.59 (6H, s), 3.68 (6H, s), 4.10 (4H, q, J = 7.5 Hz), 4.39 (4H, t, J = 7.5 Hz), 7.98 (2H, t), 8.07 (2H, d, J = 7.8 Hz), 8.98 (2H, d, J = 7.2 Hz), 9.97 (2H, s), 10.39 (2H, s). ^{13}C NMR (TFA/$CDCl_3$): δ 12.00, 17.21, 20.04, 21.88, 35.78, 53.08, 99.18, 101.16, 127.60, 129.55, 131.18, 131.34, 131.47, 136.22, 136.92, 139.65, 140.80, 142.00, 142.69, 142.93, 144.68, 144.89, 175.83. HRMS (EI): calcd for $C_{44}H_{42}N_4O_4$, 691.3284; found, 691.3282. Anal. Calcd for $C_{44}H_{42}N_4O_4 \cdot H_2O$: C, 74.55; H, 6.25; N, 7.90. Found: C, 73.86; H, 5.84; N, 7.69. Nickel(II) complex (**16a**). Dark-purple crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 288 (4.34), 344 (4.31), 388 (4.61), 434 (4.98), 530 (3.94), 558 (4.05), 602 nm (4.62). Copper(II) complex (**16b**). Dark-purple crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 288 (4.50), 416 (4.87), 436 (5.10), 540 (3.97), 562 (4.05), 610 nm (4.67). Zinc complex (**16c**). Dark-purple crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 290 (4.24), 332 (4.35), 394 (4.62), 446 (5.01), 542 (3.95), 566 (4.02), 616 nm (4.59).

8,12,13,17-Tetraethyl-7,18-dimethylthiadiazolobenzo-[3,4-*b*]porphyrin (32a). Tripyrrane **31a** (50 mg) was dissolved in TFA (1 mL) and stirred at room temperature for 10 min under nitrogen. The mixture was diluted with dichloromethane (18 mL), followed by the addition of pyrroledialdehyde **13**[23] (14 mg). The mixture was stirred under nitrogen at room temperature for an additional 2 h. The dark solution was then neutralized by the dropwise addition of triethylamine (1.8 mL), DDQ (18 mg) was added, and the solution stirred for another 1 h. The solution was diluted with dichloromethane and washed with water, and the solvent was evaporated under reduced pressure. The residue was then columned in grade 3 alumina eluting with 30% dichloromethane in toluene. A greenish-purple fraction was collected and recrystallization from chloroform/methanol giving the title porphyrin (15 mg, 31%) as purple crystals, mp >300 °C. UV−vis ($CHCl_3$): λ_{max} (log ϵ) 380 (4.85), 436 (5.06), 528 (3.86), 566 (4.45), 588 nm (4.41). UV−vis (1% TFA/$CHCl_3$): λ_{max} (log ϵ) 422 (5.34), 434 (5.37), 566 (4.25), 616 nm (4.44). ^{1}H NMR (TFA/$CDCl_3$): δ −2.81 (2H, br), −2.76 (2H, br), 1.76−1.90 (12H, m), 3.68 (3H, s), 3.70 (3H, s), 4.11−4.29 (8H, m), 8.92 (1H, d, J = 9.3 Hz), 9.69 (1H, d, J = 9.3 Hz), 10.65 (2H, s), 11.06 (1H, s), 11.99 (1H, s). ^{13}C NMR (TFA/$CDCl_3$): δ 11.96, 16.46, 16.58, 17.44, 20.07, 20.28, 20.45, 97.86, 99.63, 99.85, 101.05, 124.52, 125.14, 125.65, 134.47, 137.87, 138.96, 142.16, 142.40, 142.49, 143.04, 143.22, 143.34, 144.52, 144.64, 144.93, 145.62, 150.89, 157.07. HRMS (EI): calcd for $C_{34}H_{34}N_6S$, 558.25657; found, 558.25653. Anal. Calcd for $C_{34}H_{34}N_6S \cdot {}^3/_5H_2O$: C, 71.70; H, 6.18; N, 14.75. Found: C, 71.44; H, 6.05; N, 14.44. Nickel(II) complex. Dark-green crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 260 (4.46), 342 (4.40), 386 (4.82), 428 (4.84), 526 (3.86), 556 (4.07) 600 (4.64). Copper(II) complex. Dark-green crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 330 (4.33), 388 (4.84), 434 (4.87), 538 (3.88), 560 (4.01), 606 nm (4.61). Zinc complex. Purple crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 390 (4.84), 442 (4.84), 528 (3.88), 566 (4.01), 612 nm (4.55).

2,3-Diethyl-8,17-bis-(2-methoxycarbonylethyl)-7,18-dimethylthiadiazolobenzo[3,4-*b*]porphyrin (32b). The procedure for **32a** was adopted using **31b** (100 mg), pyrroledialdehyde **13**[23] (24.4 mg), TFA (7 mL), dichloromethane (280 mL), and DDQ (31 mg). The crude product was chromatographed on grade 3 alumina eluting with dichloromethane. A pink prefraction was collected, followed by a major green fraction. The latter was recrystallized from chloroform/methanol to give the thiadiazolobenzoporphyrin (40 mg, 44%) as long purple needles, mp >300 °C. UV−vis ($CHCl_3$): λ_{max} (log ϵ) 380 (4.85), 436 (5.12), 528 (3.93), 564 (4.49), 588 nm (4.39). UV−vis (1% TFA/$CHCl_3$): λ_{max} (log ϵ) 338 (4.36), 422 (5.37), 434 (5.39), 566 (4.27), 614 nm (4.39). ^{1}H NMR ($CDCl_3$): δ −4.03 (2H, br s), 1.91 (6H, t, J = 7.2 Hz), 3.23 (2H, t, J = 7.7 Hz), 3.37 (2H, t, J = 7.7 Hz), 3.65 (9H, s), 3.66 (3H, s), 4.01 (4H, q, J = 7.5 Hz), 4.37 (2H, t, J = 7.7 Hz), 4.45 (2H, t, J = 7.7 Hz), 8.40 (1H, d, J = 8.8 Hz), 9.25 (1H, d, J = 8.8 Hz), 9.95 (1H, s), 9.97 (1H, s), 10.06 (1H, s), 11.16 (1H, s). ^{1}H NMR (TFA/$CDCl_3$): δ −3.14 (2H, br s), −2.95 (2H, br s), 1.77 (6H, t, J = 7.5 Hz), 3.25 (2H, t, J = 7.4 Hz), 3.33 (2H, t, J = 7.7 Hz), 3.72 (3H, s), 3.74 (9H, s), 4.16 (4H, q, J = 7.5 Hz), 4.5−4.7 (4H, m), 8.96 (1H, d, J = 9.3 Hz), 9.82 (1H, d, J = 9.3 Hz), 10.70 (2H, s), 11.33 (1H, s), 12.01 (1H, s). ^{13}C NMR ($CDCl_3$/TFA): δ 12.21, 17.44, 20.07, 21.86, 21.98, 29.83, 35.67, 35.80, 53.08, 53.19, 98.50, 99.99, 100.22, 101.00, 124.74, 125.40, 125.70, 134.98, 138.19, 138.56, 140.11, 140.22, 140.66, 142.22, 142.50, 142.74, 143.25, 144.76, 144.89, 150.74, 157.16, 175.36, 175.75. HRMS (EI): calcd for $C_{38}H_{38}N_6O_4S$, 674.26753; found, 674.26707. Anal. Calcd for $C_{38}H_{38}N_6O_4S$: C, 67.63; H, 5.68; N, 12.45; S, 4.75. Found: C, 67.25; H, 5.59; N, 12.17; S, 4.58.

7,18-Bis-(2-methoxycarbonylethyl)-8,17-dimethylacenaphtho[1,2-*b*]phenanthro[9,10-*l*]porphyrin (21). Tripyrrane **12b** (100 mg) was dissolved in 10 mL of TFA, and the solution was stirred under nitrogen for 10 min. Dichloromethane (390 mL) was added, followed immediately by dialdehyde **17b** (36.4 mg), and the mixture was allowed to stir for 2 h under a nitrogen atmosphere. Triethylamine (18 mL) was slowly added to neutralize the TFA, followed by DDQ (30 mg), and the resulting solution was stirred for an additional 1 h. The solution was washed with water and evaporated under reduced pressure, and the residue was subjected to chromatographic separation on a grade 3 alumina column using dichloromethane and then chloroform as the eluent. The product was collected as a deep-green fraction. Recrystallization from chloroform/methanol gave the title porphyrin (44 mg, 42%) as a dark-green powder, mp >300 °C. UV−vis ($CHCl_3$): λ_{max} (log ϵ) 319 (4.35), 436 (5.16), 541 (4.08), 584 (4.50), 599 (4.47), 612 (4.48), 675 nm (4.08). UV−vis (1% TFA-$CHCl_3$): λ_{max} (log ϵ) 326 (4.22), 466 (5.27), 550 (3.89), 590 (4.21), 648 nm (4.73). ^{1}H NMR (TFA/$CDCl_3$): δ −3.15 (1H, br s), −2.67 (1H, br s), − 2.00 (2H, br s), 3.26 (4H, t, J = 7 Hz), 3.72 (12H, s), 4.51 (4H, t, J = 7 Hz), 8.11−8.21 (4H, m), 8.30−8.34 (4H, m), 9.26 (4H, t), 9.93 (2H, d, J = 8.4 Hz), 11.19 (2H, s), 11.44 (2H, s). ^{13}C NMR (TFA/$CDCl_3$): δ 12.18, 21.85, 35.72, 53.12, 100.69, 100.93, 125.24, 127.45, 127.67, 129.56, 129.77, 129.93, 130.51, 131.13, 131.30, 131.50, 133.82, 136.37, 136.77, 139.24, 140.42, 142.71, 143.32, 144.43, 175.83. HRMS (FAB): calcd for $C_{52}H_{40}N_4O_4$ + H, 785.3128; found, 785.3132. Anal. Calcd for $C_{52}H_{40}N_4O_4$: C, 79.57; H, 5.14; N, 7.14. Found C, 79.07; H, 5.05; N, 7.05. Nickel(II) complex. Dark-green crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 258 (4.78), 346 (4.33), 442 (5.11), 538 (3.93), 576 (4.08), 624 nm (4.79). Copper(II) complex. Dark-green powder, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 442 (5.20), 550 (3.94), 580 (4.07), 630 nm (4.89). Zinc complex. Dark-green powder, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 256 (4.71), 340 (4.37), 454 (5.15), 546 (3.95), 584 (4.06), 636 nm (4.84).

7,18-Bis-(2-methoxycarbonylethyl)-8,17-dimethyldiacenaphtho[1,2-*b*:1,2-*l*]porphyrin (20). The previous procedure was repeated using tripyrrane **12b** (100 mg), **17a** (33 mg), DDQ (30.3 mg), TFA (7 mL), and 280 mL of dichloromethane. Chromatography on neutral alumina, eluting initially with dichloromethane and finally with 10% methanol/chloroform, gave the product fraction. Recrystallization from chloroform/methanol to give the porphyrin (50 mg, 50%) as a dark-green powder, mp >300 °C. UV−vis ($CHCl_3$): λ_{max} (log ϵ) 370 (4.39), 443 (4.80), 470 (4.97), 548 (4.19), 592 (3.95), 625

(4.07), 692 nm (4.49). UV−vis (1% TFA/$CHCl_3$): λ_{max} (log ϵ) 329 (4.29), 384 (4.32), 472 (5.08), 556 (4.01), 582 (4.11), 600 (4.09), 659 nm (4.63). ^{1}H NMR (TFA/$CDCl_3$): δ −3.16 (2H, br s), −3.01 (2H, br s), 3.31 (4H, t, J = 7.5 Hz), 3.74 (6H, s), 3.81 (6H, s), 4.61 (4H, t, J = 7.5 Hz), 8.14 (4H, t), 8.35 (4H, d, J = 8.4 Hz), 9.16 (2H, d, J = 6.9 Hz), 9.27 (2H, d, J = 6.9 Hz), 11.04 (2H, s), 11.26 (2H, s). ^{13}C NMR (TFA/$CDCl_3$): δ 12.13, 21.88, 35.77, 53.12, 101.24, 101.35, 127.33, 127.70, 129.53, 129.58, 131.11, 131.25, 131.32, 131.56, 136.56, 136.83, 136.89, 140.15, 140.89, 142.68, 143.10, 144.64, 144.78, 175.80. HRMS (FAB): calcd for $C_{50}H_{38}N_4O_4$ + H, 759.2971; found, 759.2968. Anal. Calcd for $C_{50}H_{38}N_4O_4 \cdot {}^1/_2H_2O$: C, 78.21; H, 5.12; N, 7.30. Found C, 78.02; H, 4.99; N, 7.16. Nickel(II) complex. Dark-green crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 270 (4.52), 346 (4.33), 440 (5.04), 528 (3.91), 642 nm (4.76). Copper(II) complex. Green crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 342 (4.31), 446 (4.74), 532 (4.05), 650 nm (4.41). Zinc complex. Green crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 282 (4.33), 352 (4.40), 458 (4.88), 656 nm (4.59).

7,18-Bis-(2-methoxycarbonylethyl)-8,17-dimethylthiadiazolobenzo[3,4-*b*]phenanthro[9,10-*l*]porphyrin (33b). Tripyrrane **31b** (100 mg) was dissolved in TFA (7 mL) and stirred under nitrogen for 10 min. Dichloromethane (280 mL) and phenanthro[9,10-*c*]pyrrole-1,3-dicarboxaldehyde (38 mg) were added, and the mixture was allowed to stir for 2 h under nitrogen. Triethylamine was added slowly to the reaction mixture to neutralize the TFA. DDQ (31 mg) was then added, and the solution was stirred for an additional 1 h. The residue obtained after evaporation of the solution was diluted with dichloromethane, washed with water, and evaporated under reduced pressure. The residue was chromatographed in grade 3 alumina eluting initially with dichloromethane, then chloroform and 1% methanol/chloroform. Recrystallization (twice) from chloroform/methanol gave the title porphyrin (48 mg, 47%) as green crystals, mp >300 °C. UV−vis ($CHCl_3$): λ_{max} (log ϵ) 326 (4.40), 400 (sh, 4.78), 440 (5.06), 580 (4.52), 604 nm (4.53). UV−vis (1% TFA/$CHCl_3$): λ_{max} (log ϵ) 254 (4.63), 306 (4.27), 324 (4.26), 438 (5.08), 454 (5.07), 582 (4.24), 608 (4.03), 638 nm (4.56). ^{1}H NMR (TFA/$CDCl_3$): δ −2.36 (2H, br s), −1.66 (2H, br s), 3.15−3.4 (4H, m), 3.66 (3H, s), 3.68 (3H, s), 3.72 (3H, s), 3.74 (3H, s), 4.48 (2H, t), 4.55 (2H, t), 8.18 (2H, t), 8.33 (2H, t), 8.95 (1H, d, J = 9 Hz), 9.27 (2H, d, J = 8.4 Hz), 9.75 (1H, d, J = 9 Hz), 9.93 (2H, d, 7.8 Hz), 11.23 (1H, s), 11.45 (2H, s), 11.87 (1H, s). ^{13}C NMR (TFA/$CDCl_3$): δ 12.24, 21.87, 35.62, 35.75, 53.09, 98.31, 100.76, 101.48, 101.74, 124.71, 125.25, 127.36, 127.53, 129.83, 129.96, 130.41, 130.46, 133.81, 134.90, 138.50, 138.82, 138.92, 139.06, 139.66, 139.87, 140.28, 143.07, 143.23, 143.33, 144.11, 150.74, 157.23, 175.19, 175.67. HRMS (FAB): calcd for $C_{46}H_{36}N_6O_4S$ + H, 769.259 70; found, 769.260 10. Anal. Calcd for $C_{46}H_{36}N_6O_4S \cdot {}^1/_2H_2O$: C, 71.02; H, 4.79; N, 10.80; S, 4.12. Found: C, 71.05; H, 4.64; N, 10.78; S, 3.85. Nickel(II) complex. Dark-green crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 256 (4.66), 350 (4.29), 420 (sh, 4.75), 434 (4.83), 540 (3.86), 578 (4.09), 618 nm (4.61). Copper(II) complex. Dark-green crystals, mp >300 °C (chloroform/petroleum ether). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 334 (4.30), 418 (4.79), 436 (4.83), 546 (3.94), 584 (4.05), 624 nm (4.58). Zinc complex. Dark-purple flakes, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 352 (4.42),416 (4.82), 450 (5.05), 562 (3.96), 584 (3.96), 632 nm (4.77).

7,18-Bis-(2-methoxycarbonylethyl)-8,17-dimethylthiadiazolobenzo[3,4-*b*]acenaphtho[1,2-*l*]porphyrin (33a). Tripyrrane **31b** (100 mg) was dissolved in TFA (7 mL) and stirred under nitrogen for 10 min. Dichloromethane (280 mL) and acenaphtho[1,2-*c*]pyrrole-1,3-dicarboxaldehyde (33.7 mg) were added, and the mixture was allowed to stir for 2 h under nitrogen. Triethylamine was added slowly to the reaction mixture to neutralize the TFA. DDQ (31 mg) was then added, and the solution was stirred for an additional 1 h. The residue obtained after evaporation of the solution was diluted with dichloromethane, washed with water, and evaporated under reduced pressure. The residue was chromatographed on grade 3 alumina eluting with dichloromethane, then chloroform, and finally 5% methanol/chloroform. A green fraction was collected and recrystallized from chloroform/methanol to give the title porphyrin (55 mg, 55%) as green crystals, mp >300 °C. UV−vis ($CHCl_3$): λ_{max} (log ϵ) 272 (4.24), 332 (4.57), 346 (4.55), 442 (5.29), 590 (4.51), 618 (4.77), 650 (4.02), 686 nm (3.60). UV−vis (1% TFA/$CHCl_3$): λ_{max} (log ϵ) 260 (4.37), 322 (4.34), 450 (sh, 5.20), 462 (5.31), 578 (4.16), 592 (4.23), 626 (4.01), 650 nm (4.83). ^{1}H NMR (TFA/$CDCl_3$): δ −2.41 (2H, br s), −2.29 (2H, br s), 3.27−3.36 (4H, m), 3.63 (3H, s), 3.68 (3H, s), 3.79 (3H, s), 3.82 (3H, s), 4.50−4.62 (4H, m), 8.12 (2H, t), 8.31 (2H, d, J = 8.4 Hz), 9.12 (2H, d, J = 6.6 Hz), 8.95 (1H, d, J = 9.3 Hz), 9.76 (1H, d, J = 9.3 Hz), 11.10 (2H, s), 11.25 (1H, s), 11.95 (1H, s). ^{13}C NMR (TFA/$CDCl_3$): δ 12.15, 12.23, 21.92, 22.04, 35.69, 35.85, 53.28, 53.35, 98.63, 101.15, 102.28, 102.54, 124.83, 125.56, 125.87, 127.51, 129.61, 131.19, 131.27, 131.76, 135.24, 136.29, 136.51, 136.94, 138.94, 139.41, 140.47, 140.89, 140.97, 142.90, 143.07, 143.31, 144.02, 144.70, 144.82, 150.74, 157.20, 175.90, 176.23. HRMS (FAB): calcd for $C_{44}H_{34}N_6O_4S$ + H, 743.244 05; found, 743.243 90. Anal. Calcd for $C_{44}H_{34}N_6O_4S \cdot {}^1/_2H_2O$: C, 70.29; H, 4.69; N, 11.18; S, 4.26. Found: C, 70.02; H, 4.56; N, 11.00; S, 4.08. Nickel(II) complex. Dark-green powder, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 330 (4.29), 358 (4.33), 438 (4.93), 526 (3.96), 636 nm (4.69). Copper(II) complex. Dark-green crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 330 (4.40), 442 (5.06), 536 (4.02), 644 nm (4.72). Zinc complex. Dark-green crystals, mp >300 °C (chloroform/methanol). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 352 (4.54), 456 (5.23), 546 (3.95), 650 nm (4.91).

13,17-Dibutyl-12,18-dimethyldiacenaphtho[1,2-*b*:1,2-*g*]porphyrin (26b). A mixture of bis-(3-ethoxycarbonyl-1-acenaphtho[1,2-*c*]pyrrolyl)methane (**22**; 0.220 g) and potassium hydroxide (0.30 g) in ethylene glycol (30 mL) was refluxed under nitrogen for 30 min. The reaction mixture was cooled, diluted with chloroform, and washed with water. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The residue was mixed with dialdehyde **24b**[37] (0.140 g) in methanol (1.75 mL)/dichloromethane (50 mL) and added dropwise over a period of 2 h to a three-necked 250 mL round-bottom flask containing *p*-toluenesulfonic acid (0.596 g) in methanol (1.75 mL)/dichloromethane (50 mL) under an atmosphere of nitrogen. After the addition was complete, the solution was allowed to stir overnight. A saturated solution of zinc acetate in methanol (10 mL) was added, and the resulting mixture was allowed to stir open to atmospheric oxygen for an additional 24 h. The deep-red reaction mixture was washed with water, evaporated under reduced pressure, and dissolved in TFA (3 mL). The red solution was diluted with dichloromethane, washed with water, aqueous sodium bicarbonate solution, and water, and evaporated under reduced pressure. The residue was washed with methanol and filtered, and the green residue was recrystallized from chloroform/methanol to give the *adj*-diacenaphthoporphyrin (55 mg, 23%) as reddish-brown crystals, mp >300 °C. UV−vis (trace pyrrolidine/$CHCl_3$): λ_{max} (log ϵ) 288 (4.51), 344 (4.57), 406 (4.80), 476 (5.10), 550 (4.32), 590 (4.44), 610 (4.19), 672 nm (4.34). UV−vis (1%TFA/$CHCl_3$): λ_{max} (log ϵ). 262 (4.46), 330 (4.44), 366 (4.57), 470 (5.35), 596 (4.47), 618 (4.01), 648 nm (4.60). ^{1}H NMR (TFA/$CDCl_3$): δ −3.15 (4H, br s), 1.10 (6H, t, J = 6.9 Hz), 1.70 (4H, sextet), 2.15 (4H, quintet, J = 7.0 Hz), 3.75 (6H, s), 4.13 (4H, t, J = 7.5 Hz), 8.13−8.21 (4H, m), 8.35−8.39 (4H, m), 9.18 (2H, d, J = 6.9 Hz), 9.26 (2H, d, J = 6.9 Hz), 10.60 (1H, s), 11.11 (2H, s), 11.61 (1H, s). ^{13}C NMR (TFA/$CDCl_3$): δ 12.02, 13.75, 23.20, 26.67, 35.50, 98.90, 101.21, 103.41 127.42, 129.60, 131.29, 131.35, 131.64, 131.77, 136.01, 136.53, 137.04, 139.95, 143.39, 143.59, 144.60, 144.65, 145.06. HRMS (EI): calcd for $C_{50}H_{42}N_4$, 698.34095; found, 698.34078. Anal. Calcd for $C_{50}H_{42}N_4 \cdot {}^3/_4H_2O$: C, 84.30; H, 6.15; N, 7.86. Found: C, 84.17; H, 5.85; N, 7.89. Nickel(II) complex. Dark-green crystals, mp >300 °C. UV−vis (trace pyrrolidine/$CHCl_3$): λ_{max} (log ϵ) 288 (4.41), 346 (4.42), 366 (4.42), 390 (4.38), 410 (4.44), 466 (4.86), 578 (4.14), 604 (4.37), 620 nm (4.50). Zinc complex. Green crystals, mp >300 °C. UV−vis (trace pyrrolidine/

$CHCl_3$): λ_{max} (log ϵ) 296 (4.45), 342 (4.46), 374 (4.57), 414 (4.65), 468 (4.74), 496 (5.14), 596 (4.32), 646 nm (4.53).

13,17-Dibutyl-12,18-dimethyldithiadiazolobenzo[3,4-*b*:3,4-*g*]porphyrin (34). Following the previous procedure, **34** was prepared using bis-(3-ethoxycarbonyl-1-thiadiazolobenzo-[3,4-*c*]pyrrolylmethane **35** (200 mg) and 3,3′-dibutyl-4,4′-dimethyl-2,2′-dipyrrylmethane-5,5′-dicarboxyaldehyde (**24b**)[37] (134 mg). The residue was washed with methanol, filtered, and recrystallized from chloroform/methanol to give the *adj*-dithiadiazolobenzoporphyrin (19 mg, 7%) as green crystals, mp >300 °C. The product was contaminated by an isomeric species, but this could be removed by careful flash chromatography eluting with 0.5% methanol/dichloromethane to give a pure sample of porphyrin **34**. UV−vis ($CHCl_3$): λ_{max} (log ϵ) 367 (4.62), 400 (4.67), 465 (4.97), 549 (4.10), 583 (4.33), 662 nm (4.16). UV−vis (1% TFA/$CHCl_3$): λ_{max} (log ϵ) 342 (4.40), 442 (5.32), 451 (5.28), 580 (4.24), 624 (4.45), 632 (4.46). ^{1}H NMR ($CDCl_3$/TFA): δ −2.15 (4H, br), 1.07 (6H, t, J = 7.3 Hz), 1.63 (4H, m), 2.12 (4H, m), 3.74 (6H, s), 4.14 (4H, t, J = 7.8 Hz), 8.99 (2H, d, J = 8.8 Hz), 9.72 (2H, d, J = 9.8 Hz), 10.69 (1H, s), 11.13 (2H, s), 13.28 (1H, s). HRMS (FAB): calcd for $C_{38}H_{34}N_8S_2$ + H, 667.2428; found, 667.2426.

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Supporting Information Available: Copies of UV−vis spectra for porphyrins **14**, **20**, **21**, **26**, and **32**−**34** and their nickel(II), copper(II), and zinc chelates and ^{1}H and selected ^{13}C NMR spectra for compounds **5**, **10**−**12**, **14**, **17**−**22**, **26**, and **28**−**35** are provided (93 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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