Porphyrins with Exocyclic Rings. 14.[1] Synthesis of Tetraacenaphthoporphyrins, a New Family of Highly Conjugated Porphyrins with Record-Breaking Long-Wavelength Electronic Absorptions

John D. Spence[†] and Timothy D. Lash*

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160

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The Soret band for porphyrins is usually observed in the near-ultraviolet at approximately 400 nm, and few examples of "nonexpanded" porphyrins with this major absorption band at values above 500 nm have previously been reported in the literature. Ring fusion with aromatic ring systems such as naphthalene, anthracene, or phenanthrene generally only produces minor bathochromic shifts to this diagnostic absorption band. In this paper, the synthesis of a series of tetraacenaphthoporphyrins and their metal chelates is reported. The compact nature of the acenaphthylene ring system allows the introduction of meso substituents using the Lindsey methodology. *meso*-Tetraphenylporphyrin **10a** shows the presence of a Soret band at 556 nm, while *p*-methoxy and *p*-nitro substituents in **10f** and **10g**, respectively, further shift this band to 560 and 570 nm. Addition of TFA produces the corresponding dications with slightly higher wavelength Soret bands at 565, 573, and 588 nm. These values compare to 525 nm for the dication of tetraacenaphthylene **8**, which lacks the *meso*-aryl substituents, indicating that steric crowding and its resulting distortion of the macrocyclic conformation is responsible for a significant albeit minor portion of these shifts. The nickel(II), copper(II), and zinc chelates of **10a** produce Soret bands at 528, 545, and 558 nm, respectively, demonstrating that the trend for increasing red shifts in metalloporphyrins across the periodic table is retained for this series. The lead(II) chelate **19d** gave an additional "hyper" shift that brought the Soret band to 604 nm. A similar red shift could be achieved by introducing four phenylethynyl substituents at the meso positions, and this highly conjugated porphyrin (**20**) also showed a Soret band at 604 nm, while the corresponding dication afforded this absorption band at 629 nm. The essentially additive "hyper" shift due to lead chelation brought the Soret band for the related lead(II) complex **22d** to 642 nm. These effects are by far the largest ever observed for true porphyrins and demonstrate that the Soret band can be fined tuned to virtually any part of the visible spectrum.

Introduction

Alteration of the porphyrin chromophore to produce strong absorptions in the far-red region of the visible spectrum has been pursued by many research groups in recent years due to the potential application of these modified structures in photodynamic therapy,[2] as well as in the development of novel optical materials.[3] This has been accomplished by a variety of methods including partial reduction of the tetrapyrrolic macrocycle (chlorins, bacteriochlorins, and isobacteriochlorins),[4] the introduction of *meso*-alkynyl substituents,[5−7] expansion of the conjugated core (expanded porphyrins such as sapphyrins),[8] subunit (core) modification,[9] linkage isomerization,[10] and so on. Octaalkylporphyrins show a strong absorption in the near-ultraviolet at approximately 400 nm known as the Soret band, together with a series of four Q-bands that peter out around 625 nm.[11] In many of the modified structures, efforts have been focused on bathochromic shifts associated with the Q-bands rather than the generally more intense Soret band. In fact, apart from core-expanded systems, the Soret band is very rarely observed at wavelengths greater than 500 nm. This value has been exceeded when four *meso*-alkynyl substuents are placed on the meso bridges, but little work has been reported to suggest that this value can be pushed much further.[5−7] Steric crowding due to peripheral substituents can lead to nonplanar structures that retain their aromatic properties as assessed by proton NMR spectroscopy but these nonetheless show moderate red shifts by UV−vis spectroscopy.[12] Perhaps one of the

* To whom correspondence should be addressed. E-mail: tdlash@ilstu.edu.

[†] Present address: Department of Chemistry, Trinity University, 715 Stadium Drive, San Antonio, TX 78212-7200.

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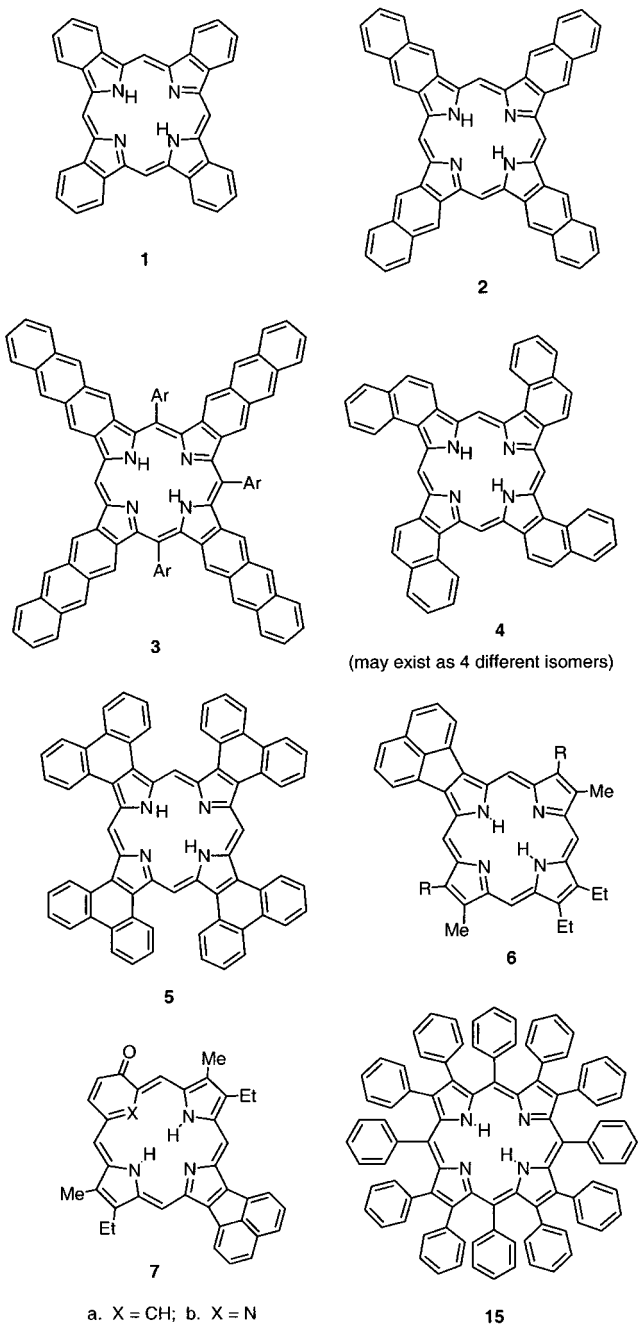
Chart 1



most obvious approaches to inducing red shifts in porphyrinoid systems is to fuse additional aromatic rings onto the pyrrolic subunits.[13] While the series naphthalene-anthracene-naphthacene shows major bathochromic shifts as the π-conjugation is extended,[14] tetrabenzoporphyrin **1** (Chart 1) shows only modest effects due to the presence of four fused benzene rings.[13,15] In 5% THF−pyridine, a split Soret band is observed at 412 and 427 nm while the longest wavelength absorption (Q-band 1) is shifted to 662 nm.[15] The zinc complex of linearly annealed tetranaphthoporphyrin **2** is reported to show a Soret band at 439 nm and a longer wavelength Q-band at 701 nm.[16] In this system, the longer wavelength band becomes more intense relative to the Soret band, a trend that is continued in the tetraanthraporphyrin **3** whose zinc chelate shows a Soret band at 462 and an intense band in the far red at 770 nm (in many respects these chromophores more closely resemble phthalocyanines than porphyrins).[17] On the other hand, angularly fused tetranaphthoporphyrin **4** shows a slightly bigger red shift for the Soret band (438 nm for the free base and 452 nm for its zinc complex) while Q-band 1 is less affected.[18] The tetraphenanthroporphyrin **5** proved to be too insoluble in organic solvents to give a UV−vis spectrum, but in TFA−chloroform the corresponding dication gave a Soret band at 482 nm.[19] Although this shift is significant, it is remarkable that this degree of ring fusion has such a limited influence of the porphyrin chromophore.[19,20] In essence, conjugation to four phenanthrene moieties introduces 48 additional π-electrons, but the Soret band of $\mathbf{5}H_2^{2+}$ is bathochromically shifted by only 80 nm compared to the dication of octaethylporphyrin. Porphyrins with one or two fused aromatic rings have also been investigated, but in most cases only minor shifts to the UV−vis absorptions have been noted.[20−24]

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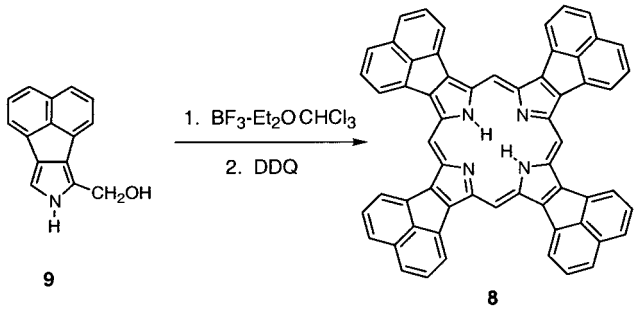
Scheme 1



For some years, we have been investigating the effects of various fused aromatic rings on the porphyrin chromophore.[1,13,19,20,22−26] During the course of these studies, the presence of a fused acenaphthylene ring was found to have a disproportionate effect on the porphyrin system.[1,26−28] For instance, monoacenaphthoporphyrin **6** showed three Soret bands at 387, 431, and 454 nm while Q-band 1 shifted to 656 nm.[1,26] This effect was magnified in diacenaphthoporphyrins[1,26] and was also observed when the same unit was placed onto porphyrin analogues such as oxybenzi- and oxypyriporphyrins **7a** and **7b**,[29] or expanded porphyrins such as the sapphyrins.[30] Following on from these observations, a tetraacenaphthoporphyrin **8** was prepared by cyclotetramerization of acenaphtho[1,2-*c*]pyrrole **9** in the presence of BF_3 etherate in chloroform (Scheme 1).[27,28] Unfortunately, the synthesis of **8** was plagued by difficulties due to the insolubility of **8** in all organic solvents. In our study, moderate yields of impure **8** were obtained but the UV−vis spectra demonstrated that the dication, generated in TFA−chloroform, showed a Soret band at a remarkable 525 nm.[27,28] In independent work by Ono and co-workers,[18] purer samples of **8** were obtained under slightly different conditions, and absorptions at λ_{max} = 528 (Soret), 647, and 702 nm were reported for their material in TFA−chloroform. While this represented one of the highest values ever observed for the Soret band of a nonexpanded porphyrin structure, the highly insoluble nature of this compound made further investigations impractical. We have overcome this problem by introducing substituents at the meso-bridge carbon atoms, and this greatly increases the solubility of the resulting porphyrins.[27,28] In the present study, a series of novel tetraacenaphthoporphyrins are reported that show unprecedented bathochromic shifts to both the Soret band and the Q-band absorptions. Indeed, examples of porphyrins with Soret bands above 600 nm are reported for the first time.

Results and Discussion

Tetraaryltetraacenaphthoporphyrins. The synthesis of meso-substituted tetraacenaphthoporphyrins **10** (Scheme 2) was adapted from the procedures developed by Lindsey and co-workers.[31] Ethyl ester **11** is readily available from the reaction of ethyl isocyanoacetate with 1-nitroacenaphthylene **12** in the presence of the nonnucleophilic base DBU.[1,26,27] Cleavage of the ester unit with KOH in ethylene glycol at 180 °C afforded the unsubstituted tetracycle **13** in excellent yields. This was condensed with benzaldehyde in the presence of catalytic boron trifluoride in chloroform to generate the porphyrinogen **14**, and subsequent oxidation with DDQ produced the desired tetraphenylporphyrin **10a** in 56% yield. Given the highly crowded nature of this system, this yield is quite exceptional. The new porphyrin produced deep violet solutions in organic solvents such as chloroform and crystallized as a dark green solid. The UV−vis spectrum for **10a** in chloroform showed a Soret band at a record-breaking value of 556 nm, while three Q-bands were observed at 638, 705, and 790 nm (Figure 1A). This represents a shift for the Soret band of over 140 nm compared to *meso*-tetraphenylporphyrin[11] while retaining a strong molar extinction coefficient of nearly 2×10^5. The high degree of crowding due to the peripheral phenyl substuents must induce a considerable amount of distortion to the porphyrin nucleus, and indeed, molecular mechanics simulations indicate that the system takes on a saddle-shaped conformation.[27] While this appears to be responsible for a certain amount of the red shifts observed, the highly distorted dodecaphenylporphyrin **14** (Chart 1) shows a Soret band at only 468 nm,[32] and it is clear from the data for **6**−**8** that the acenaphthylene rings are primarily responsible for the observed bathochromic shifts. Addition of TFA to a solution of **10a** in chloroform produced a new chromophore with an intensified Soret band ($\epsilon = 3.6 \times 10^5$) that is slightly red shifted to 565 nm, while additional absorptions were present at longer wavelengths (Figure 1B). This compares to a value for the Soret band of 528 nm for the meso-unsubstituted tetraacenaphthoporphyrin dication $\mathbf{8}H_2^{2+}$, suggesting that the distortion due to the meso substituents is responsible for a shift of 30−40 nm. This confirms that the shift due to the four acenaphthylene rings alone is of on the order of >100 nm.

The ease of synthesis and high yields obtained for **10a** encouraged us to examine a series of related compounds with substituted aryl substituents. A series of 4-substituted benzaldehydes (R = Me, Cl, Br, I, OMe) were condensed with acenaphthopyrrole **13** as described previously to give the related porphyrins **10b**−**f** in 32−66% yield. In the case of 4-nitrobenzaldehyde, poor yields were obtained and the tetrakis(4-nitrophenyl)porphyrin **10g**

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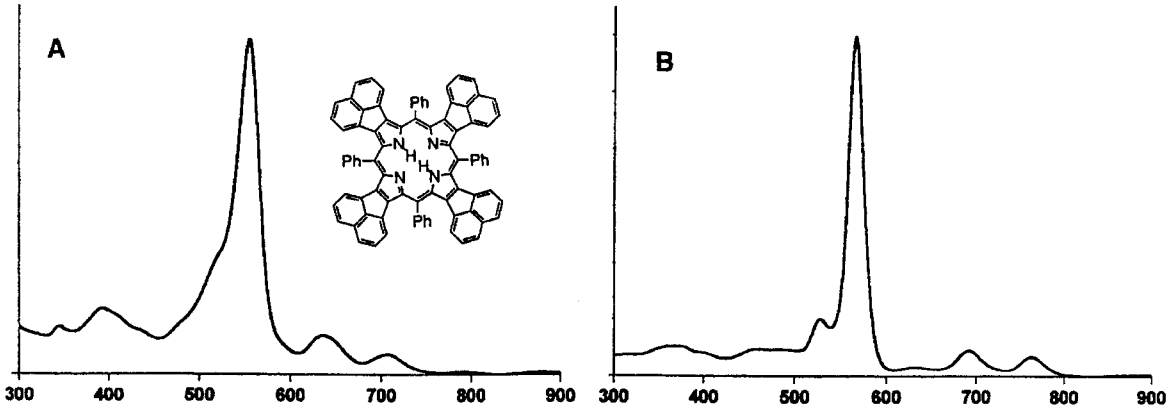
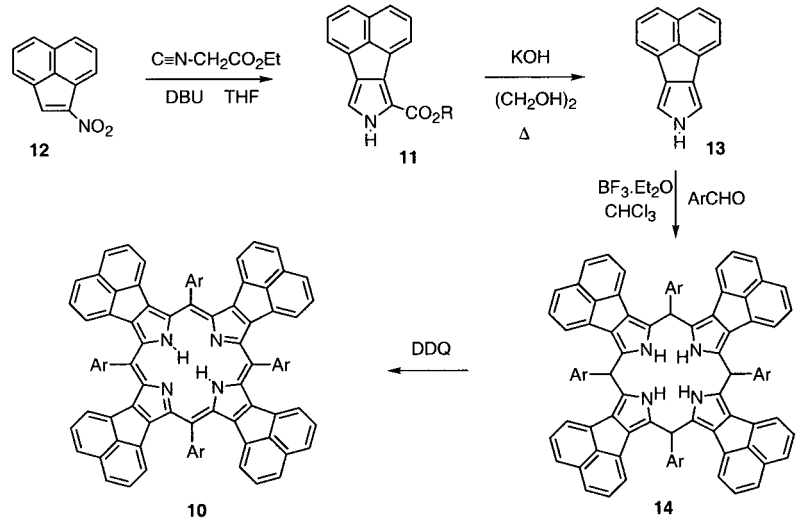


Figure 1. UV−vis spectra of tetraacenaphthoporphyrin **10a**: (A) free base in chloroform; (B) dication in 5% TFA−chloroform.

Scheme 2



a. R = Ph; b. R = 4-MeC_6H_4; c. R = ClC_6H_4; d. R = 4-BrC_6H_4; e. R = 4-IC_6H_4; f. R = 4-$MeOC_6H_4$;
g. R = 4-$NO_2C_6H_4$; h. R = Mes; i. R = n-Bu; j. R = 9-anthracenyl; k. R = 3-MeC_6H_4

was isolated in only 7% yield. However, it is worth noting that this aldehyde has previously been observed to give poor yields under the Lindsey conditions for porphyrin synthesis.[31] Mesitaldehyde gave no porphyrin under these conditions, possibly due to the increased crowding that would result in **10h**, although a compound with a molecular ion by FAB mass spectrometry of *m*/*z* 1149 was noted. This compound has been tentatively assigned as corrole **16** (Scheme 3) and is presumably formed by oxidative coupling. This type of chemistry has been increasing reported over the last several years,[33] although further studies will be necessary to confirm this structure. The analogous phenanthropyrrole **17**[1,20,34] was also reacted with benzaldehyde (Scheme 3), and a fraction was isolated that showed the correct molecular ion by FAB MS for tetraphenanthroporphyrin **18** (calcd for $C_{92}H_{54}N_4$ + H *m*/*z* 1215.4427, found 1215.4424). However, the UV−vis spectrum of this fraction showed no Soret-like band, and NMR data could not be obtained. The "wider" phenanthrene units presumably prevent the system from attaining sufficient coplanarity to allow aromatic character, and indeed, it is surprising that this species is even detectable by mass spectrometry. Finally, valeraldehyde and 9-anthracenecarboxaldehyde gave no trace of any macrocyclic products, again presumably due to the highly congested nature of the substituents in tetrabutyl- and tetraanthracenylporphyrins **10i** and **10j**.

The UV−vis spectra for this series of porphyrins showed some minor shifts for both the free bases and dications (Table 1), although the most significant changes were noted for the tetrakis(4-methoxyphenyl) and tetrakis(4-nitrophenyl)porphyrins **10f** and **10g**. For **10f**, the Soret band was present at 560 nm in the free base and further shifted to 573 nm for the related dication, while the tetranitro compound **10g** gave values of 570 and 588 nm, respectively. These data indicates that the electron donating *p*-methoxy and electron-withdrawing *p*-nitro units can extend the chromophore to a limited extent. In addition, the observed Soret bands are approaching

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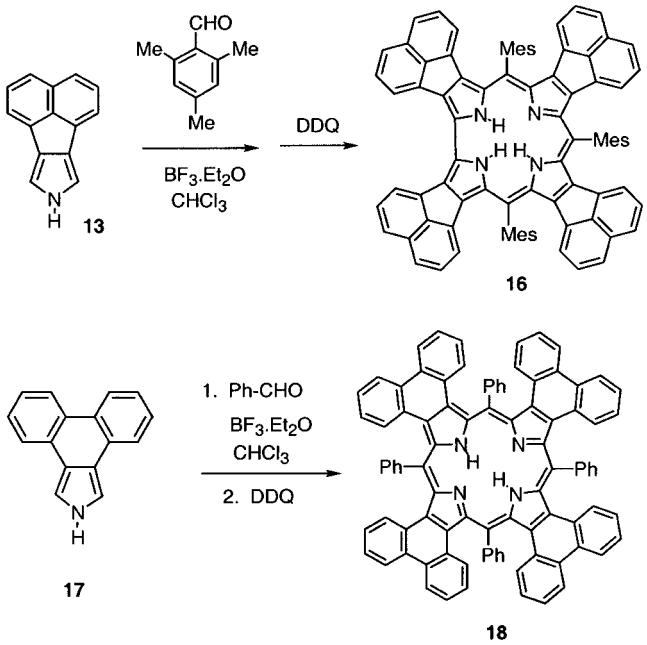
Table 1. UV−Vis Spectra of Meso-Tetrasubstituted Tetraacenaphthoporphyrins

porphyrin (solvent)	λ_{max} (nm) (log ϵ)		Soret band	Q-bands		
10a ($CHCl_3$)	395 (4.59)		556 (5.28)	638 (4.27)	705 (3.84)	790 (3.22)
10a (dication) (1% TFA−$CHCl_3$)	365 (4.56)	525 (4.81)	565 (5.56)	630 (4.06)	700 (4.44)	760 (4.32)
10b ($CHCl_3$)	345 (4.52)	396 (4.64)	557 (5.31)	639 (4.33)	705 (4.14)	793 (3.63)
10b (dication) (1% TFA−$CHCl_3$)	368 (4.63)	529 (4.81)	569 (5.56)	634 (4.11)	697 (4.40)	771 (4.52)
10c ($CHCl_3$)	345 (4.55)	390 (4.59)	557 (5.19)	637 (4.43)	705 (4.18)	786 (3.71)
10c (dication) (1% TFA−$CHCl_3$)	362 (4.66)	534 (4.76)	573 (5.45)		696 (4.51)	770 (4.41)
10d ($CHCl_3$)	345 (4.59)	390 (4.63)	557 (5.32)	638 (4.44)	706 (4.20)	791 (3.54)
10d (dication) (1% TFA−$CHCl_3$)	368 (4.70)	535 (4.84)	574 (5.58)		699 (4.53)	771 (4.47)
10e ($CHCl_3$)	348 (4.61)	389 (4.60)	558 (5.21)	638 (4.40)	707 (4.24)	800 (v weak)
10e (dication) (1% TFA−$CHCl_3$)	376 (4.66)	535 (4.76)	576 (5.45)		699 (4.50)	770 (4.50)
10f ($CHCl_3$)	352 (4.520	399 4.59)	560 (5.13)	641 (4.35)	709 (4.23)	790 (3.93)
10f (dication) (1% TFA−$CHCl_3$)	368 (4.57)	534 (4.73)	573 (5.330	648 (4.44)	711 (4.38)	787 (4.56)
10g ($CHCl_3$)	348 (4.56)		570 (5.17)	651 (4.43)	719 (4.24)	800 (v weak)
10g (dication) (1% TFA−$CHCl_3$)	391 (4.57)	547 (4.76)	588 (5.43)	708 (4.57)	779 (4.20)	896 (4.050
20 ($CHCl_3$)	379 (4.620	417 (4.61)	604 (5.34)	698 (4.28)	776 (4.36)	889 (3.86)
20 (dication) (1% TFA−$CHCl_3$)	388 (4.660		629 (5.50)		778 (4.29)	872 (4.71)

Scheme 3



600 nm, suggesting that still larger bathochromic shifts can be accomplished for this series (see below).

The 400 MHz proton NMR spectrum of **10a** in $CDCl_3$ at 40 °C showed a broad resonance for the internal NH at −0.5 ppm. The acenaphthylene protons closest to the porphyrin nucleus were relatively shielded to 5.7 ppm due to the proximity of the *meso*-phenyl substituent. On the other hand, the ortho protons for the phenyl units produced a downfield doublet at 8.8 ppm due to deshielding from the surrounding π-system. The spectrum showed only six types of aromatic protons, three each for the acenaphthylene and phenyl moieties, indicating that NH tautomerization is rapid at 40 °C (Figure 2). However, at 20 °C the resonances were somewhat broadened, and at 0 °C two sets of signals resolved (Figure 2). As the porphyrin must take on a highly nonplanar conformation, most likely a deep saddle-type distortion, several dynamic processes must be considered to explain these data: (1) NH tautomerization; (2) saddle to saddle inversion; (3) phenyl rotation. Initially, we suggested that the NMR data were consistent with a coincidental slowing of the NH tautomerization and saddle to saddle inversion.[27] However, a reassessment of these results with further data available from the metal chelates has led to the conclusion that this may be due to a slowing of the NH tautomerization alone. In a deep saddle conformation, the barrier to inversion is high and the phenyl substituents are held in an environment that will not allow free rotation. This geometry can nevertheless take on pseudo-symmetry when NH tautomerization is rapid; only when this is slowed will the frozen conformation distinguish between the chemical environments for the various sets of aromatic protons. To gain further insight into the dynamics for this system, the *meso*-tetrakis(3-methylphenyl)porphyrin **10k** was synthesized by reacting 3-tolualdehyde with acenaphthopyrrole **13** (49%). This porphyrin gave a more complex 400 MHz proton NMR spectrum with two singlets for the methyl substituents,[35] implying that the aryl substituent could not undergo free rotation. The barrier must be quite substantial, as these peaks do not coalesce at 100 °C in toluene-d_8. Saddle to saddle inversion would also result in coalescence, again suggesting that the conformation is fixed. At lower temperatures (<0 °C) further resolution is observed as the NH tautomerization is slowed.

In the presence of TFA, the dication **10a**H_2^{2+} gave a well-resolved proton NMR spectrum where the shielded acenaphthylene protons appeared at 6.1 ppm while the ortho protons of the phenyl substituents were further deshielded to approximately 9.0 ppm (Figure 3). Unlike the free base, the symmetry observed for this spectrum was not effected by temperature, and this lends additional support to the view that this is a "frozen" saddle-shaped structure. The carbon-13 NMR spectrum for **10a** in TFA−$CDCl_3$ shows the presence of 13 aromatic carbon resonances in accord with expectations for this highly symmetrical structure. Further evidence for the structure

(35) A number of atropisomers are possible for this structure and further resolution of these signals may be possible. The two singlets presumably correspond to two types of local environments.

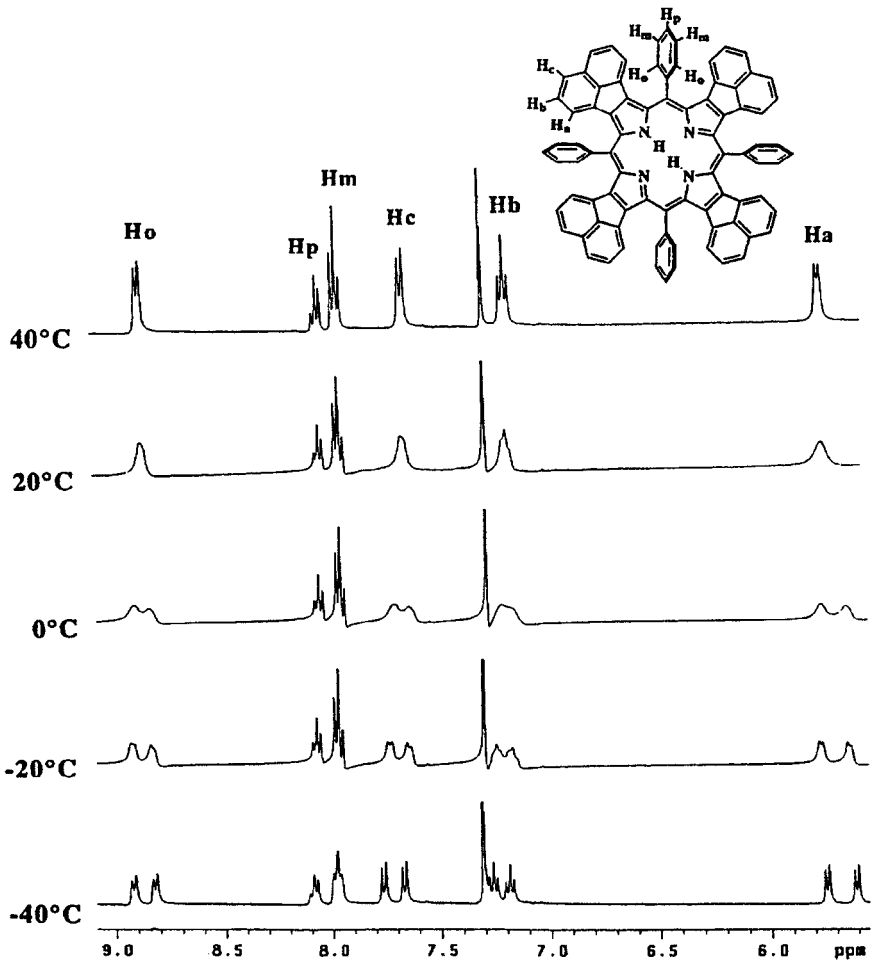


Figure 2. Variable-temperature 400 MHz proton NMR spectra of tetraacenaphthoporphyrin **10a** at +40, +20, 0, −20, and −40 °C. The acenaphthylene protons and the *o*-phenyl protons resolve into two sets of peaks at lower temperatures. This is attributed to a slowing of NH tautomerization.

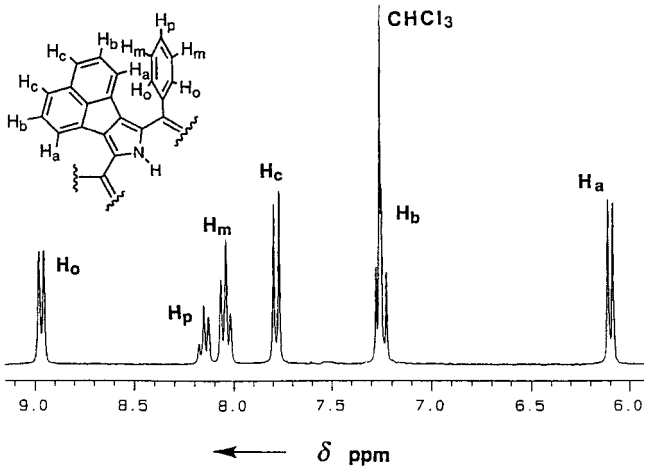


Figure 3. 400 MHz proton NMR spectum of the tetraacenaphthoporphyrin dication **10a**H_2^{2+} in TFA−$CDCl_3$.

comes from FAB MS which gave the expected [M + H] peak at *m*/*z* 1111. Porphyrins **10b**−**g** gave comparable spectroscopic data, although a satisfactory mass spectrum for **10g** could only be obtained by FD MS.

Metal Complexes

Reaction of tetraphenylporphyrin **10a** with nickel(II), copper(II), and zinc acetates gave the related metal chelates **19a**−**c** in excellent yields (Scheme 3). These were isolated as green powders and gave strong Soret bands at 528, 545, and 558 nm, respectively (Figure 4). This red shift for metal(II) porphyrins across the periodic table (Ni−Cu−Zn) is well recognized for metalloporphyrins.[11] Less typical were the changes for the longer wavelength bands: two bands are noted between 600 and 700 nm for the nickel(II) complex, whereas one predominates for the copper chelate, and this region shows only one band for the zinc porphyrin **19c**. The structures were confirmed by mass spectrometry (the zinc complex demetalated in FAB MS, but the correct molecular ion was observed by FD MS) and for the diamagnetic species **19a** and **19c** also by proton NMR spectroscopy. Metalloporphyrins **19a** and **19c** showed three types of acenaphthylene and three types of phenyl protons, and these chelates showed no indication of additional peaks even at −80 °C. These data are again consistent with a fixed saddle-shaped conformation.

Lead chelates of porphyrins are known to induce further shifts to the electronic absorptions for metalloporphyrins ("hyper" spectral shifts").[7,36,37] For instance,

(36) Albers, V. M.; Knorr, H. *J. Chem. Phys.* **1941**, *9*, 497. Schaffer, A. M.; Gouterman, M. *Theor. Chim. Acta* **1970**, *18*, 1. See also: Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3, Chapter 1.

(37) Barkigia, K. M.; Fajer, J.; Adler, A. D.; Williams, G. J. B. *Inorg. Chem.* **1980**, *19*, 2057.

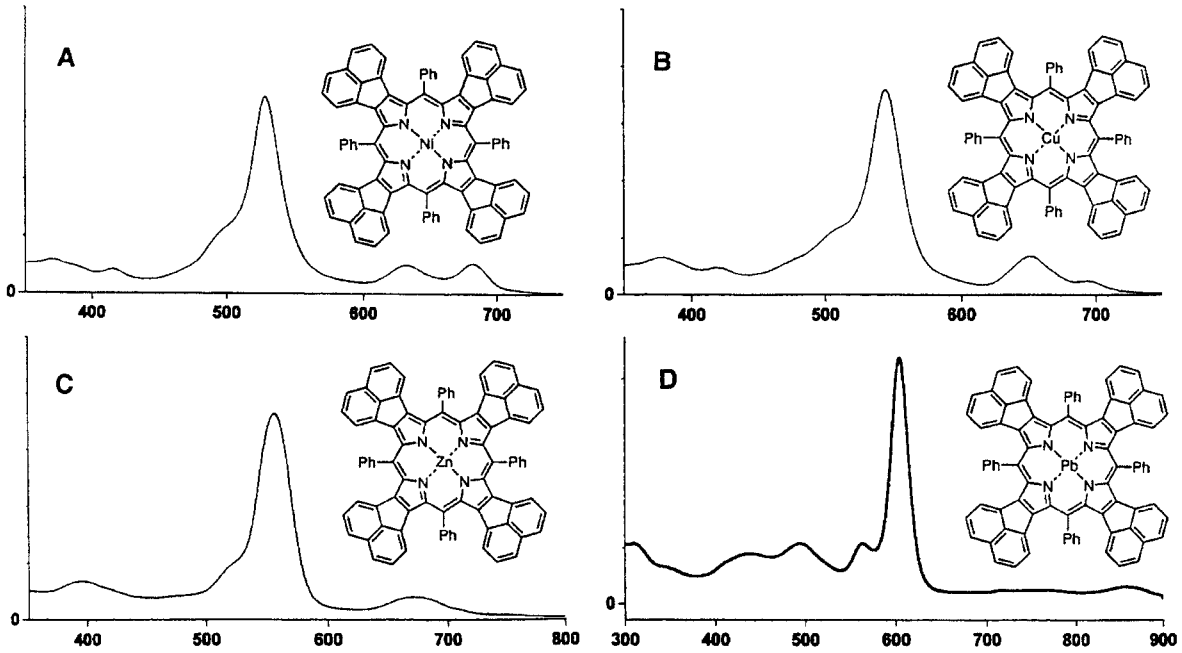
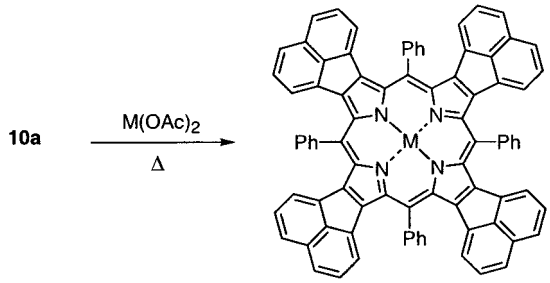


Figure 4. UV−vis spectra of tetraacenaphthoporphyrin metal chelates **19** in chloroform: (A) nickel(II) complex; (B) copper(II) complex; (C) Zinc complex; (D) lead(II) complex.

solutions of the lead(II) complex of octaethylporphyrin in benzene afford a Soret band at 462 nm, a shift of 62 nm compared to the parent free base porphyrin in the same solvent.[11] Clearly, it was of some interest to see whether this effect would further exaggerate the influence of the acenaphthylene rings. The lead(II) complex **19d** was prepared by reacting **10a** with lead(II) acetate in refluxing pyridine−chloroform. This compound proved to demetalate in chloroform solutions and was best isolated by precipitation from the reaction mixture. The electronic spectrum of **19d** in DMSO showed the expected bathochromic shifts with the Soret band for the first time crossing 600 nm (Figure 4). This remarkable spectrum is still very much like those obtained for typical porphyrins but with the bands red shifted by 200 nm. The proton NMR spectrum of lead chelate **19d** showed a doubling up of many of the resonances, suggesting that it takes on a somewhat different conformation than **19a**−**c**, something that is also true for lead(II) 5,10,15,20-tetrapropylporphyrin, which takes on a folded or "roof" shaped geometry.[37]

Bathochromic Shifts Due to Phenylethynyl Substituents. The presence of *meso*-ethynyl substituents on the porphyrin nucleus is also known to induce significant bathochromic shifts,[5−7] and we sought to find out whether this factor would also add on to the "acenaphthylene effect". Condensation of phenylpropargaldehyde with **13** in the presence of boron trifluoride etherate gave low yields of the desired porphyrin (Scheme 4); at lower reaction temperatures[7] (−35 °C) small improvements were noted, but the tetrakis(phenylethynyl)porphyrin **20** was still only isolated in 3% yield. This was obtained as an intense blue fraction from column chromatography and crystallized as a dark brown solid. The UV−vis spectrum of **20** in chloroform showed that the phenylethynyl substituents had further shifted the Soret band to 604 nm (Figure 5), while the dication in 1% TFA−chloroform produced an intense Soret absorption at 629 nm. The Soret band for *meso*-tetrakis(phenylethynyl)-porphyrin **21a** has been reported at 463 nm for the free

Scheme 4



base and 485 nm for the related dication,[6] while the related para-substituted arylethynylporphyrins **21b** and **21c** afford this band at 466 and 468 nm, respectively.[6,7] The *p*-alkoxy substituents of **21d** slightly enhance the effect, affording a Soret band at 472 nm for the free base and 496 for the related dication.[6] In every case, the bathochromic shift due to the four arylethynyl units is >40 nm.[5−7]

A series of metal complexes were prepared by reacting **20** with metal(II) acetates as described above. The nickel(II) and copper(II) chelates **22a** and **22b** gave spectra with broadened Soret absorptions at 600 nm (Figure 5). However, the zinc complex **22c** afforded a far narrower and more intense Soret band at 614 nm. The structure of porphyrin **20** was confirmed by proton and carbon-13 NMR spectroscopy and mass spectrometry. The NMR data were in accord with a highly symmetrical species; for instance, the carbon-13 spectrum in TFA−$CDCl_3$ showed 15 resonances for the 92 carbon atoms in this structure. In the proton NMR spectra, the upfield acenaphthylene doublet observed for the tetraaryltetraacenaphthoporphyrins **10a**−**g** (Figures 2 and 3), both for the free base and diprotonated structures, was not present for **20**. Instead, a downfield doublet was present

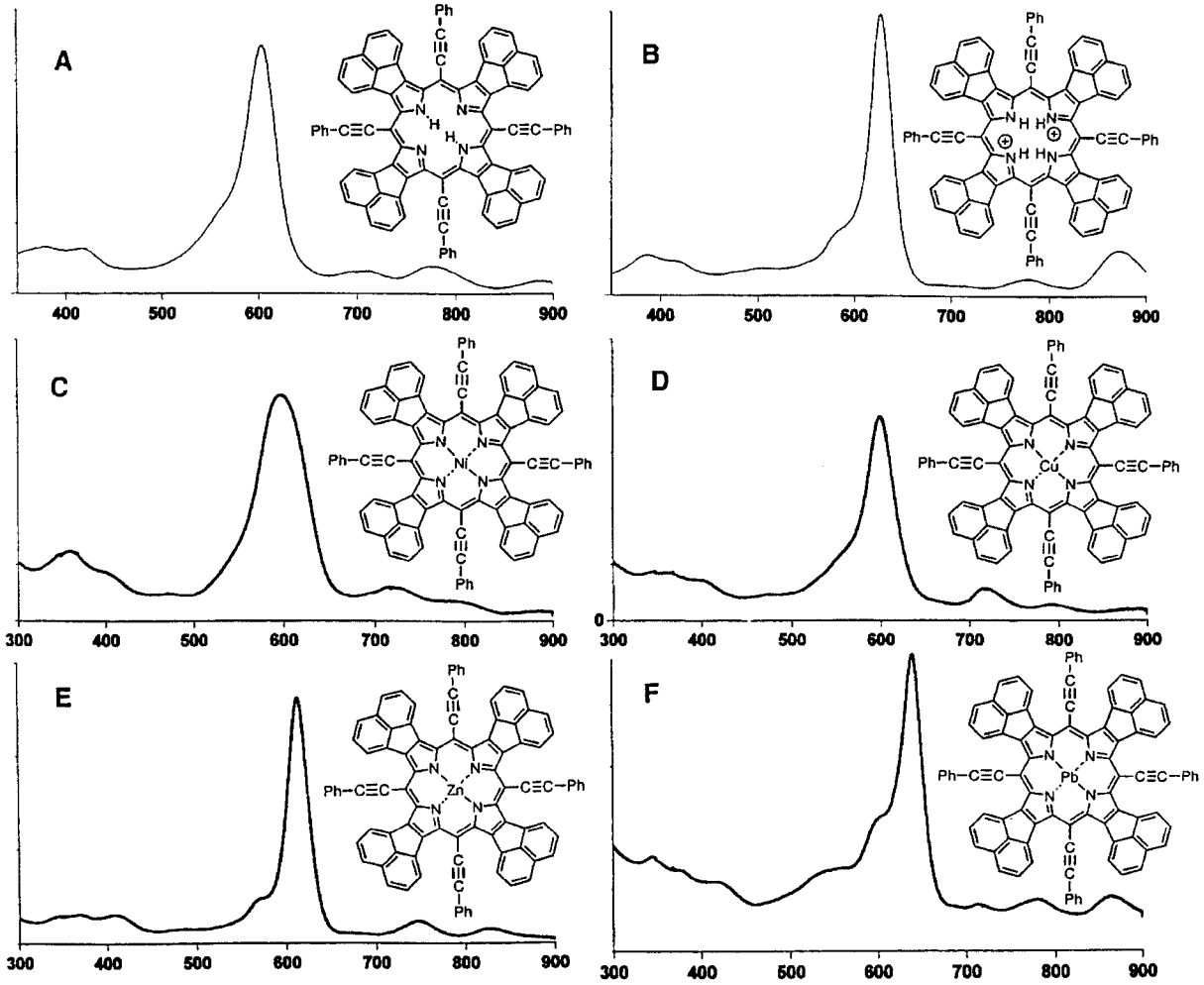


Figure 5. UV−vis spectra of tetrakis(phenylethynyl)porphyrin **20** and its metal chelates **21a**−**d** in chloroform: (A) free base in chloroform; (B) dication in 5% TFA−chloroform; (C) nickel(II) complex **22a** in chloroform; (D) copper(II) complex **22b** in chloroform; (E) zinc complex **22c** in chloroform; (F) lead(II) complex **22d** in chloroform. Lead chelate **22d** shows the longest wavelength Soret band ever observed for a nonexpanded metalloporphyrin.

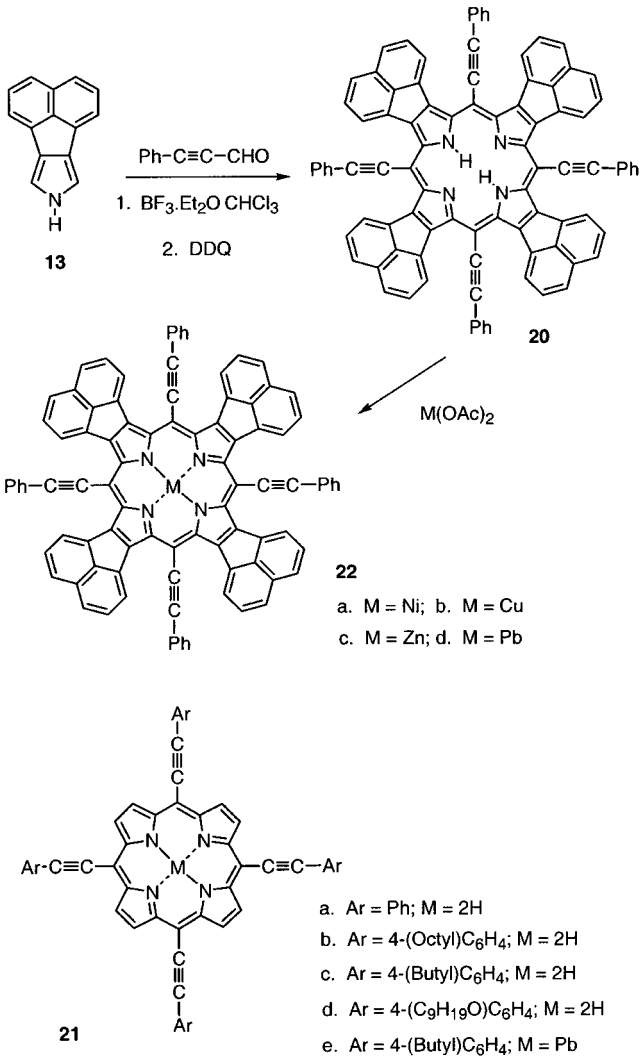
at 9.2 ppm for the free base in $CDCl_3$, while the related dication in TFA−$CDCl_3$ gave a similar resonance at approximately the same value. These data demonstrate that the acenaphthylene protons are deshielded by the nearby phenylethynyl substituents, as would be expected for this structure.

The lead chelate **21e** of *meso*-tetrakis(arylethynyl)-porphyrin **21c** has been reported[7] to give a Soret absorption at 509 nm, a "hyper" shift of 41 nm compared to the parent porphyrin, demonstrating that the influence due to the coordinated lead(II) adds on to the bathochromic shifts from the arylethynyl substituents. It remained to be seen whether these combined effects would further add on to those due to the four fused acenaphthylene moieties. With this in mind, lead(II) chelate **22d** was synthesized by reacting **20** with $Pb(OAc)_2$ in pyridine−chloroform. This compound proved to be far more stable than the analogous tetraphenyl species **19d** and showed the largest bathochromic shifts so far observed in these investigations. In chloroform, this complex gave a Soret band at 642 nm, while a series or smaller bands extended to 862 nm (Figure 5). For the time being, this complex holds the record for the longest wavelenth Soret band of any nonexpanded porphyrin structure.

Conclusions

Acenaphthylene has a remarkably large effect on the porphyrin chromophore compared to any other ring systems, including naphthalene, anthracene, and phenanthrene, and also has the advantage of being sufficiently compact to tolerate the presence of meso substituents. While linearly annealed naphthalene and anthracene units greatly affect the Q-band absorptions, the Soret band is only slightly altered by this type of ring fusion. Fused acenaphthylene produces major bathochromic shifts to the Soret absorption that are essentially additive with other factors. Structures with one, two, or four acenaphthylene rings show increasingly large effects, and shifts due to steric crowding and the presence of *meso*-phenylethynyl substituents further increase these values. The "hyper" spectral shifts due to lead chelation also adds on to these factors and in the lead(II) chelate **22d** of tetrakis(phenylethynyl)tetraacenaphthoporphyrin **20** produces the longest wavelength value yet observed for the Soret band at 642 nm. In fact, prior to our work no examples of "nonexpanded" porphyrins with Soret absorptions above 520 nm had been reported in the literature. While the lead chelates are not compatible with medicinal applications, the results indicate that the Soret band can be "tuned" to virtually any part of the visible

Scheme 5



spectrum. In addition, there is no reason to assume that the limit has been reached for these bathochromic shifts and it may be possible to push the Soret band from its historical starting point in the near-ultraviolet[38] into the far red beyond 700 nm.

Experimental Section

5,10,15,20-Tetraphenyltetraacenaphtho[1,2-*b*:1′,2′-*g*:1″,2″-*l*:1‴,2‴-*q*]porphyrin (10a). Benzaldehyde (29.5 μL, 0.29 mmol) was added to a stirred solution of acenaphtho[1,2-*c*]pyrrole (55 mg, 0.29 mmol) in chloroform (30 mL), and the resulting solution was purged with nitrogen for 10 min. Boron trifluoride etherate (7.1 μL, 0.058 mmol) was then added and the reaction stirred for 2 h in the dark. DDQ (49 mg, 0.22 mmol) was added and the solution stirred an additional 1 h. One drop of Et_3N was then added, and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with 1% Et_3N−$CHCl_3$, and the product was collected as a dark violet fraction. Recrystallization from chloroform/methanol afforded the tetraphenyltetraacenaphthoporphyrin (45 mg; 56%) as dark green crystals, mp > 300 °C. UV−vis (DMSO): λ_{max} (log ϵ) 347 (4.07), 402 (4.13), 558 (4.59), 629 (3.97), 708 (3.76). ^{1}H NMR ($CDCl_3$): δ −0.5 (2H, br s), 5.74 (8H, d, J = 7.0 Hz), 7.17 (8H, t, J = 7.5 Hz), 7.63 (8H, d, J = 8.0 Hz), 7.93 (8H, t, J = 7.5 Hz), 8.03 (4H, t, J = 7.5 Hz), 8.84 (8H, d, J = 7.0 Hz). ^{1}H NMR (TFA-$CDCl_3$): δ 6.10 (8H, d, J = 6.7 Hz), 7.27 (8H, t, J = 7.3 Hz), 7.79 (8H, d, J = 8.5 Hz), 8.06 (8H, t, J = 7.3 Hz), 8.16 (4H, t, J = 7.3 Hz), 9.01 (8H, d, J = 7.3 Hz). ^{13}C NMR (TFA−$CDCl_3$): δ 120.9, 126.5, 127.9, 129.7 (2), 130.6, 130.7, 131.7, 135.6, 138.0, 139.4, 139.6, 141.4. HRMS (FAB): calcd for $C_{84}H_{46}N_4$ + H m/z 1111.3801, found 1111.3811. **General Procedure for the Synthesis of Metal Chelates.** To a stirred solution of TATPP (10 mg) in chloroform (10 mL) was added a saturated solution of the metal(II) acetate in methanol (3 mL) and the solution refluxed for 1 h. The solution was cooled, diluted with chloroform, washed with water, and evaporated in vacuo. The residue was purified by chromatography on alumina (CH_2Cl_2 to $CHCl_3$) and recrystallized from chloroform−methanol to afford the pure metal complex. **Ni(II) Complex 19a.** TATPP (10 mg) and nickel(II) acetate afforded the complex as a green powder (10 mg; 95%). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 371 (4.51), 416 (4.37), 528 (5.26), 632 (4.43), 682 (4.45). ^{1}H NMR ($CDCl_3$): δ 5.68 (8H, d, J = 7.0 Hz), 7.18 (8H, t, J = 7.5 Hz), 7.65 (8H, d, J = 8.0 Hz), 7.88 (8H, t, J = 7.5 Hz), 7.99 (4H, t, J = 7.0 Hz), 8.58 (8H, d, J = 7.0 Hz). HRMS (FAB): calcd for $C_{84}H_{44}N_4Ni$ + H m/z 1167.2998, found 1167.2996. **Cu(II) Complex 19b.** TATPP (10 mg) and copper(II) acetate afforded the complex as a green powder (10 mg; 95%). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 377 (4.57), 420 (4.44), 545 (5.30), 650 (4.57), 694 (4.13). HRMS (FAB): calcd for $C_{84}H_{44}N_4Cu$ + H m/z 1172.2940, found 1172.2938. **Zn(II) Complex 19c.** TATPP (11 mg) and zinc acetate afforded the complex as a green powder (10 mg; 86%). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 343 (4.50), 396 (4.62), 558 (5.35), 672 (4.39). ^{1}H NMR (CD_2Cl_2): δ 5.64 (8H, d, J = 7.0 Hz), 7.19 (8H, t, J = 7.5 Hz), 7.65 (8H, d, J = 8.0 Hz), 7.97 (8H, t, J = 7.5 Hz), 8.08 (4H, t, J = 7.5 Hz), 8.76 (8H, d, J = 7.0 Hz). FD MS: m/z 1174 (M^+). **Pb(II) Complex 19d.** A saturated solution of lead(II) acetate in pyridine was added to a solution of TATPP (10 mg) in chloroform (5 mg) and the resulting mixture stirred under reflux for 7 h. The solution was poured into cold methanol and the resulting precipitate filtered off and dried in vacuo to give the lead(II) chelate (7 mg; 59%) as a dark purple powder. UV−vis (DMSO): λ_{max} (log ϵ) 311 (4.62), 437 (4.58), 494 (4.65), 564 (4.65), 604 (5.25), 717 (3.93), 760 (3.97), 853 (4.03). ^{1}H NMR (C_6D_6): δ 5.82 (4H, d, J = 7.5 Hz), 6.04 (4H, d, J = 7.0 Hz), 7.15−7.25 (8H, m), 7.42 (4H, d, J = 8.4 Hz), 7.48 (4H, d, J = 8.0 Hz), 7.57 (4H, t, J = 7.3 Hz), 7.6−7.69 (8H, m), 8.70 (4H, d, J = 7.5 Hz), 8.95 (4H, d, J = 7.5 Hz). FAB MS: m/z 1316.5 (M^+).

5,10,15,20-Tetrakis(4-methylphenyl)tetraacenaphtho[1,2-*b*:1′,2′-*g*:1″,2″-*l*:1‴,2‴-*q*]porphyrin (10b). Compound **10b** was prepared from the previous procedure from *p*-tolualdehyde (24.7 μL, 0.21 mmol), acenaphtho[1,2-*c*]pyrrole (40 mg, 0.21 mmol), BF_3·Et_2O (5.2 μL, 0.042 mmol), and DDQ (36 mg, 0.16 mmol) in chloroform (21 mL). Chromatography on silica, eluting with Et_3N−methanol−chloroform (1:2:97), afforded blue and purple prefractions followed by a major purple fraction corresponding to **10b**. Recrystallization from chloroform−methanol afforded the title tetraacenaphthoporphyrin (21 mg; 34%) as dark green crystals, mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ −0.5 (2H, br s), 2.84 (12H, s), 5.80 (8H, br d), 7.17 (8H, t, J = 8.1 Hz), 7.63 (8H, d, J = 7.5 Hz), 7.75 (8H, d, J = 7.5 Hz), 8.68 (8H, d, J = 7.2 Hz). ^{1}H NMR (TFA−$CDCl_3$): δ 2.89 (12H, s), 6.160 (8H, d, J = 6.7 Hz), 7.27 (8H, t, J = 7.3 Hz), 7.79 (8H, d, J = 7.9 Hz), 7.86 (8H, d, J = 7.9 Hz), 8.83 (8H, d, J = 7.9 Hz). ^{13}C NMR (TFA−$CDCl_3$): δ 21.9, 120.8, 126.5, 127.8, 129.6, 129.7, 130.7, 131.3, 135.6, 136.9, 137.7, 139.6, 141.4, 142.7. HRMS (FAB): calcd for $C_{88}H_{54}N_4$ + H m/z 1167.4427, found 1167.4424.

5,10,15,20-Tetrakis(4-chlorophenyl)tetraacenaphtho[1,2-*b*:1′,2′-*g*:1″,2″-*l*:1‴,2‴-*q*]porphyrin (10c). Compound **10c** was prepared as described above from *p*-chlorobenzaldehyde (25 mg, 0.18 mmol), acenaphtho[1,2-*c*]pyrrole (35 mg, 0.18 mmol), BF_3·Et_2O (4.4 μL, 0.036 mmol), and DDQ (31 mg, 0.14 mmol) in $CHCl_3$ (18 mL). Column chromatography on silica gel, eluting with Et_3N−methanol−chloroform (1:2:97), followed by recrystallization from chloroform−methanol afforded the tetraacenaphthoporphyrin derivative **10c** (38 mg; 66%) as dark brown crystals, mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ −0.5 (2H,

(38) Soret, J. L. *Comput. Rend.* **1883**, *97*, 1267.

br s), 5.88 (8H, d, J = 6.3 Hz), 7.27 (8H, t), 7.69 (8H, d, J = 8.1 Hz), 7.94 (8H, d, J = 8.4 Hz), 8.76 (8H, d, J = 8.4 Hz). ^{1}H NMR (TFA−$CDCl_3$): δ 6.25 (8H, d, J = 7.3 Hz), 7.36 (8H, t, J = 7.9 Hz), 7.84 (8H, d, J = 7.9 Hz), 8.04 (8H, d, J = 8.5 Hz), 8.60 (8H, d, J = 8.5 Hz). ^{13}C NMR (TFA−$CDCl_3$): δ 119.7, 126.2, 128.1, 129.9 (2), 130.6, 130.9, 135.6, 137.6, 138.9, 139.0, 139.7, 141.0. HRMS (FAB): calcd for $C_{84}H_{42}Cl_4N_4$ + H m/z 1247.2242, found 1247.2237.

5,10,15,20-Tetrakis(4-bromophenyl)tetraacenaphtho-[1,2-*b*:1′,2′-*g*:1″,2″-*l*:1‴,2‴-*q*]porphyrin (10d). Compound **10d** was prepared as described previously from 4-bromobenzaldehyde (37 mg, 0.20 mmol), acenaphtho[1,2-*c*]pyrrole (38 mg, 0.20 mmol), BF_3·Et_2O (4.9 μL, 0.040 mmol), and DDQ (34 mg, 0.15 mmol). Column chromatography on silica gel, eluting with Et_3N−methanol−chloroform (1:2:97), followed by recrystallization from chloroform−methanol afforded the porphyrin (25 mg; 35%) as dark brown crystals, mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ −0.5 (2H, br s), 5.88 (8H, d, J = 6.6 Hz), 7.28 (8H, t, J = 7.8 Hz), 7.70 (8H, d, J = 8.1 Hz), 8.10 (8H, d, J = 8.1 Hz), 8.69 (8H, d, J = 8.1 Hz); ^{1}H NMR (TFA-$CDCl_3$): δ 6.25 (8H, d, J = 7.0 Hz), 7.37 (8H, t, J = 8.0 Hz), 7.84 (8H, d, J = 8.4 Hz), 8.20 (8H, d, J = 8.4 Hz), 8.85 (8H, d, J = 8.4 Hz). ^{13}C NMR (TFA-$CDCl_3$): δ 119.8, 126.2, 127.4, 128.1, 129.9, 130.0, 130.4, 133.9, 135.6, 137.8, 139.1, 139.4, 141.2. HRMS (FAB): calcd for $C_{84}H_{42}Br_4N_4$ + H m/z 1423.0221, found 1423.0228.

5,10,15,20-Tetrakis(4-iodophenyl)tetraacenaphtho[1,2-*b*:1′,2′-*g*:1″,2″-*l*:1‴,2‴-*q*]porphyrin (10e). Compound **10e** was prepared as described previously from 4-iodobenzaldehyde (42.5 mg, 0.18 mmol), acenaphtho[1,2-*c*]pyrrole (35 mg, 0.18 mmol), BF_3·Et_2O (4.4 μL, 0.036 mmol), and DDQ (30.6 mg, 0.135 mmol). Column chromatography on silica gel, eluting with Et_3N−methanol−chloroform (1:2:97), followed by recrystallization from chloroform−methanol, afforded the porphyrin (23 mg; 32%) as dark brown crystals, mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ −0.6 (2H, br s), 5.86 (8H, d, J = 6.6 Hz), 7.28 (8H, t, J = 7.8 Hz), 7.70 (8H, d, J = 7.8 Hz), 8.28 (8H, d, J = 8.1 Hz), 8.54 (8H, d, J = 7.8 Hz); ^{1}H NMR (TFA-$CDCl_3$): δ 6.24 (8H, d, J = 7.3 Hz), 7.36 (8H, t, J = 7.3 Hz), 7.84 (8H, d, J = 7.9 Hz), 8.42 (8H, d, J = 8.5 Hz), 8.69 (8H, d, J = 7.9 Hz). ^{13}C NMR (TFA−$CDCl_3$): δ 99.2, 120.1, 126.4, 128.1, 129.9, 130.1, 130.5, 135.6, 138.4, 139.2, 139.3, 140.0, 141.3. HRMS (FAB): calcd for $C_{84}H_{42}I_4N_4$ + H m/z 1614.9667, found 1614.9667.

5,10,15,20-Tetrakis(4-methoxyphenyl)tetraacenaphtho-[1,2-*b*:1′,2′-*g*:1″,2″-*l*:1‴,2‴-*q*]porphyrin (10f). Compound **10f** was prepared as descibed previously from 4-methoxybenzaldehyde (25 mg, 0.18 mmol), acenaphtho[1,2-*c*]pyrrole (35 mg, 0.18 mmol), BF_3·Et_2O (4.5 μL, 0.037 mmol), and DDQ (31 mg, 0.14 mmol). Chromatography on silica, eluting first with $CHCl_3$ and then 1% Et_3N−$CHCl_3$, afforded a purple prefraction followed by a deep violet product fraction. Recrystallization from chloroform−methanol afforded the porphyrin (18 mg; 32%) as dark green crystals, mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ −0.5 (2H, br s), 4.17 (12H, s), 5.87 (8H, br d), 7.22 (8H, t, J = 7.5 Hz), 7.47 (8H, d, J = 9.0 Hz), 7.64 (8H, d, J = 8.1 Hz), 8.70 (8H, d, J = 8.4 Hz). ^{1}H NMR (TFA−$CDCl_3$): δ 4.21 (12H, s), 6.24 (8H, d, J = 7.3 Hz), 7.31 (8H, t, J = 7.3 Hz), 7.56 (8H, d, J = 8.6 Hz), 7.79 (8H, d, J = 8.6 Hz), 8.85 (8H, d, J = 7.9 Hz). ^{13}C NMR (TFA−$CDCl_3$): δ 56.2, 116.2, 120.2, 126.3, 127.9, 129.4, 129.8, 130.5, 130.8, 133.0, 135.7, 139.3, 140.1, 141.1. HRMS (FAB): calcd for $C_{88}H_{54}N_4O_4$ + H m/z 1231.4223, found 1231.4228.

5,10,15,20-Tetrakis(4-nitrophenyl)tetraacenaphtho-[1,2-*b*:1′,2′-*g*:1″,2″-*l*:1‴,2‴-*q*]porphyrin (10g). Compound **10g** was prepared as descibed previously from 4-nitrobenzaldehyde (32 mg, 0.21 mmol), acenaphtho[1,2-*c*]pyrrole (40 mg, 0.21 mmol), BF_3·Et_2O (5.2 μL, 0.042 mmol), and DDQ (36 mg, 0.157 mmol). Chromatography on silica with Et_3N−MeOH−$CHCl_3$ (1:2:97) afforded a dirty purple fraction that proved to be highly impure by proton NMR spectroscopy. This material was rechromatographed on silica, initially using chloroform until a brown fraction had been collected, and then with 1% triethylamine−chloroform. The product eluted as a purple fraction. Recrystallization from chloroform−methanol afforded the porphyrin (5 mg; 7%) as dark brown crystals, mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ −0.3 (2H, br s), 5.80 (8H, d, J = 6.6 Hz), 7.18 (8H, t, J = 7.6 Hz), 7.70 (8H, d, J = 8.1 Hz), 8.81 (8H, d, J = 8.4 Hz), 9.09 (8H, d, J = 8.7 Hz); ^{1}H NMR (TFA−$CDCl_3$): δ 6.21 (8H, d, J = 7.3 Hz), 7.31 (8H, t, J = 7.9 Hz), 7.86 (8H, d, J = 8.6 Hz), 8.90 (8H, d, J = 8.5 Hz), 9.27 (8H, d, J = 8.6 Hz). ^{13}C NMR (TFA−$CDCl_3$): δ 119.3, 125.4, 126.1, 128.3, 129.9, 130.1, 130.9, 135.6, 138.6, 139.0, 141.4, 143.0, 149.7. FD MS: m/z 1291.5 ([M + H]$^+$).

5,10,15,20-Tetrakis(phenylethynyl)tetraacenaphtho-[1,2-*b*:1′,2′-*g*:1″,2″-*l*:1‴,2‴-*q*]porphyrin (20). Phenylpropargylaldehyde (176 μL, 1.44 mmol) was added to a stirred solution of acenaphtho[1,2-*c*]pyrrole (275 mg, 1.44 mmol) in chloroform (145 mL), and the resulting solution was cooled to −35 °C and purged with nitrogen. Boron trifluoride etherate (53 μL, 0.432 mmol) was then added and the reaction mixture stirred for 12 h in the dark while it slowly warmed to room temperature. DDQ (245 mg, 1.08 mmol) was added and the solution stirred for an additional 1 h. Two drops of triethylamine were added and the solvents removed in vacuo. The residue was purified by column chromatography first on grade 3 alumina, eluting first with CH_2Cl_2 and then 1% Et_3N−CH_2Cl_2, and then silica eluting with dichloromethane with 0.1−3.0% Et_3N. Following a green forerun, the product was collected as a dark blue fraction. Following evaporation of the solvents under reduced pressure, the residue was recrystallized from chloroform/methanol to afford the tetrakis(phenylethynyl)porphyrin (12 mg; 2.8%) as a brown solid, mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ 7.62−7.65 (20H, m), 7.91 (8H, m), 7.98 (8H, d, J = 8.0 Hz), 9.27 (8H, d, J = 7.0 Hz). ^{1}H NMR (TFA−$CDCl_3$): δ 7.67−7.71 (20H, m), 7.95 (8H, m), 8.12 (8H, d, J = 7.9 Hz), 9.16 (8H, d, J = 7.3 Hz). ^{1}H NMR (CD_2Cl_2): δ 7.54 (8H, t, J = 7.3 Hz), 7.59 (12H, m), 7.82 (8H, m), 7.87 (8H, d, J = 7.3 Hz), 9.23 (8H, d, J = 6.7 Hz). ^{1}H NMR (TFA−CD_2Cl_2): δ 7.71−7.75 (20H, m), 7.97 (8H, m), 8.19 (8H, d, J = 8.5 Hz), 9.20 (8H, d, J = 7.3 Hz). ^{13}C NMR (TFA−$CDCl_3$): δ 92.3, 102.1, 107.1, 122.6, 128.0, 128.3, 129.2, 130.3, 130.6 (2), 130.8, 134.0, 136.1, 139.5, 139.8. HRMS (FAB): calcd for $C_{92}H_{46}N_4$ + H m/z 1207.3801, found 1207.3797. **Ni(II) Complex 22a.** UV−vis ($CHCl_3$): λ_{max} (log ϵ) 360 (4.58), 463 (4.17), 600 (5.08), 717 (4.19), 721 (4.14). FD MS: m/z 1264.4 (M$^+$). **Cu(II) Complex 22b.** UV−vis ($CHCl_3$): λ_{max} (log ϵ) 363 (4.36), 394 (4.29), 471 (4.08), 600 (4.99), 717 (4.12), 792 (3.83). FD MS: m/z 1268.7 (M$^+$). MALDI MS: m/z 1266.29 (M$^+$). **Zn Complex 22c.** UV−vis ($CHCl_3$): λ_{max} (log ϵ) 363 (4.58), 408 (4.57), 491 (4.25), 614 (5.50), 747 (4.41), 826 (4.20); HRMS (FAB): calcd for $C_{92}H_{44}N_4$-Zn + H m/z 1270.3014, found 1270.2993. **Pb(II) Complex 22d.** ^{1}H NMR (C_5D_5N): δ 7.6 (4H, obscured by solvent), 7.73 (8H, t, J = 7.5 Hz), 7.98 (8H, t, J = 7.5 Hz), 8.19 (8H, d, J = 7.8 Hz), 8.23 (8H, d, J = 7.8 Hz), 10.15 (8H, d, J = 6.8 Hz). UV−vis ($CHCl_3$): λ_{max} (log ϵ) 347 (4.56), 368 (4.51), 416 (4.44), 642 (5.22), 711 (4.27), 780 (4.36), 862 (4.35). FD MS: m/z 1412.3 (M$^+$).

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Supporting Information Available: Copies of UV−vis spectra for porphyrins **10a**−**g** and ^{1}H and selected ^{13}C NMR spectra for compounds **10a**−**g**, **19a**,**d**, **20**, and **22d** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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