Porphyrins with Exocyclic Rings. 16.[1] Synthesis and Spectroscopic Characterization of Fluoranthoporphyrins, a New Class of Highly Conjugated Porphyrin Chromophores

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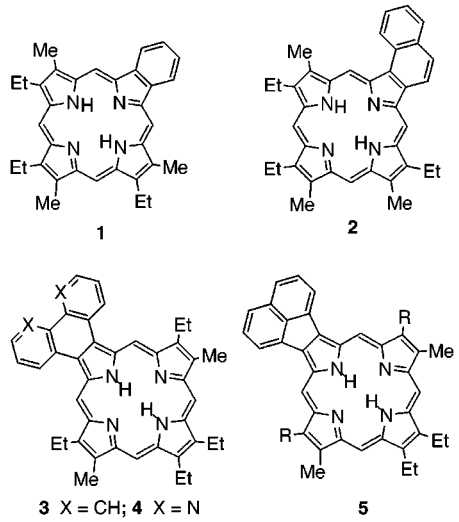
Porphyrins with fused aromatic rings are under detailed investigation due to their unique spectroscopic properties. To gain more insights into the effects due to ring annealation on the porphyrin chromophore, a series of fluoranthoporphyrins have been synthesized. Reaction of 3-nitrofluoranthene with isocyanoacetate esters in the presence of a phosphazene base afforded good yields of the fluorantho[2,3-*c*]pyrrole esters **8**. Cleavage of the ester moiety with KOH in ethylene glycol afforded the parent heterocycle **9**, and this condensed with 2 equiv of acetoxymethylpyrroles **10** in refluxing acetic acid-2-propanol to afford tripyrranes **11**. Following cleavage of the *tert*-butyl ester protective groups with TFA, "3 + 1" condensation with pyrrole dialdehyde **12** gave the fluoranthoporphyrins **13** in good overall yields. In addition, reaction of tripyrrane **11** with acenaphthopyrrole dialdehyde **16** gave the mixed acenaphthofluoranthoporphyrin **17** in excellent yields. A difluoranthoporphyrin **18** was also prepared via a "2 + 2" MacDonald condensation. Reaction of fluoranthopyrrole **8a** with dimethoxymethane in the presence of *p*-toluenesulfonic acid gave the symmetrical dipyrrylmethane **19**, and following ester saponification, this was condensed with a dipyrrylmethane dialdehyde to afford the *adj*-difluoranthoporphyrin **18**. The UV−vis spectra for these fluoranthoporphyrins gave a series of three broadened absorptions in the Soret band region, although the Q-bands were little effected by ring fusion. The nickel(II), copper(II), and zinc chelates were more unusual, showing strong absorptions near 600 nm. Difluoranthoporphyrin **18** showed many of the same spectroscopic features, although the presence of two ring fusions gave rise to an increase in the spectroscopic shifts. The mixed system **17** gave spectra that showed larger red shifts due to the acenaphthylene unit combined with the features due to the fluoranthene rings. This work further demonstrates the utility of aromatic ring fusion in altering the properties of porphyrinoid systems.

Introduction

There is presently a high level of interest in exploring porphyrin-type systems with strong absorptions in the far red/near-infrared for various applications ranging from sensors and novel optical materials[2] to the development of superior photosensitizers for photodynamic therapy.[3] Although extension of the chromophore by introducing fused aromatic rings might be expected to produce major bathochromic shifts for the porphyrin system, in many cases the effects are actually rather small.[4] Monobenzoporphyrin **1** (Chart 1) gives a Soret band at 404 nm and a longest wavelength Q-band at 628 nm,[4,5] values that are only slightly higher than those reported for octaalkylporphyrins such as octaethylporphyrin (OEP) (400 and 622 nm, respectively).[6,7] Naphtho-

Chart 1



[1,2-*c*]porphyrin **2** gave a Soret band at 415 nm and Q-band 1 at 630 nm,[5,8] again demonstrating that aromatic ring fusion has a minimal effect, and many other fused units such as phenanthrene (e.g., porphyrin **3**),[9,10] phenanthroline (e.g., porphyrin **4**),[11] quinoline,[1] and isoquinoline[1] also little alter the electronic spectra for

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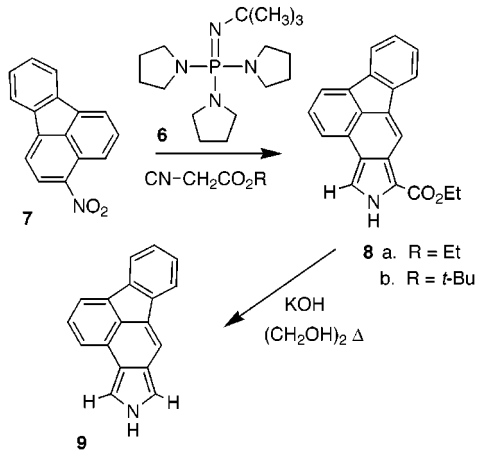
these modified porphyrins. On the other hand, acenaphthoporphyrins **5** have very different electronic spectra[12−14] showing three strong Soret bands at 387, 431, and 454 nm (for R = Et), while Q-band 1 is further red shifted to 658 nm and intensified.[12] Fusion of two acenaphthylene units to the porphyrin chromophore have still larger effects,[12] while tetraacenaphthoporphyrins produce by far the largest bathochromic shifts yet reported for porphyrin systems.[13,14] The very different effects caused by acenaphthylene compared to benzene, naphthalene, phenanthrene, and related systems are presently not well understood,[4] and further examples of ring-fused porphyrins are needed to examine these disparate influences. With this in mind, we targeted the synthesis of porphyrins with fused fluoranthene rings.[15] Fluoranthene contains the elements of both naphthalene and acenaphthylene moieties and hence represents a structural unit that could potentially produce intermediary effects on the UV−vis absorption spectra.

Results and Discussion

To synthesize fluoranthoporphyrins, pyrroles with fused fluoranthene rings were required as the key intermediates. In previous studies, we have adapted the Barton−Zard chemistry[16] to synthesize *c*-annelated pyrroles from nitroaromatic compounds.[9−14,17−20] This chemistry involves the condensation of isocyanoacetate esters with nitroaromatic compounds in the presence of a nonnucleophilic base such as DBU. The initial reaction involves a conjugate addition to the nitroarene, and for this reason, the degree of nitroalkene character in the intermediates is a critical factor.[9−19] Hence, while 9-nitrophenanthrene reacts with ethyl isocyanoacetate in the presence of DBU to give excellent yields of phenanthropyrroles,[9,10,17] 1-nitronaphthalene gave low yields of pyrrolic products under these conditions[18] and nitrobenzene failed to react at all to give the related isoindoles. While this is to be expected, the use of phosphazene base **6**[21] (Scheme 1) in this chemistry has been shown to extend the range of isolatable pyrrolic products[19] and indeed 1-nitronaphthalene gives good yields of naphthopyrrole using this reagent.[19] 3-Nitrofluoranthene (**7**) failed to react with ethyl isocyanoacetate in the presence of DBU, but gave the required fluorantho[2,3-*c*]pyrrole **8a** in 45% yield when phosphazene **6** was used as the base (Scheme 1). Similarly, *tert*-butyl isocyanoacetate[10] condensed with **7** in the presence of **6** to give the related *tert*-butyl ester **8b** in good yields. The ethyl ester **8a** was recrystallized from toluene to give the pure fluoranthopyrrole. However, traces of toluene were tenaciously retained even when the sample was vacuum-dried for several days at room temperature, and it was necessary to dry the fluoranthopyrrole in a vacuum oven at 60 °C for several days in order to obtain solvent free samples of **8a**. The proton NMR spectra for pyrroles **8a** and **8b** showed most of the aromatic resonances between 7.3 and 8.0 ppm, with the pyrrole CH showing up as a doublet (J = 3.2 Hz) at 7.8 ppm. The isolated fluoranthene proton overlies the ester unit and hence is further deshielded to produce a 1H singlet at 8.6 ppm, while the NH appears as a broad singlet near 10 ppm in $CDCl_3$ (this latter resonance is further deshielded due to hydrogen bonding to near 12 ppm in DMSO-d_6). The structures were further confirmed by carbon-13 NMR spectroscopy, electron impact MS, and combustion analyses.

Scheme 1



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(15) Results were presented, in part, at the following meetings: 213th National ACS Meeting, San Francisco, CA, April 1997 (Werner, T. M.; Lash, T. D. *Book of Abstracts*, CHED 441); 216th National ACS Meeting, Boston, MA, August 1998 (Thompson, M. L.; Spence, J. D.; Lash, T. D. *Book of Abstracts*, CHED 256); 31st Central Regional ACS Meeting, Ohio State University, Columbus, OH, June 1999 (Thompson, M. L.; Lash, T. D. *Program and Abstracts*, Abstract No. 266).

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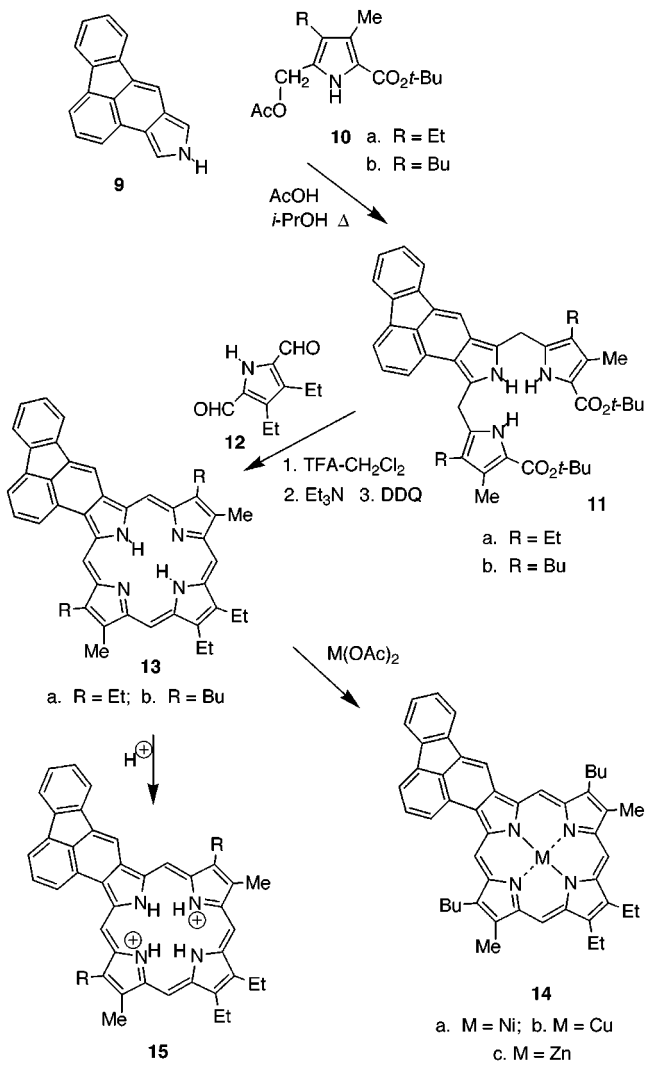
The fluoranthopyrroles **8** could be used to synthesize porphyrin products using a variety of synthetic routes,[22] but our previous work has demonstrated that the "3 + 1" variant[11,23,24] on the MacDonald condensation[25] is particularly well suited for the synthesis of porphyrins with fused aromatic rings.[1,4,11,12,18] To generate the required tripyrrolic intermediates, it was first necessary to cleave the ester moiety. This was accomplished by heating **8a** with KOH in ethylene glycol in the presence of a small amount of hydrazine to give the fluoranthopyrrole **9** (Scheme 1). Good yields could be obtained for this transformation but the conditions used were critical to isolate the pure parent pentacycle **9**. Pyrrole **9** was condensed with acetoxymethylpyrroles **10** in refluxing acetic acid−isopropyl alcohol under nitrogen for 16 h (Scheme 2). The resulting tripyrranes **11** were isolated in crude form as brown powders following precipitation in ice−water, suction filtration, and drying in vacuo. Attempts to purify the tripyrranes by recrystallization were unsuccessful and as these compounds are too unstable to survive chromatography they were used in crude form for porphyrin synthesis. The *tert*-butyl ester protective groups of **11a** and **11b** were cleaved with TFA. The solutions were then diluted with dichloromethane, one equivalent of pyrrole dialdehyde **12** was added and the resulting mixture stirred at room temperature under nitrogen for 2 h. Following neutralization with triethylamine, 1.05 equiv of DDQ was added and the mixture stirred for a further 1 h. Following extraction, chromatography, and recrystallization from chloroform−methanol, the fluoranthoporphyrins **13a** and **13b** were isolated in good overall yields (>20% from fluoranthopyrrole **9**). Dibutylporphyrin **13b** was further reacted with nickel(II), copper(II), and zinc acetate, respectively, under standard conditions[26,27] to generate the related metal(II) chelates **14** (Scheme 2).

The proton NMR spectra for **13a** and **13b** showed typical shifts due to the powerful diatropic ring current for the porphyrin nucleus. For **13a**, the four bridging methine or *meso*-protons showed up as a series of four 1H singlets between 10.0 and 11.2 ppm (two of these singlets are slightly deshielded by the proximate fluoranthene ring to 10.6 and 11.1 ppm). The alkyl substituents are also deshielded to typical values for porphyrin systems, with the methyl groups appearing as a singlet at 3.7 ppm. The internal NH appeared as a broad upfield signal near −3.6 ppm. In the presence of TFA, the related dications **15** (Scheme 2) also demonstrated powerful aromatic ring current effects by proton NMR spectroscopy. The carbon-13 NMR spectra in TFA−$CDCl_3$ were also well resolved and showed four resonances for the

Scheme 2



meso-carbons between 96 and 100 ppm. The structures were also confirmed by mass spectrometry.

The UV−vis spectrum for **13a** showed a broadened Soret band region with strong absorptions at 380, 414, and 436 nm. However, while the Soret region was quite unusual, the Q-band region was little affected and showed Q-band 1 as weak absorptions at 634 nm (Figure 1A). The dications **15** in 10% TFA−chloroform gave fairly ordinary spectra showing a strong Soret band at 426 nm and Q-bands at 570 and 616 nm (Figure 1B). While the UV−vis spectra for the fluoranthoporphyrins were for the most part unexceptional, the related metal chelates **14a**−**c** gave far more unusual spectra (Figure 1C−E). Nickel(II) porphyrin **14a** gave three Soret bands at 390, 416, and 431 nm and a strong absorption (α band[28]) at 592 nm. Although the α band is substantially red shifted compared to the related absorption for nickel(II) OEP, which appears at 551 nm,[7] its most notable feature is that it has almost two-thirds the intensity of the principal Soret absorption with a molar absorptivity of 6×10^4 $cm^{-1}\cdot mol^{-1}\cdot L$. NiOEP in dioxane solution gives an α band with a relative intensity compared to the Soret band of

(22) 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.

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(24) Related "3 + 1" procedures were independently developed by Boudif and Momenteau: Boudif, A.; Momenteau, M. *J. Chem. Soc., Chem. Commun.* **1994**, 2069; *J. Chem. Soc., Perkin Trans. 1* **1996**, 1235. For an alternative "3 + 1" porphyrin synthesis, see: Nguyen, L. T.; Senge, M. O.; Smith, K. M. *J. Org. Chem.* **1996**, *61*, 998.

(25) The "3 + 1" methodology has also proven to be exceptionally valuable in the synthesis of porphyrin analogues: Lash, T. D. *Synlett* **2000**, 279 and references therein.

(26) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; p 798.

(27) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

(28) Metalloporphyrins generally show two significant absorption bands at higher wavelengths than the Soret band and these are designated as the α (higher wavelength) and β bands. See: Smith, K. M. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; pp 3−28.

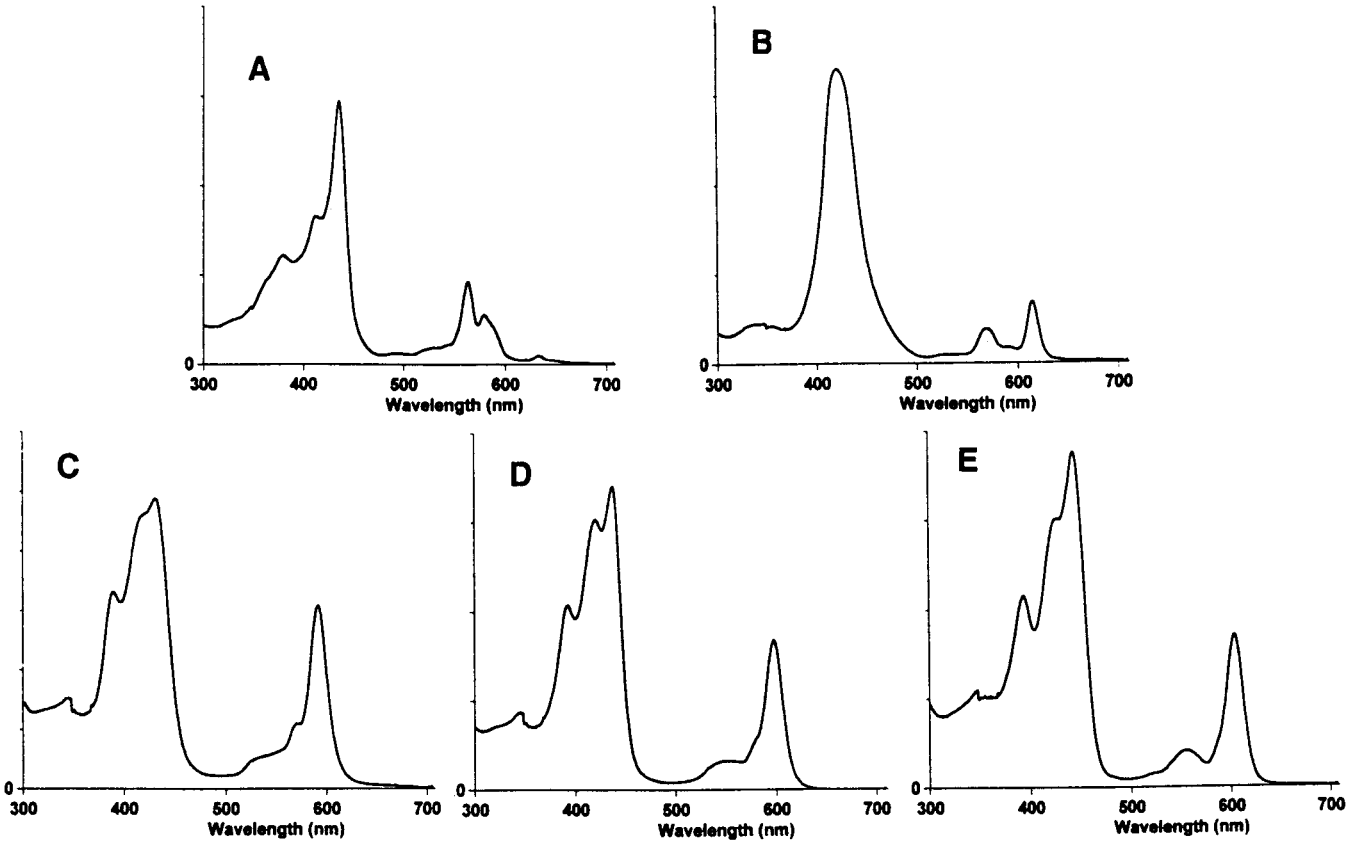
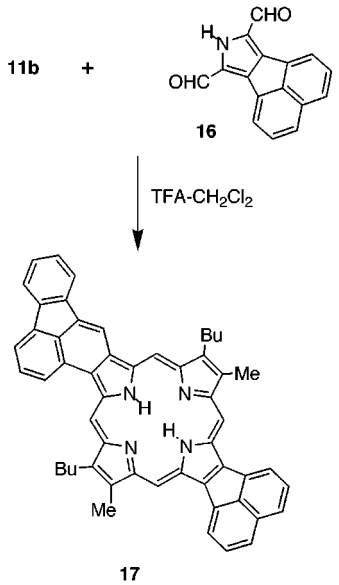


Figure 1. UV−vis spectra of fluoranthoporphyrin **13b** and related metal chelates: (A) free base in 1% Et_3N−chloroform; (B) dication in 10% TFA−chloroform; (C) nickel(II) chelate **14a** in chloroform; (D) copper(II) chelate **14b** in chloroform; (E) zinc chelate **14c** in chloroform.

only 0.15 and a molar extinction coefficient of 3.3×10^4 $cm^{-1}\cdot mol^{-1}\cdot L$.[7] In the case of the copper(II) chelate **14b**, the main Soret band is shifted to longer wavelength (438 nm), while the α band shifts to 598 nm, albeit with a slightly reduced extinction coefficient (5.6×10^4). These trends continue with the zinc complex, where the main Soret band appears at 444 nm, and the main longer wavelength absorption appears at 604 nm ($\epsilon = 5.2 \times 10^4$). The zinc complex shows some signs of aggregation in solution. Pyrrolidine is sometimes added to solutions to disrupt aggregation and the UV−vis spectrum was rerun in the presence of 2% pyrrolidine. In this case, the main Soret band intensified and shifted to 458 nm and the α band moved to 613 nm, although a broad band became evident at 678 nm. Interestingly, addition of pyrrolidine to solutions of the nickel(II) and copper(II) complexes, **14a** and **14b**, had little effect on the UV−vis spectra of these chelates. The diamagnetic nickel(II) complex **14a** gave a well-resolved 400 MHz proton NMR spectrum, although the macrocyclic ring current appeared to be slightly reduced for this species compared to the free base **13**. For instance, the *meso*-protons appeared in the range of 9.6−10.5 ppm for **14a**, compared to 9.9−11.3 ppm for **13**, while the methyl resonances shifted approximately 0.2 ppm upfield to give two 3H singlets with values of 3.38 and 3.41 ppm. The zinc complex **14c** was sparingly soluble in $CDCl_3$ but gave a proton NMR spectrum that was in accord with the structure. The solubility markedly improved when a drop of pyrrolidine was added to the NMR tube and the spectrum sharpened up considerably. This was associated with an upfield shift of many of the aromatic resonances in the deaggregated solutions.

Scheme 3



The unique spectroscopic properties of fluoranthoporphyrins, particularly for the metal chelates, prompted us to investigate the synthesis of a porphyrin with both a fused fluoranthene and an acenaphthylene unit (Scheme 3). Acenaphthylene produces superior red shifts,[12−14] but the fluoranthoporphyrin metal complexes produce intense α bands and it was of interest to see whether these two properties could be combined. Crude tripyrrane **11b** was condensed with acenaphthopyrrole dialdehyde **16** under the usual "3 + 1" conditions. In this case, superior

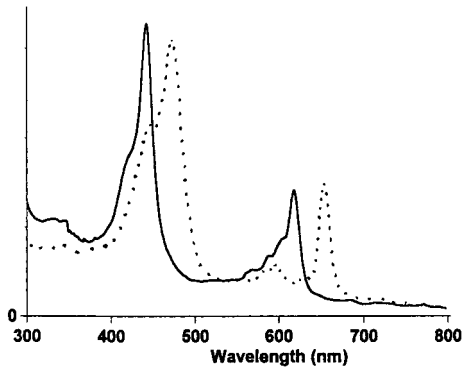


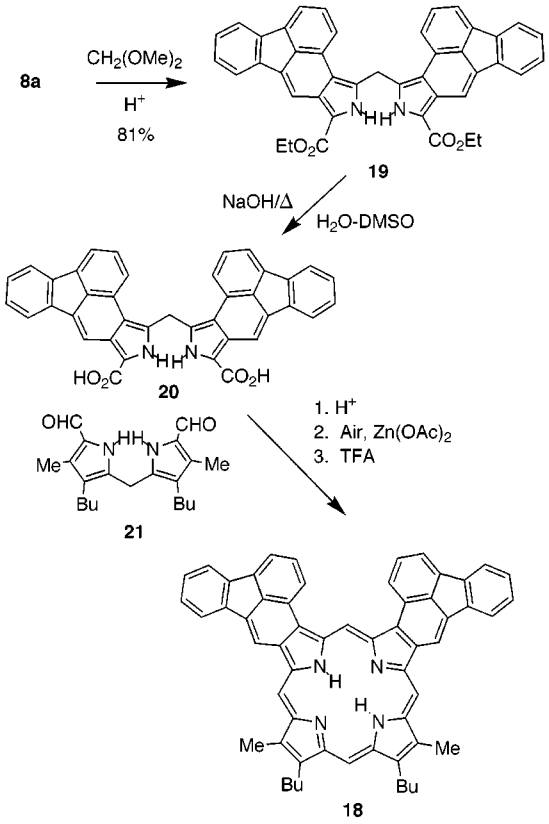
Figure 2. UV−vis spectra of acenaphthofluoranthoporphyrin **17** (3.02×10^{-5} M). Bold line: free base in 1% Et_3N−chloroform. Dotted line: dication in 10% TFA−chloroform.

results were obtained when the final oxidation was carried out by washing the reaction solution with 0.1% aqueous ferric chloride solution. Following recrystallization from chloroform−methanol, the highly insoluble acenaphthofluoranthoporphyrin **17** was obtained in excellent yields (Scheme 3). Although the porphyrin was not sufficiently soluble to run the proton NMR spectrum of the free base, addition of TFA afforded the corresponding dication and this was sufficiently soluble to allow proton and carbon-13 NMR data to be obtained. The structures were also confirmed by high-resolution mass spectrometry. The nickel(II), copper(II), and zinc complexes were also synthesized, although these were all rather insoluble in organic solvents.

The UV−vis spectrum for **17** in chloroform demonstrated the predicted red shifts due to the acenaphthylene moiety, and the main Soret band appeared at 442 nm (Figure 2). The effects were rather more significant for the dication **17**H_2^{2+} in 10% TFA−chloroform where the Soret band shifted to 472 nm while a strong band appeared at 653 nm. The metal chelates were insufficiently soluble for molar absorptivity values to be obtained, but spectra were obtained for each chelate in chloroform and in 2% pyrrolidine−chloroform. The nickel(II) complex gave a Soret band at 441 nm and a strong longer wavelength band at 637 nm, but these values shifted to 476 and 656 nm, respectively, in the presence of pyrrolidine. The copper(II) complex in chloroform gave a Soret band at 439 nm and two major longer wavelength bands at 613 and 642 nm, but in this case addition of pyrrolidine only slightly modified the observed UV−vis spectrum. Finally, the zinc complex afforded a Soret band at 468 nm in chloroform, together with a strong band at 654 nm; again, the spectrum was only slightly altered upon addition of pyrrolidine, although the bands are somewhat sharpened. The spectra reveal that the additive effects that were anticipated (combination of red shifts and intensification of the longer wavelength bands) are indeed observed, although the UV−vis spectrum for Ni**17** in 2% pyrrolidine−chloroform appears to be anomalous.

The effect of fusing the fluoranthene ring system onto a porphyrin nucleus was further probed by synthesizing a difluoranthoporphyrin **18** (Scheme 4). The "3 + 1" approach was ill-suited for synthesizing difluoranthoporphyrins due to the asymmetry of fluoranthene itself. One of the condensing units must be symmetrical to avoid isomer formation, and this could not be readily achieved in these studies. Instead, the "2 + 2" MacDonald condensation[25,29] was used to prepare the *adj*-difluoranthoporphyrin **18**. Reaction of fluoranthopyrrole **8a** with dimethoxymethane in the presence of *p*-toluenesulfonic acid afforded the symmetrical dipyrrylmethane **19** in excellent yields (Scheme 4). This intermediate proved to be highly insoluble, although a proton NMR spectrum could be obtained in DMSO-d_6. Attempts to cleave the ester groups with KOH in ethylene glycol at 180 °C led to extensive decomposition. Instead, the ethyl esters were saponified with NaOH in H_2O−DMSO under nitrogen. Following neutralization with glacial acetic acid, suction filtration, and vacuum-drying, the corresponding dicarboxylic acid **20** was obtained in crude form as a pale blue powder. Condensation with dialdehyde **21** in the presence of *p*-toluenesulfonic acid,[29] followed by addition of zinc acetate and air oxidation for 2 days, gave the *adj*-difluoranthoporphyrin as a mixture of the free base and its zinc complex in moderate yield. Demetalation with TFA afforded the diannelated porphyrin, while reaction with zinc acetate in refluxing DMF gave the corresponding zinc complex Zn**18**. The UV−vis spectrum for **18** showed a broad Soret region with multiple bands and a fairly ordinary Q-band region where band 1 appears at 659 nm (Figure 3). This agrees with expectations if the effects due to the individual rings are essentially additive. In TFA−chloroform, a strong Soret band appears at 449 nm, together with weaker absorptions at 589 and 638 nm. Zn**18** was highly insoluble and gave only broadened absorptions at 467 and 633 nm (Figure 4). However, addition of pyrrolidine greatly improved the solubility and a strong Soret band appeared at 475 nm (Figure 4).

Scheme 4



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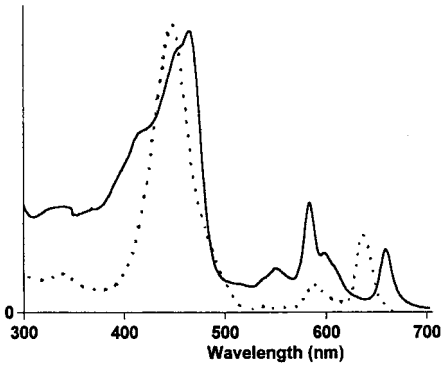

Figure 3. UV−vis spectra of *adj*-difluoranthoporphyrin **18**. Bold line: free base in 1% Et_3N−chloroform. Dotted line: dication in 2% TFA−chloroform.

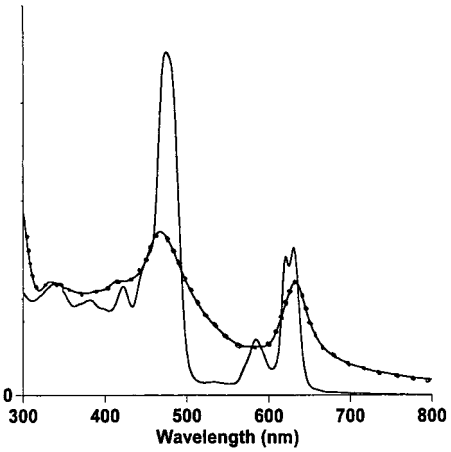

Figure 4. UV−vis spectra of zinc *adj*-difluoranthoporphyrin Zn**18** (2.33×10^{-5} M). Dotted line: Highly aggregated complex in chloroform. Bold line: Zn**18** in 2% pyrrolidine−chloroform.

At longer wavelengths two moderately strong bands were present at 621 and 631 nm.

Conclusions

The synthesis of monofluorantho-, difluorantho-, and acenaphthofluoranthoporphyrins has been achieved starting from commercially available 3-nitrofluoranthene. The monofluoranthoporphyrins exhibit highly broadened Soret regions with multiple absorption bands, but the Q-bands are little influenced. However, the metal chelates are far more unusual, showing strong absorptions near 600 nm. Addition of an acenaphthylene unit further red shifts the UV−vis absorptions but the intensification of the α bands in the metal chelates is retained. The *opp*-difluoranthoporphyrin system also shows spectroscopic trends that suggest that the effect of the second ring fusion is essentially additive. These results demonstrate a further diversity in the effects on the porphyrin chromophore due to ring fusion, although some limitations due to solubility considerations have been encountered. The methodology that we have developed using the Barton−Zard condensation to construct *c*-annelated pyrroles from nitroarenes,[16] coupled with the "3 + 1" methodology for porphyrin formation,[11,22] has now been shown for the first time to allow a tetracyclic benzenoid aromatic unit to be fused onto the porphyrin macrocycle, and this approach is likely to lead to still further modified or extended structures. Fluoranthene is structurally closely related to the highly studied corrannulene system[30] and our results suggest that this type of "buckybowl" might also be attached onto the porphyrin ring system. Apart from further extending the chromophore, this would have the additional advantage of potentially increasing the porphyrin's solubility due to the nonplanar nature of these benzenoid structures.

Experimental Section

3-Nitrofluoranthene, TFA, DDQ, triethylamine, and dimethoxymethane were obtained from Aldrich Chemical Co. Phosphazene base P_1-*t*-Bu-tris(tetramethylene) (**6**) was purchased from Fluka Chemie AG. These reagents 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[26] or DMF.[27] 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 Fluorantho[2,3-*c*]pyrrole-1-carboxylate (8a). Phosphazene base **6** (1.71 g) was added dropwise to a solution of ethyl isocyanoacetate[31] (0.59 g) and 3-nitrofluoranthene (1.08 g) in THF (20 mL; freshly distilled from calcium hydride), and the resulting mixture was stirred under reflux overnight. The solution was diluted with chloroform, washed with water, dried over sodium sulfate, and evaporated under reduced pressure. The residue was chromatographed on silica, eluting with dichloromethane. Recrystallization from toluene afforded the fluoranthopyrrole (467 mg; 45%) as a light brown powder; mp 230−232 °C dec; IR (Nujol mull) ν 3256 (NH str.), 1667 cm^{-1} (C=O str.); ^1H NMR ($CDCl_3$) δ 1.53 (3H, t, J = 7.2 Hz), 4.53 (2H, q, J = 7.2 Hz), 7.38−7.42 (2H, m), 7.65 (1H, t, J = 7.6 Hz), 7.85−7.90 (3H, m), 7.99−8.02 (2H, m), 8.58 (1H, s), 9.96 (1H, br s); ^1H NMR (DMSO-d_6−$CDCl_3$) δ 1.54 (3H, t, J = 7.0 Hz), 4.52 (2H, q, J = 7.0 Hz), 7.36−7.41 (2H, m), 7.64 (1H, t, J = 7.8 Hz), 7.83−7.89 (3H, m), 7.97−8.01 (2H, m), 8.60 (1H, s), 12.12 (1H, br s); ^{13}C NMR (DMSO-d_6−$CDCl_3$) δ 14.6, 60.0, 115.2, 115.4, 115.9, 117.5, 121.0, 121.2, 121.3, 121.4, 125.0, 127.0, 127.1, 127.4, 127.9, 131.0, 134.5, 136.5, 138.5, 140.4, 161.5; MS (EI, 70 eV) *m*/*z* 313 (93) [M^+], 267 (100) [M^+ − EtOH], 239 (52), 213 (37). Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47. Found: C, 80.30; H, 4.66; N, 4.11.

***tert*-Butyl Fluorantho[2,3-*c*]pyrrole-1-carboxylate (8b).** The title compound was prepared from 3-nitrofluoranthene (0.250 g), *tert*-butyl isocyanoacetate[10] (0.216 g), and phosphazene base **6** (0.423 g) by the previous procedure. Recrystallization from toluene gave the *tert*-butyl ester (127 mg; 37%) as pale yellow crystals: mp 210 °C dec; IR (Nujol mull) ν 3249 (NH str.), 1664 cm^{-1} (C=O str.); ^1H NMR ($CDCl_3$) δ 1.76 (9H, s), 7.36−7.41 (2H, m), 7.64 (1H, t, J = 7.8 Hz), 7.81 (1H, d, J = 3.2 Hz), 7.84−7.89 (2H, m), 7.94−7.97 (1H, m), 7.99 (1H, d, J = 8.0 Hz), 8.57 (1H, s), 10.18 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 28.9, 81.9, 114.9, 115.4, 117.1, 118.2, 121.4, 121.6, 121.9, 122.1, 125.3, 127.5, 128.0, 128.4, 131.8, 135.5, 137.3, 139.0, 141.0, 160.9; MS (EI, 70 eV) *m*/*z* 341 (36) [M^+], 285 (100) [M^+ − $(CH_3)_2C{=}CH_2$], 267 (89) [M^+ − *t*-BuOH], 239 (46), 213 (44). Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.80; H, 5.68; N, 4.26.

Fluorantho[2,3-*c*]pyrrole (9). Nitrogen gas was bubbled through a mixture of **8a** (197 mg) and potassium hydroxide (0.50 g) in ethylene glycol (10 mL) for 15 min, seven drops of

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hydrazine were added, and the resulting solution was stirred under reflux on a preheated oil bath at 190 °C under an atmosphere of nitrogen for a further 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 pyrrole (117 mg; 77%) was obtained as a light brown powder: mp 95 °C dec, darkened at 55 °C; ^{1}H NMR (DMSO-d_6) δ 7.36 (2H, m), 7.56 (1H, br s), 7.59 (1H, t, J = 7.5 Hz), 7.85−7.89 (1H, m), 7.95−8.01 (2H, m), 8.05 (1H, d, J = 7.6 Hz), 8.21 (1H, s), 12.15 (1H, br s); ^{13}C NMR (DMSO-d_6) δ 116.3, 119.5, 122.4, 122.6, 124.5, 126.6, 126.8, 128.5, 131.1, 132.1, 132.4, 132.6, 135.0, 136.3, 141.1, 143.8, 145.0; MS (EI, 70 eV) m/z 241 (100) [M$^+$], 214 (9), 213 (24), 120 (17), 106 (16). Anal. Calcd for $C_{18}H_{11}N\cdot{}^1/_4H_2O$: C, 87.96; H, 4.71; N, 5.70. Found: C, 88.21; H, 4.54; N, 5.88.

Diethyl 1,1′-Difluorantho[2,3-*c*]pyrrolylmethane-3,3′-dicarboxylate (19). Ethyl fluorantho[2,3-*c*]pyrrole-1-carboxylate (**8a**; 786 mg), dimethoxymethane (190 mg), and *p*-toluenesulfonic acid (75 mg) were dissolved in 37 mL of glacial acetic acid. The reaction vessel was purged with nitrogen, and the mixture was stirred under an atmosphere of nitrogen at room temperature for 3 days. The cloudy mixture was poured into 200 mL of ice/water and allowed to stand at room temperature for 2 h. The resulting precipitate was suction filtered, washed with water, and recrystallized from ethanol to give the dipyrrylmethane (652 mg; 81%) as a pale green powder: mp > 300 °C; ^{1}H NMR (d$_6$-DMSO) δ 1.41 (6H, t, J = 7 Hz), 4.40 (4H, q, J = 7 Hz), 5.40 (2H, s), 7.35−7.43 (6H, m), 7.84−7.89 (4H, m), 7.96 (2H, m), 8.06 (2H, m), 8.65 (2H, s). Anal. Calcd for $C_{43}H_{30}N_2O_4$: C, 80.86; H, 4.73; N, 4.39. Found: C, 80.58; H, 4.76; N, 4.45.

Bis-1,3-(5-*tert*-butoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)fluorantho[2,3-*c*]pyrrole (11a). Nitrogen was bubbled through a mixture of fluoranthopyrrole **9** (100 mg) and acetoxymethylpyrrole **10a**[32] (233 mg) in 2-propanol (8 mL) and acetic acid (1.5 mL) for 10 min. The mixture was refluxed with stirring under a nitrogen atmosphere for 16 h. The solution was poured into ice−water and the resulting precipitate suction filtered and dried in vacuo to give the crude tripyrrane (254 mg; 90%) as a brown powder. This material was used without further purification. For the 400 MHz ^{1}H NMR ($CDCl_3$), see the Supporting Information.

Bis-1,3-(5-*tert*-butoxycarbonyl-3-butyl-4-methyl-2-pyrrolylmethyl)fluorantho[2,3-*c*]pyrrole (11b). Tripyrrane **11b** was prepared by the previous procedure from **9** (100 mg) and **10b** (256 mg). Again, the resulting crude tripyrrane, which was obtained as a brown powder (248 mg; 81%), was used without further purification. For the 400 MHz ^{1}H NMR ($CDCl_3$), see the Supporting Information.

7,12,13,18-Tetraethyl-8,17-dimethylfluorantho[2,3-*b*]-porphyrin (13a). Tripyrrane **11a** (100 mg) was dissolved in TFA (1 mL) and stirred at room temperature for 10 min under nitrogen. The mixture was diluted with dichloromethane (19 mL), followed immediately by the addition of pyrroledialdehyde **12**[23] (26 mg). The mixture was stirred under nitrogen for a further 2 h. Then, the mixture was neutralized by the dropwise addition of triethylamine, DDQ (35 mg) was added, and the solution was stirred for another 1 h. The solution was then diluted with chloroform and washed with water, and the solvent was evaporated under reduced pressure. The residue was chromatographed on a Grade 3 alumina column, eluting with dichloromethane, and then on silica again eluting with dichloromethane. A deep red fraction was collected and evaporated under reduced pressure. Recrystallization of the residue from chloroform−methanol gave the fluoranthoporphyrin (33 mg; 36%) as purple crystals: mp > 300 °C; UV−vis (1% E_3N−$CHCl_3$) λ_{max} (log ϵ) 380 (4.81), 414 (4.95), 436 (5.19), 530 (3.51), 564 (4.69), 580 (4.45), 634 nm (3.61); UV−vis (10% TFA-$CHCl_3$) λ_{max} (log ϵ) 274 (4.48), 354 (4.40), 426 (5.25), 570 (4.31), 616 nm (4.56); ^{1}H NMR ($CDCl_3$) δ −3.57 (2H, s), 1.92 (6H, t, J = 7.1 Hz), 1.99 (3H, t, J = 7.6 Hz), 2.02 (3H, t, J = 7.4 Hz), 3.74 (6H, s), 4.04 (4H, q, J = 7.2 Hz), 4.26−4.34 (4H, 2 overlapping quartets), 7.54 (1H, t, J = 7.6 Hz), 7.60 (1H, t, J = 7.0 Hz), 8.11 (1H, d, J = 6.8 Hz), 8.19−8.25 (2H, m), 8.43 (1H, d, J = 6.8 Hz), 9.80 (1H, d, J = 7.6 Hz), 9.84 (1H, s), 10.09 (1H, s), 10.11 (1H, s), 10.58 (1H, s), 11.13 (1H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −3.22 (1H, br s), −2.74 (1H, br s), −2.52 (1H, br s), −2.31 (1H, br s), 1.71−1.76 (6H, 2 overlapping triplets), 1.80 (6H, t, J = 7.8 Hz), 3.66 (3H, s), 3.67 (3H, s), 4.12 (4H, q, J = 7.6 Hz), 4.22 (4H, q, J = 7.7 Hz), 7.59−7.65 (2H, m), 8.10 (1H, d, J = 6.8 Hz), 8.34−8.36 (2H, m), 8.43 (1H, d, J = 6.4 Hz), 9.65−9.69 (1H, m), 9.94 (1H, s), 10.58 (2H, s), 11.09 (1H, s), 11.44 (1H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.1, 16.7, 17.6, 20.1, 20.4, 20.5, 96.3, 98.6, 99.3, 99.5, 114.4, 122.0, 122.4, 123.2, 124.9, 126.3, 128.9, 129.2, 130.0, 131.8, 135.5, 136.4, 137.7, 137.9, 138.6, 139.2, 139.3, 139.8, 141.3, 141.6, 142.1, 142.2, 142.4, 142.5, 142.7, 143.2, 143.4; HRMS (FAB) calcd for $C_{44}H_{40}N_4$ + H 625.3331, found 625.3332.

7,18-Dibutyl-12,13-diethyl-8,17-dimethylfluorantho-[2,3-*b*]porphyrin (13b). Prepared from tripyrrane **11b** (100 mg) and **12** (24 mg) by the previous procedure. Following chromatography as described for **13a**, the product was recrystallized from chloroform−methanol to give the title porphyrin (26 mg; 28%) as dark purple crystals: mp 264−266 °C; UV−vis (1% E_3N−$CHCl_3$) λ_{max} (log ϵ) 380 (4.83), 413 (4.97), 436 (5.22), 529 (3.99), 564 (4.70), 579 (4.48), 633 nm (3.67); UV−vis (10% TFA-$CHCl_3$) λ_{max} (log ϵ) 423 (5.26), 569 (4.33), 615 nm (4.58); ^{1}H NMR ($CDCl_3$) δ −4.06 (2H, br s), 1.08−1.14 (6H, 2 overlapping triplets), 1.69−1.78 (4H, m), 1.92−1.97 (6H, 2 overlapping triplets), 2.17−2.26 (4H, m), 3.53 (3H, s), 3.59 (3H, s), 3.84−3.92 (4H, m), 4.03 (4H, q, J = 7.6 Hz), 7.55 (1H, t, J = 7.2 Hz), 7.61 (1H, t, J = 7.2 Hz), 8.02 (1H, t, J = 7.4 Hz), 8.08 (1H, d, J = 7.6 Hz), 8.13 (1H, d, J = 6.8 Hz), 8.30 (1H, d, J = 6.8 Hz), 9.27 (1H, s), 9.39 (1H, d, J = 7.6 Hz), 9.93 (2H, s), 9.95 (1H, s), 10.53 (1H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −3.31 (1H, br s), −3.10 (1H, br s), −2.88 (1H, br s), −2.8 (1H, vb), 1.05−1.11 (6H, 2 overlapping triplets), 1.68−1.76 (10H, m), 2.11−2.22 (4H, m), 3.68 (6H, s), 4.14 (4H, q, J = 7.7 Hz), 4.22 (4H, t, J = 7.4 Hz), 7.60−7.67 (2H, m), 8.10−8.13 (1H, m), 8.36−8.38 (2H, m), 8.45−8.48 (1H, m), 9.65−9.69 (1H, m), 9.96 (1H, s), 10.63 (2H, s), 11.15 (1H, s), 11.49 (1H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.2, 14.0, 17.5, 20.1, 23.3, 26.8, 26.9, 34.5, 96.5, 98.8, 99.4, 99.6, 114.3, 122.1, 122.4, 123.3, 124.7, 126.2, 129.0, 129.3, 130.2, 131.9, 135.5, 136.5, 138.5 (2), 138.7, 139.3 (2), 139.8, 141.3 (2), 141.6, 142.0, 142.4 (2), 142.5, 142.6, 142.8, 143.0, 143.6, 143.8. Anal. Calcd for $C_{48}H_{48}N_4\cdot H_2O$: C, 82.48; H, 7.21; N, 8.02. Found: C, 82.46; H, 7.05; N, 8.03. Nickel(II) complex (**14a**): dark green crystals; mp > 300 °C, dec (chloroform−methanol); UV−vis ($CHCl_3$) λ_{max} (log ϵ) 390 (4.81), 416 (4.95), 431 (4.98), 529 (3.97), 569 (4.32), 592 nm (4.77); ^{1}H NMR ($CDCl_3$) δ 1.08−1.15 (6H, 2 overlapping triplets), 1.68−1.77 (4H, m), 1.82 (6H, t, J = 7.4 Hz), 2.10−2.23 (4H, m), 3.38 (3H, s), 3.41 (3H, s), 3.79 (4H, t, J = 7.4 Hz), 3.90 (4H, q, J = 7.6 Hz), 7.50−7.59 (2H, m), 8.01−8.07 (2H, m), 8.13 (1H, d, J = 6.8 Hz), 8.28 (1H, d, J = 7.2 Hz), 9.33−9.35 (2H, overlapping singlet and doublet), 9.64 (1H, s), 9.65 (1H, s), 9.89 (1H, s), 10.45 (1H, s); HRMS (EI) calcd for $C_{48}H_{46}N_4Ni$ 736.3076, found 736.3079. Copper(II) complex (**14b**): dark green crystals; mp > 300 °C (chloroform−methanol); UV−vis ($CHCl_3$) λ_{max} (log ϵ) 393 (4.84), 421 (5.01), 438 (5.06), 550 (4.06), 598 nm (4.75); HRMS (EI) calcd for $C_{48}H_{46}N_4Cu$ 741.3018, found 741.3021. Zinc complex (**14c**): green crystals; mp > 300 °C (chloroform−methanol); UV−vis ($CHCl_3$) λ_{max} (log ϵ) 394 (4.83), 425 (4.98), 444 (5.07), 555 (4.11), 604 nm (4.72); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (log ϵ) 398 (4.78), 432 (4.85), 458 (5.15), 528 (3.72), 565 (4.21), 613 (4.74), 678 nm (3.70); ^{1}H NMR ($CDCl_3$) δ 1.14 (6H, t, J = 7.2 Hz), 1.70−1.80 (4H, m), 1.91−1.97 (2 overlapping triplets), 2.1−2.2 (4H, m), 3.35 (3H, s), 3.45 (3H, s), 3.62−3.68 (2H, br t), 3.68−3.75 (2H, br t), 4.03−4.07 (4H, 2 overlapping quartets), 7.56 (1H, t, J = 7.2 Hz), 7.63 (1H, t, J = 6.4 Hz), 8.00 (1H, t, J = 7.2 Hz), 8.06 (1H, d, J = 7.2 Hz), 8.09 (1H, d, J = 6.4 Hz), 8.33 (1H, d, J = 7.2 Hz), 9.21 (1H, s), 9.27 (1H, br d), 9.60 (1H, br s), 9.70 (1H, s), 9.79 (1H, s), 10.14 (1H, br s); ^{1}H NMR (pyrrolidine−$CDCl_3$; downfield region only) δ 7.52 (1H, t, J = 7.4 Hz), 7.58 (1H, obscured by solvent impurity), 8.11 (1H, d, J = 7.2 Hz), 8.21−8.27 (2H, m), 8.46

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(1H, d, J = 7.2 Hz), 9.98 (1H, d J = 6.4 Hz), 10.01 (1H, s), 10.02 (1H, s), 10.03 (1H, s), 10.57 (1H, s), 11.13 (1H, s); FAB MS *m*/*z* (rel int) 747 (9), 746 (19), 745 (19), 744 (27), 743 (25), 742 (34), 741 (6), 703 (5), 702 (5), 701 (7), 700 (5), 699 (8); HRMS (EI) calcd for $C_{48}H_{46}N_4Zn$ 742.3014, found 742.3013.

8,17-Dibutyl-7,18-dimethylacenaphtho[1,2-*b*]fluoranthо[2,3-*l*]porphyrin (17). Tripyrrane **11b** (74 mg) was dissolved in TFA (1 mL) and the mixture stirred at room temperature for 10 min under nitrogen. The mixture was diluted with dichloromethane (65 mL), followed immediately by the addition of acenaphthopyrroledialdehyde **16**[12] (26 mg), and the mixture stirred under nitrogen for a further 2 h. The solution was washed with water and vigorously shaken with a 0.1% v/v aqueous ferric chloride solution for 10 min. The mixture was further washed with water and 5% aqueous sodium bicarbonate solution and the solvent removed under reduced pressure. The residue was recrystallized from chloroform−methanol to give the fluoranthoacenaphthoporphyrin (51 mg; 68%) as dark green crystals: mp > 300 °C; UV−vis (1% E_3N−$CHCl_3$) λ_{max} (log ϵ) 420 (sh, 4.78), 442 (5.03), 565 (4.18), 588 (4.31), 603 (4.43), 618 (4.64), 683 nm (3.66); UV−vis (10% TFA−$CHCl_3$) λ_{max} (log ϵ) 445 (4.86), 472 (5.01), 579 (4.23), 595 (4.27), 626 (4.15) 653 nm (4.68); ^{1}H NMR (TFA−$CDCl_3$) δ −2.58 (2H, br s), −2.25 (1H, br s), −2.05 (1H, br s), 1.08−1.15 (6H, 2 overlapping triplets), 1.68−1.76 (4H, m), 2.18−2.26 (4H, m), 3.75 (6H, s), 4.22 (4H, t), 7.61−7.67 (2H, m), 8.09−8.13 (3H, m), 8.28 (2H, m), 8.36−8.39 (2H, m), 8.47 (1H, m), 9.10 (2H, m), 9.65−9.69 (1H, m), 9.92 (1H, s), 11.00 (2H, s), 11.04 (1H, s), 11.40 (1H, s); ^{13}C NMR (TFA-$CDCl_3$) δ 12.2, 14.0, 23.3, 26.8, 26.9, 27.0, 34.5, 34.6, 96.8, 99.1, 101.7, 102.0, 114.2, 122.4, 122.5, 123.5, 124.6, 126.3, 127.1, 129.2, 129.4, 130.5, 131.2, 131.4, 132.2, 135.3, 135.6, 136.9, 137.0, 138.5, 139.5, 139.7, 139.9, 140.4, 141.5, 142.4, 142.8, 143.2, 143.3, 143.4, 143.8, 144.0, 144.1; HRMS (FAB) calcd for $C_{54}H_{44}N_4$ + H 749.3644, found 749.3645. Nickel(II) complex: dark purple crystals; mp > 300 °C (chloroform−methanol); UV−vis ($CHCl_3$) λ_{max} (rel int.) 424 (sh), 441 (1), 526 (0.08), 594 (0.13), 637 nm (0.46); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (rel int) 445 (0.72), 476 (1), 634 (sh), 656 nm (0.59). Copper(II) complex: dark purple crystals; mp > 300 °C (chloroform−methanol); UV-vis ($CHCl_3$) λ_{max} (rel int.) 395 (0.40), 418 (0.63, sh), 439 (1), 537 (0.06), 563 (0.07), 613 (0.32), 642 nm (0.15); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (rel int) 394 (0.40), 418 (sh, 0.63), 440 (1), 535 (0.06), 561 (0.06), 613 (0.29), 643 nm (0.20). Zinc complex: green crystals; mp > 300 °C ($CHCl_3$−MeOH); UV−vis ($CHCl_3$) λ_{max} (rel int) 468 (1), 552 (0.05), 602 (0.05), 654 nm (0.47); UV−vis (2% pyrrolidine−$CHCl_3$) λ_{max} (rel int) 442 (0.27), 468 (1), 554 (0.04), 604 (0.04), 656 nm (0.43).

13,17-Dibutyl-12,18-dimethyldifluoranthо[2,3-*b*:3,2-*g*]porphyrin (18). A solution of sodium hydroxide (0.80 g) in water (4 mL) was added to a solution of dipyrrylmethane **19** (200 mg) in DMSO (10 mL) and the resulting mixture stirred at 100 °C under a nitrogen atmosphere for 5 h. The dark orange colored solution was cooled to room temperature, diluted with water (30 mL), and further cooled to <5 °C with the aid of a salt−ice bath. The mixture was neutralized to a litmus end point with glacial acetic acid while the temperature was maintained at <5 °C. The resulting precipitate was suction filtered and washed repeatedly with water to remove all traces of acid. Following vacuum-drying overnight, the crude dicarboxylic acid **20** was obtained as a light blue solid (161 mg; 88%). A solution of *p*-toluenesulfonic acid (360 mg) in methanol (15 mL) was added to a stirred mixture of **20** (175 mg) and dialdehyde **21**[29c] (97.8 mg) in methanol (15 mL) and dichloromethane (330 mL) and the resulting solution stirred in the dark under nitrogen for 24 h. A saturated solution of zinc acetate in methanol (10 mL) was then added to the dark red solution and the resulting mixture stirred open to the air for 2 days. The solvent was evaporated under reduced pressure, and the residue was taken up in dichloromethane (75 mL). The insoluble materials were suction filtered and washed with copious quantities of methanol. The residue (30 mg; 12%) appeared to be a mixture of difluoranthoporphyrin **18** and the related zinc complex. The green solid was dissolved in TFA (2 mL), and the solution diluted with chloroform and washed successively with water, 10% aqueous sodium bicarbonate solution, and water. The organic solution was evaporated under reduced pressure and the residue recrystallized from chloroform−methanol to give the difluoranthoporphyrin as a dark green powder (10 mg): mp > 300 °C; UV−vis (1% E_3N−$CHCl_3$) λ_{max} (log ϵ) 414 (4.82), 454 (sh, 4.99), 466 (5.02), 551 (4.21), 584 (4.61), 598 (4.34), 659 nm (4.37); UV−vis (10% TFA−$CHCl_3$) λ_{max} (log ϵ) 449 (5.33), 589 (4.32), 638 nm (4.76); ^{1}H NMR (TFA−$CDCl_3$) δ −2.35 (4H, br s), 1.07 (6H, t, J = 7.3 Hz), 1.63−1.69 (4H, m), 2.09−2.13 (4H, m), 3.74 (6H, s), 4.12 (4H, t, J = 7.5 Hz), 7.64−7.67 (4H, m), 8.13 (2H, d, J = 7.0 Hz), 8.37−8.48 (6H, m), 9.82 (2H, d, J = 7.9 Hz), 9.97 (2H, s), 10.56 (1H, s), 11.13 (2H, s), 12.40 (1H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 12.0, 13.7, 23.1, 26.7, 34.5, 97.6, 99.5, 100.4, 114.1, 122.3, 122.5, 123.4, 124.6, 126.1, 128.9, 129.2, 130.4, 132.4, 135.7, 137.0, 137.9, 138.3, 139.4, 139.5, 141.0, 141.1, 141.4, 142.9, 143.2, 144.4; HRMS (FAB) calcd for $C_{58}H_{46}N_4$ + H 799.3801, found= 799.3803. Zinc Complex Zn**18**. Crude partially metalated porphyrin (10 mg) from the previous procedure and zinc acetate (20 mg) in DMF (10 mL) were heated under reflux under a nitrogen atmosphere for 2 h. The solution was cooled to room temperature and poured into ice−water. The resulting precipitate was suction filtered and washed successively with water and methanol to give Zn**18** (7.5 mg) as a green powder: mp > 300 °C; UV−vis (chloroform) λ_{max} 467, 633 nm; UV−vis (2% pyrrolidine−chloroform) λ_{max} (log ϵ) 422 (4.68), 449 (sh, 4.76), 475 (5.18), 584 (4.38), 621 (4.77), 631 nm (4.80).

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Supporting Information Available: Copies of UV−vis spectra for porphyrins **13**, **17**, and **18**, their nickel(II), copper(II), and zinc chelates, and ^{1}H and selected ^{13}C NMR spectra and MS data for compounds **8**−**11**, **13**, **14a**,**c**, and **17**−**19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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