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Porphyrin on a Half-Shell! Synthesis and Characterization of Corannulenoporphyrins†

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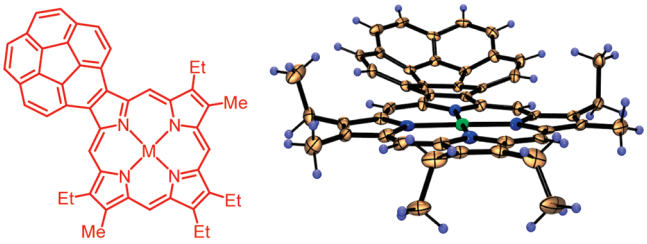

An efficient synthetic method for preparing corannulenoporphyrins is described. Nitrocorannulene was reacted with ethyl isocyanoacetate in the presence of a phosphazene base to generate the pivotal corannulenopyrrole intermediate. Following cleavage of the ethyl ester moiety with KOH in ethylene glycol at 180−190 °C, the heptacyclic system was reacted with acetoxymethylpyrroles under mildly acidic conditions to afford tripyrranes. The proton NMR spectra for these tripyrrolic intermediates suggest that they can take on helical geometries, but the conformations are dependent on the nature of the terminal ester groupings and may be altered by solvent interactions. Treatment of a di-*tert*-butyl ester tripyrrane with TFA cleaved the protective groups, and subsequent condensation with diformylpyrroles in TFA-CH_2Cl_2, followed by oxidation with DDQ or ferric chloride, gave excellent yields of corannulenoporphyrins. Nickel(II), copper(II), and zinc complexes of this system were also prepared, and the nickel derivative was also further characterized by X-ray crystallography. The same synthetic strategy was also used to prepare a porphyrin with fused acenaphthylene and corannulene subunits. The fused bowl-shaped corannulene provides these porphyrins with a unique structural component that increases solubility by reducing $\pi-\pi$ stacking interactions.

Introduction

Corannulene (**1**) is a bowl-shaped hydrocarbon that has attracted considerable attention since it was first described by Barth and Lawton in 1966.[1] Although the original synthesis involved 16 consecutive steps, more direct routes were subsequently developed using flash vacuum pyrolysis.[2] Fairly recently, more convenient solution phase syntheses have been developed.[3,4] The continued interest in the corannulene system is due in part to its unusual curved geometry, which corresponds to one-third of the cage-like structure found in buckminsterfullerene (C_{60}). Now that gram quantities of corannulene can be synthesized using currently available methodologies, the chemistry of this "buckybowl" can be explored in detail.[5] Furthermore, these methods have allowed numerous derivatives to be synthesized that exhibit unique properties, including liquid crystalline materials,[6] dendimers,[7] bicorannulenes,[8] and fused

† Part 26 in the series "Porphyrins with Exocyclic Rings".

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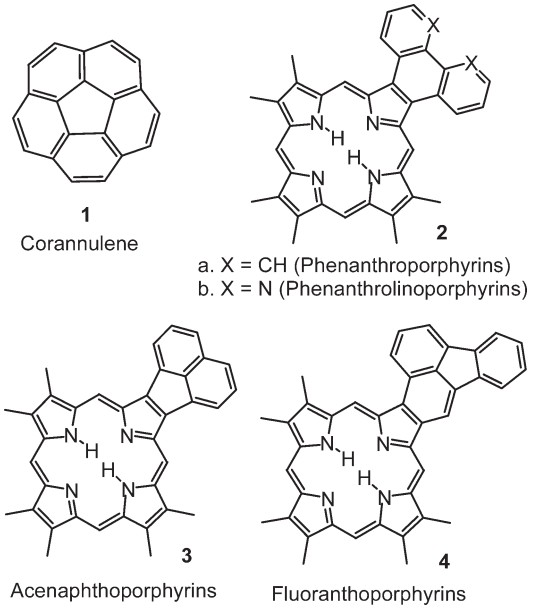
dicorannulenes.[9] Corannulenes have also been incorporated into "molecular tweezers"[10] and have been mooted as model compounds for hydrogen storage by carbon nanotubes.[11] Corannulene retains benzenoid aromatic properties, but the strain due to the five-membered ring compromises these aromatic properties and increases its reactivity. The curved structure of corannulene also undergoes a facile bowl-to-bowl inversion[12] that can be modulated by ring fusion.[13] Furthermore, in contrast to C_{60}, a variety of η^6 coordination complexes of corannulene have been described.[14]



Given the remarkable characteristics of this system, we were interested in the possibility of synthesizing porphyrins with fused corannulene moieties. In previous investigations, syntheses of porphyrins with fused benzene,[15,16] naphthalene,[17,18] phenanthrene (**2a**),[19,20] phenanthroline (**2b**),[21] acenaphthylene (**3**),[22] fluoranthene (**4**),[23a] pyrene,[23b] and heteroaromatic subunits[24] have been conducted using a variety of synthetic strategies.[15] These extended conjugated systems show modified spectroscopic properties and may have value as new classes of photosensitizers for medicinal applications,[25] as biological sensors,[26] or in the development of novel optical materials.[27] Porphyrins also have molecular recognition properties[28,29] that can lead to applications, such as in the development of stationary phase materials for the chromatographic separation of fullerenes.[30,31]

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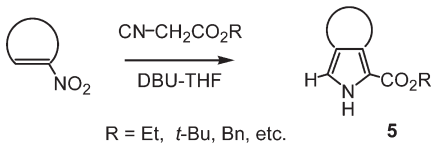
SCHEME 1

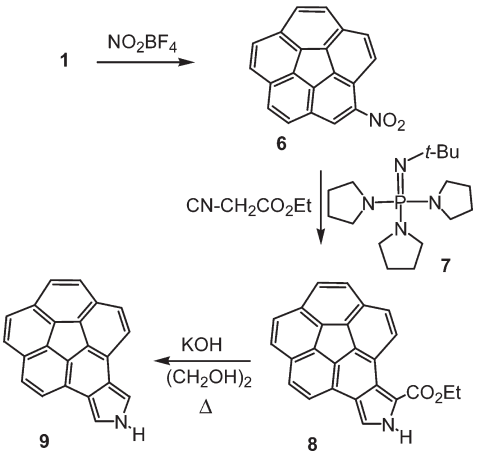


These properties also make the incorporation of porporphyrins into nanomolecular systems desirable, particularly given the well-defined geometry of the porphyrin macrocycle.[32] Ring fusion allows this desirable geometry to be extended and can thereby lead to the construction of molecular wires or nanoscale devices.[33] However, ring-fused porphyrins of this type are often poorly soluble in organic solvents, and this places limitations on their applications. The curved geometry of a fused corannulene unit would decrease $\pi-\pi$ stacking interactions and could potentially increase the solubility of annulated porphyrins. Furthermore, the curved architecture of corannulene will greatly affect intermolecular associations and could lead to an enhancement of fullerene−porphyrin interactions. Hence, the development of a synthetic route to corannulenoporphyrins would represent a significant departure from previous investigations in this area.

Results and Discussion

Nitroalkenes react with esters of isocyanoacetic acid in the presence of a non-nucleophilic base such as DBU to give pyrrole esters.[34,35] In some cases, this chemistry can be extended to the reaction of isocyanoacetates with nitroaromatic compounds, and this provides a convenient route to *c*-annelated pyrroles **5** (Scheme 1). This strategy has been applied in the synthesis of naphthopyrroles, phenanthropyrroles, acenaphthopyrroles, fluoranthopyrroles, and many other ring-fused pyrroles,[36] and these heterocyclic derivatives have been used as intermediates in the synthesis of ring-fused porphyrins.[15] This approach therefore provides a viable methodology for the synthesis of corannulenopyrroles from nitrocorannulene (**6**, Scheme 2). Although a synthesis of **6** has been noted,[37] no details on the preparation of this compound are available in the literature. We found that the treatment of corannulene with nitronium tetrafluoroborate gave good yields of reasonably pure samples of **6** that could be taken on directly for the Barton−Zard pyrrole synthesis. However, a small sample was further purified by column chromatography and fully characterized. In other work, we had obtained superior yields of pyrrolic products using phosphazene base **7** in place of DBU in the Barton−Zard chemistry.[38] Hence, in order to maximize the efficiency of this synthesis, crude nitrocorannulene was reacted with ethyl isocyanoacetate in the presence of **7** in THF, and the related corannulenopyrrole **8** was isolated in 50% yield. The ester group of **8** could then be saponified with concomitant decarboxylation using KOH in ethylene glycol at 180−190 °C to give the unsubstituted corannulenopyrrole **9** in quantitative yields. This pyrrole was reasonably stable, but the surface of the solid material became discolored over the period of several hours, and prolonged exposure to air led to a significant amount of decomposition.

SCHEME 2



Corannulenopyrroles **8** and **9** are representatives of a new heterocyclic system and were therefore carefully characterized. In DMSO-d_6, the proton NMR spectrum of **8** showed the pyrrole CH at 8.32 ppm and the NH at 13.0 ppm, values that are consistent with a pyrrolic structure of this type. The corannulene unit is asymmetrical, and the eight associated protons give rise to eight different doublets or AB quartets in the range of 7.9−8.9 ppm. The carbon-13 NMR spectrum showed 22 resonances for the aromatic carbons between 116 and 136 ppm, an ester carbonyl peak at 160.7 ppm, and the aliphatic ester carbons at 14.7 and 60.4 ppm. The IR spectrum showed the ester carbonyl stretch at 1657 cm^{-1}, a value that is typical for pyrrole esters and which reflects the highly electron-donating characteristics of the pyrrole nucleus. The EIMS for **8** showed loss of EtOH as the primary fragmentation pathway, followed by loss of CN radical and CO to give a tropylium-type species **10** (Scheme 3). Corannulenopyrrole **9** also showed properties that were similar to the constituent pyrrole and corannulene subunits. The NMR data clearly demonstrated the presence of a plane of symmetry, and the carbon-13 NMR spectra in $CDCl_3$ or DMSO-d_6 showed a total of 12 resonances in the aromatic region. The EIMS for **9** showed a strong molecular ion at m/z 289 together with a moderately strong doubly charged ion. The favored fragmentation pathway in this case involved sequential loss of $H^{\bullet}$ and HCN to again give cation **10** (Scheme 3).

The synthesis of the desired corannulenoporphyrin **11** was accomplished by using the "3 + 1" variant of the MacDonald methodology (Scheme 4).[21,39,40] Corannulenopyrrole **9** was

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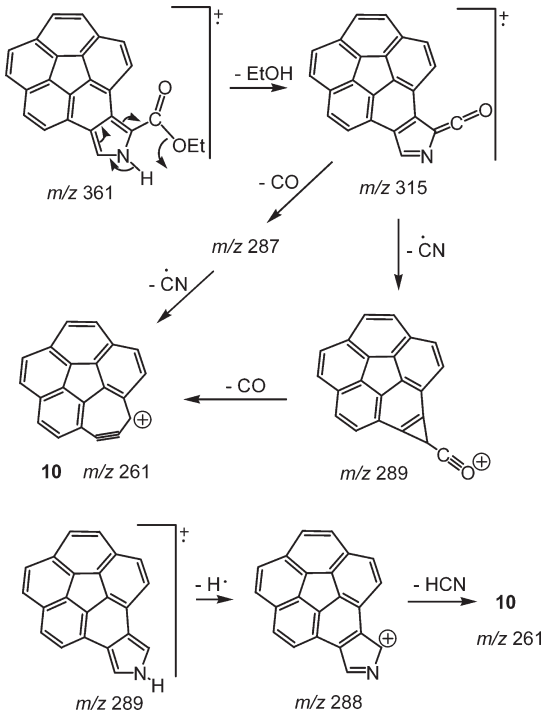
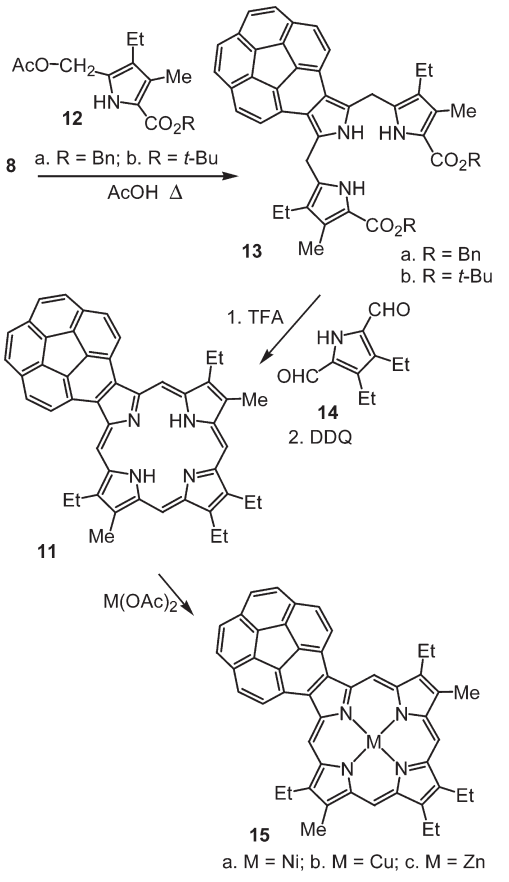
SCHEME 3



SCHEME 4



reacted with 2 equiv of an acetoxymethylpyrrole **12** and acetic acid in an alcohol solvent to give the corresponding tripyrranes **13**. When **9** was reacted with benzyl ester **12a**[41] in refluxing ethanol, the insoluble product **13a** could be filtered off in 73% yield. However, when **9** was reacted with **12b**,[42] the corresponding di-*tert*-butyl ester **13b** remained in solution and had to be precipitated out by pouring the reaction mixture into ice−water. In this fashion, the crude tripyrrane could be isolated in 86% yield. As tripyrranes of this type are not sufficiently stable to allow purification by column chromatography, this intermediate had to be used directly for porphyrin synthesis. Nevertheless, the di-*tert*-butyl ester was a convenient intermediate in our studies as the ester protective groups can be cleaved and taken on for macrocycle formation in a one-step procedure. Dibenzyl ester **13a** can also easily be deprotected by hydrogenolysis over 10% Pd/C, but this would require the isolation of an intermediary dicarboxylic acid. Although **13a** was not used to prepare corannulenoporphyrins, it was isolated in pure form and fully characterized. The proton NMR data for **13a** in $CDCl_3$ gave broadened resonances, and the bridge methylenes and benzyl ester CH_2 units gave rise to a very broad 6H absorption between 4.1 and 4.7 ppm and a further broad 2H peak at 3.6 ppm. The complexity of this spectrum, together with the upfield shift for the benzyl CH_2 resonances, is typical for tripyrranes and is attributable to the tripyrrolic unit taking on a helical geometry.[43] This conformation is also beneficial for macrocycle formation. Another feature of the spectrum is that the terminal benzyl ester units are shielded because they fall over the π-system for the other end of the tripyrrole. The *ortho*-, *meta*-, and *para*-protons for the benzyl ester gave rise to resonances at 6.64, 6.93, and 7.06 ppm, significantly upfield from the expected values and again consistent with the tripyrrane taking on a helical conformation. Interestingly, the proton NMR spectrum of **13a** in DMSO-d_6 was well-resolved and showed none of the atypical upfield shifts observed in $CDCl_3$. In DMSO-d_6, the bridge CH_2 units appeared at 4.55 ppm (4H, s), the benzyl methylenes were observed as a 4H singlet at 5.27 ppm, and the terminal C_6H_5 groups gave rise to multiplets between 7.30 and 7.45 ppm. The marked differences in the spectra are due to the DMSO hydrogen bonding to the NH protons, which in turn alters the conformation of the tripyrrolic system. Tripyrrane **13b** also shows a well-resolved proton NMR spectrum in $CDCl_3$ and gave no unusual upfield shifts that were consistent with the compound taking on a helical conformation. This appears to be typical for the *tert*-butyl ester derivatives of tripyrranes[21,22] and is most likely due to unfavorable steric interactions due to the bulky ester units. Nevertheless, following the loss of the *tert*-butyl esters, the deprotected tripyrrane can again take on a required conformation for porphyrin formation.

Tripyrrane **13b** was stirred with TFA for 10 min at room temperature, the solution diluted with dichloromethane, pyrrole dialdehyde **14** immediately added, and the mixture stirred under nitrogen for 16 h. The resulting mixture was oxidized with ferric chloride[44] or DDQ. Following

(41) Johnson, A. W.; Kay, I. T.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1959**, 3416–3424.

(42) Clezy, P. S.; Crowley, R. J.; Hai, T. T. *Aust. J. Chem.* **1982**, *35*, 411–421.

(43) Jiao, W.; Lash, T. D. *J. Org. Chem.* **2003**, *68*, 3896–3901.

(44) Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973–7982.

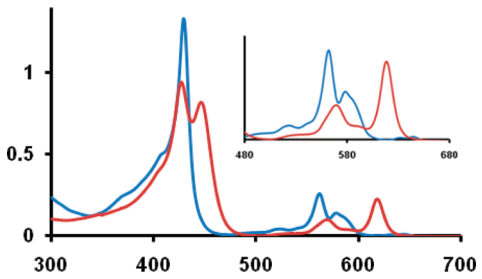


FIGURE 1. UV−vis spectra of corannulenoporphyrin **11**. Blue line: free base in 1% Et_3N-chloroform. Red line: Dication $\mathbf{11}H_2^{2+}$ in 1% TFA-chloroform.

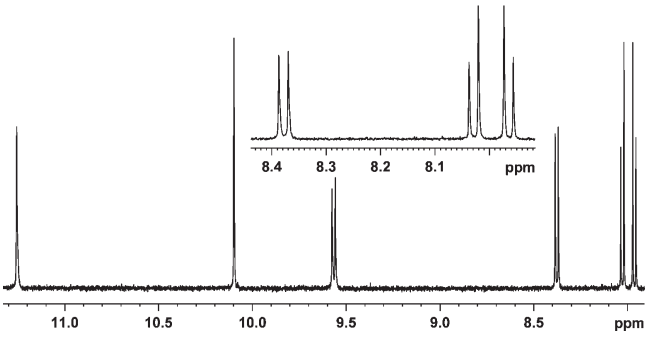


FIGURE 2. Partial 500 MHz proton NMR spectrum of corannulenoporphyrin **11** in $CDCl_3$ showing details of the downfield region.

extraction, purification by column chromatography on neutral alumina, and recrystallization from chloroform−methanol, corannulenoporphyrin **11** was isolated in 68% yield. The UV−vis absorption spectrum for **11** in chloroform gave a strong Soret band at 429 nm and a series of Q bands from 523 to 644 nm (Figure 1). Although these absorptions are bathochromically shifted compared to octaethylporphyrin, the presence of a fused corannulene moiety has a minimal effect on the porphyrin chromophore. Addition of TFA gives a dication $\mathbf{11}H_2^{2+}$ with a split Soret band at 427 and 446 nm and weaker absorptions at 569 and 619 nm (Figure 1). Again, this spectrum is somewhat modified compared to porphyrin dications without fused aromatic rings, but the wavelength shifts are still minor. Although some annelated porphyrins are greatly affected by ring fusion, phenanthroporphyrins, fluoranthoporphyrins, and related systems have similar spectroscopic properties.[45] Hence, the presence of a fused buckybowl structure does not significantly alter the electronic properties of the porphyrin macrocycle. Porphyrin **11** is reasonably soluble in chlorinated solvents and gave a high-quality proton NMR spectrum in $CDCl_3$ (Figure 2). As would be expected for an aromatic porphyrin system,[46] the internal NHs gave rise to a 2H upfield resonance at −3.4 ppm, whereas the *meso*-protons were shifted downfield to give two 2H singlets at 10.10 and 11.26 ppm.[47] The latter resonance is further deshielded due to its proximity to the corannulene moiety. The related dication $\mathbf{11}H_2^{2+}$ in TFA-$CDCl_3$ showed the *meso*-protons further downfield at 10.63 and 11.68 ppm, while the NH resonances were observed near −3 ppm. These results suggest that the diatropic ring current for the dication is enhanced compared to the free base structure, as is commonly the case for protonated porphyrins, but the shifts are also modulated by the presence of two positive charges. An indirect measure of the porphyrin diatropicity can be taken from the downfield shift of nearby protons, and by this measure, $\mathbf{11}H_2^{2+}$ actually shows a decreased ring current. The methyl substituents in **11** gave a 6H singlet at 3.75 for the free base in $CDCl_3$, but this peak shifted slightly upfield to 3.69 ppm for the dication in TFA-$CDCl_3$. The CH_2 units for the ethyl substituents showed a similar upfield shift upon protonation. This effect is also mirrored for the corannulene protons that are nearest to the porphyrin macrocycle as they give rise to a 2H doublet at 9.57 ppm for the free base form of **11** in $CDCl_3$, but this resonance shifts upfield to 9.32 ppm for the dication $\mathbf{11}H_2^{2+}$ in TFA-$CDCl_3$.[47] Therefore, the overall data indicate that the diatropicity is slightly lowered for the dication. The proton NMR data in $CDCl_3$ or TFA-$CDCl_3$ were consistent with the presence of a plane of symmetry. This was confirmed by the carbon-13 NMR spectrum of $\mathbf{11}H_2^{2+}$ in TFA-$CDCl_3$, which showed 5 sp^3 carbon resonances between 12 and 21 ppm, two resonances for the *meso*-bridge carbons at 98.9 and 99.3 ppm, and 17 of the 18 expected resonances for the pyrrole and corannulene carbons between 126 and 145 ppm.

Metalation of **11** was accomplished with nickel(II), copper(II), or zinc acetate in refluxing DMF. The resulting nickel(II) and copper(II) porphyrins **15a** and **15b**, respectively, were reasonably soluble, unlike metallo-derivatives of phenanthroporphyrins **2a**, acenaphthoporphyrins **3**, or related systems (e.g., **4**),[19,22,23] but the zinc complex **15c** was only sparingly soluble in chloroform. Proton NMR data could be obtained for the diamagnetic nickel(II) and zinc porphyrins **15a** and **15c**, but it is not possible to characterize paramagnetic copper(II) porphyrins by NMR spectroscopy. The proton NMR spectrum for the nickel(II) complex showed the *meso*-protons as two 2H singlets at 9.63 and 10.63 ppm, significantly upfield from the values obtained for the free base porphyrin, and the reduced ring current effect can also be discerned from the chemical shifts for closely connected units.[47] The methyl groups give a 6H resonance at 3.42 ppm, compared to 3.75 ppm for **11**, while the proximal corannulene protons show up at 9.17 ppm, a 0.4 ppm upfield shift compared to the free base porphyrin. Only poor-quality NMR spectra could be obtained for the zinc complex **15c** in $CDCl_3$, but the highly aggregated metalloporphyrin showed two very broad peaks for the *meso*-protons at 9.67 and 10.53 ppm. However, addition of a drop of pyrrolidine to the NMR tube greatly increased the solubility of the zinc porphyrin and allowed well-resolved NMR spectra to be obtained. Zinc porphyrins coordinate with the secondary amine, and this disrupts $\pi-\pi$ stacking interactions. The proton NMR spectrum now showed two sharp 2H singlets for the *meso*-protons at 9.90 and 11.07 ppm, and these results indicate that the diatropic character of **15c** lies midway between the free base porphyrin **11** and the nickel(II) complex **15a**. This interpretation is supported by the chemical shifts for nearby protons. The methyl resonance for **15c** is observed at 3.56 ppm, while the downfield corannulene

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(46) Medforth, C. J. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 5, pp 1−80.
(47) Proton NMR spectra for **11**, $\mathbf{11}H_2^{2+}$, **15a**, and **16** were fully assigned using $^1H-^1H$ COSY and NOE difference proton NMR spectroscopy. For details, see Supporting Information.

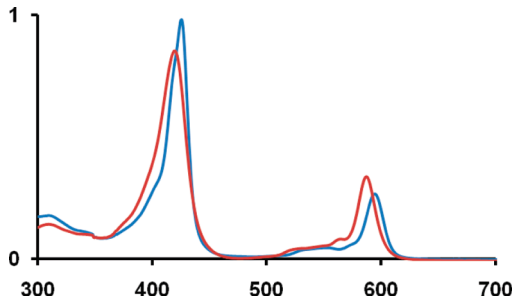


FIGURE 3. UV−vis spectra of metallocorannulenoporphyrins in chloroform. Red line: nickel(II) complex **15a**. Blue line: copper(II) complex **15b**.

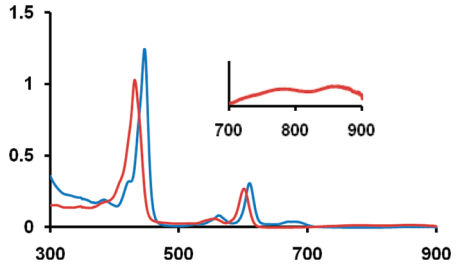


FIGURE 4. UV−vis spectra of zinc corannulenoporphyrin **15c**. Red line: **15c** in chloroform. The inset shows the weak absorptions at longer wavelengths. Blue line: **15c** in 1% pyrrolidine-chloroform.

doublet shifts to 9.55 ppm. The plane of symmetry in metalloporphyrins **15a** and **15c** is also evident in both the proton and carbon-13 NMR spectra, and all of the expected aromatic carbons resolved as separate peaks for these derivatives. The *meso*-carbon resonances for both complexes again show up between 96 and 100 ppm. The UV−vis absorption spectra for these metalloporphyrins were also insightful. The nickel(II) complex **15a** showed a Soret band at 420 nm and weaker absorptions at 565 and 589 nm (Figure 3). These bands were bathochromically shifted in the copper(II) chelate **15b** to 426, 552, and 595 nm (Figure 3). Metalloporphyrins show a trend of bathochromic shifts across the periodic table from nickel to copper to zinc,[48] and these trends are commonly also seen in modified porphyrin systems.[45] The zinc complex **15c** did indeed show a further shift to longer wavelength, giving a Soret band at 431 nm and the principal Q bands at 554 and 601 nm (Figure 4). However, weak absorptions were also noted at 780 and 854 nm. This spectrum, which corresponds to aggregated zinc porphyrin **15c**, is significantly modified and bathochromically shifted on addition of pyrrolidine. The Soret band is intensified and shifted to 446 nm, and minor bands are now observed at 562, 610, and 669 nm (Figure 4).

Slow evaporation of a solution of nickel(II) complex **15a** in $CDCl_3$ gave crystals that were suitable for X-ray crystallographic analysis (Figure 5). The porphyrin macrocycle is essentially planar and shows bond lengths that are very similar to the values reported for nickel(II) octaethylporphyrin

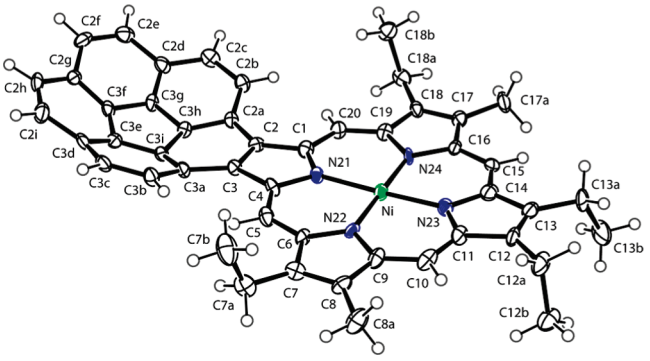


FIGURE 5. ORTEP-3 drawing (50% probability level, hydrogen atoms drawn arbitrarily small) of compound **15a**. Selected bond lengths (Å): Ni−N(23) 1.943(5), Ni−N(24) 1.959(5), Ni−N(21) 1.960(5), Ni−N(22) 1.964(5), N(21)−C(1) 1.376(8), N(21)−C(4) 1.400(7), N(22)−C(9) 1.376(8), N(22)−C(6) 1.377(7), N(23)−C(11) 1.387(8), N(23)−C(14) 1.403(8), N(24)−C(16) 1.384(7), N(24)−C(19) 1.389(7), C(1)−C(20) 1.402(8), C(1)−C(2) 1.437(8), C(2)−C(3) 1.398(8), C(3)−C(4) 1.442(8), C(4)−C(5) 1.366(8), C(5)−C(6) 1.363(8), C(6)−C(7) 1.442(9), C(7)−C(8) 1.358(9), C(8)−C(9) 1.451(9), C(9)−C(10) 1.376(9), C(10)−C(11) 1.369(9), C(11)−C(12) 1.446(8), C(12)−C(13) 1.333(9), C(13)−C(14) 1.442(9), C(14)−C(15) 1.360(9), C(15)−C(16) 1.371(9), C(16)−C(17) 1.430(9), C(17)−C(18) 1.345(8), C(18)−C(19) 1.449(8), C(19)−C(20) 1.356(8), C(2)−C(2a) 1.454(8), C(2a)−C(2b) 1.447(8), C(2b)−C(2c) 1.368(9), C(2c)−C(2d) 1.450(8), C(2d)−C(3 g) 1.363(8), C(2d)−C(2e) 1.456(9), C(2e)−C(2f) 1.380(9), C(2f)−C(2g) 1.444(9), C(2g)−C(3f) 1.352(8), C(2g)−C(2h) 1.457(9), C(2h)−C(2i) 1.379(9), C(2i)−C(3d) 1.436(9), C(3)−C(3a) 1.463(8), C(3a)−C(3i) 1.368(8), C(3a)−C(3b) 1.452(8), C(3b)−C(3c) 1.379(8), C(3c)−C(3d) 1.439(9), C(3d)−C(3e) 1.389(8), C(3e)−C(3i) 1.402(8), C(3e)−C(3f) 1.410(9), C(3f)−C(3g) 1.434(8), C(3g)−C(3h) 1.406(8), C(3h)−C(3i) 1.438(8).

(NiOEP).[49] The corannulene unit also shows bond lengths that closely resemble other corannulene structures,[50] apart from the bond length for ring fusion (C2−C3), which is approximately 0.02 Å longer than the other "rim" bonds.[50] Even the bowl shape is essentially isostructural with corannulene, as evidenced by the 0.81 Å separation between the centroid defined by the 10 peripheral carbon atoms. This corresponds to the 0.89 and 0.86 Å distances observed in two crystallographically independent molecules in pure corannulene.[50] Most nickel(II)-containing porphyrins are significantly ruffled or saddled,[49,51,52] although crystal packing forces may be sufficient to induce planar conformations in the solid state.[49] For instance, NiOEP has been characterized in three crystalline forms, two of which are near planar while the other one of these is highly ruffled.[49] Nevertheless, the ruffled conformation of NiOEP has also been shown to be favored in solution,[51] and this may also be the case for **15a** based on the reduced downfield shifts for the external protons in the proton NMR spectra for the nickel(II) complex.

Acenaphthoporphyrins **3** show highly modified UV−vis absorptions and strong Q absorptions between 650 and 700 nm.[22] These valuable characteristics made the hybrid corannulenoacenaphthoporphyrin **16** a worthwhile target for

(48) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed., Elsevier: Amsterdam, 1975; pp 871−889.

(49) (a) Meyer, E. F., Jr. *Acta Crystallogr., Sect. B* **1972**, *28*, 2162–2167. (b) Cullen, D. L.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2095–2102. (c) Brennan, T. D.; Scheidt, W. R.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3919–3924.

(50) (a) Petrukhina, M. A.; Andreini, K. W.; Mack, J.; Scott, L. T. *J. Org. Chem.* **2005**, *70*, 5713–5716. (b) Sevryugina, Y.; Rogachev, A. Y.; Jackson, E. A.; Scott, L. T.; Petrukhina, M. A. *J. Org. Chem.* **2006**, *71*, 6615–6618.

(51) Alden, R. G.; Crawford, B. A.; Doolen, R.; Ondrias, M. R.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2070–2072.

(52) Grigg, R.; Trocha-Grimshaw, J.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1978**, 571–572.

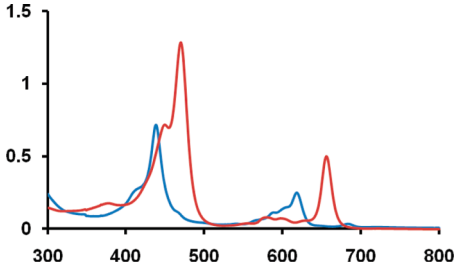
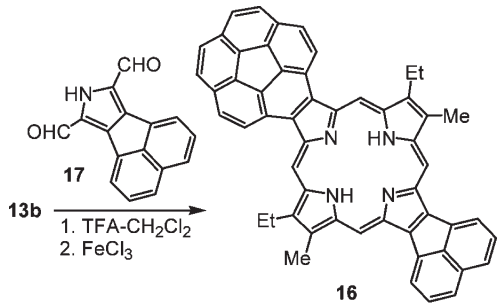


FIGURE 6. UV−vis spectra of acenaphthoporphyrin **16**. Blue line: free base in 1% Et_3N-chloroform. Red line: Dication $\mathbf{16}H_2^{2+}$ in 1% TFA-chloroform.

SCHEME 5



synthesis. This porphyrin was prepared by reacting tripyrrane **13b** with acenaphthopyrrole dialdehyde **17**[22c] in the presence of TFA, followed by oxidation with ferric chloride (Scheme 5). Following purification by column chromatography and recrystallization from chloroform−methanol, the π-extended porphyrin was isolated in 33% yield. The UV−vis absorption spectrum showed a weakened Soret band at 438 nm, followed by a series of weaker absorptions extending to 683 nm (Figure 6). In 1% TFA-chloroform, a split Soret band at 449 and 470 nm is observed followed by several weaker bands culminating in a relatively strong absorption at 656 nm (Figure 6). These results demonstrate that **16** has a similarly modified chromophore to other acenaphthoporphyrins. Corannulenoacenaphthoporphyrin **16** has poor solubility in chloroform and gave only a weak aggregated NMR spectrum in $CDCl_3$, but the dication $\mathbf{16}H_2^{2+}$ in TFA-$CDCl_3$ gave a well-resolved proton NMR spectrum showing the internal NHs as two broad 2H resonances between −2 and −3.5 ppm. The *meso*-protons are shifted downfield to give two 2H singlets at 11.08 and 11.65 ppm, and the remaining data are consistent with a highly diatropic system.[47] The carbon-13 NMR spectrum in TFA-$CDCl_3$ confirms the presence of a plane of symmetry and also shows the *meso*-carbon resonances at 99.4 and 101.1 ppm. These results demonstrate that this synthetic strategy allows access to porphyrins with two different fused aromatic subunits, but the curvature of the corannulene system does not significantly enhance the solubility of further π-extended systems.

The association of nickel(II) corannulenoporphyrin **15a** with C_{60} was also briefly examined. Addition of 1 equiv of C_{60} in toluene-d_8 to a solution of **15a** in $CDCl_3$ gave rise to no significant shifts in the proton NMR spectrum. Similarly, a spectroscopic titration of C_{60} in toluene to a dilute solution of **15a** in toluene showed no shifts in the UV−vis absorptions, but this experiment could only be taken to 20 equiv of C_{60} before the buckminsterfullerene absorptions obscured the peaks due to the corannulenoporphyrin. Nevertheless, interactions with fullerenes are likely to be fairly weak, and these molecules may need to be further elaborated to provide suitable cavities for these interactions.

Conclusions

Nitrocorannulene has been shown to undergo a Barton−Zard pyrrole condensation with ethyl isocyanoacetate in the presence of a phosphazene base to give a a novel corannulenopyrrole. The carboxylate group was cleaved in virtually quantitative yield to afford the unsubstituted *c*-annelated pyrrole, and further reaction with acetoxymethylpyrroles in the presence of acetic acid gave tripyrranes. The terminal ester units were cleaved, and further reaction with pyrrole dialdehydes in TFA-CH_2Cl_2 afforded excellent yields of corannulenoporphyrins **11** and **16**. Nickel(II), copper(II), and zinc complexes of corannulenoporphyrin **11** were also easily prepared. The new porphyrin systems retained highly diatropic characteristics and showed only minor modifications to their UV−vis spectra. The nickel(II) complex gave crystals that were suitable for X-ray crystallographic analysis and showed the expected curved architecture for the fused corannulene unit. These results show that corannulenoporphyrins are easily prepared from corannulene and the novel shell-like geometry of the fused corannulene system may provide access to more complex supramolecular systems.

Experimental Section

Nitrocorannulene (6). A solution of nitronium tetrafluoroborate (133 mg, 1.00 mmol) in anhydrous acetonitrile (25 mL) was added over a 30 min period to a stirred solution of corannulene (250 mg, 1.00 mmol) in dichloromethane (45 mL), and the resulting mixture was stirred under reflux overnight. The mixture was washed with water (×3), dried over sodium sulfate, and evaporated to give a yellow-orange residue (290 mg, 0.983 mmol, 98%). A pure sample of nitrocorannulene was obtained by running the crude material through a silica column, eluting with cyclohexane. Recrystallization from toluene gave the nitro compound as a yellow solid: mp 248−249 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82−7.90 (4H, 2 overlapping AB quartets, J = 8.7 Hz), 7.89−7.93 (2H, AB quartet, J = 8.8 Hz), 7.98 (1H, d, J = 9.0 Hz), 8.54 (1H, d, J = 9.0 Hz), 8.97 (1H, s); ^{13}C NMR ($CDCl_3$) δ 123.3, 126.6, 127.47, 127.52, 127.65, 127.70, 128.3, 128.5, 128.7, 129.2, 130.0, 131.2, 131.4, 132.9, 134.90, 134.93, 135.7, 136.8, 138.0, 146.2; HRMS (EI) m/z calcd for $C_{20}H_9NO_2$ 295.0633, found 295.0629.

Ethyl corannuleno[1,2-*c*]pyrrole-1-carboxylate (8). Phosphazene base **7** (1.58 g) was added dropwise to a stirred solution of nitrocorannulene (1.20 g, 4.06 mmol) and ethyl isocyanoacetate (460 mg, 4.07 mmol) in freshly distilled THF (100 mL), and the resulting solution was stirred at room temperature overnight. The solution was diluted with dichloromethane, washed with water, and evaporated under reduced pressure. The residue was purified by flash chromatography on a silica column, eluting initially with 25% cyclohexane/dichloromethane and then increasing proportions of dichloromethane. The product fraction was evaporated under reduced pressure and recrystallized from toluene to give the corannulenopyrrole ethyl ester (0.712 g, 2.03 mmol, 50%) as a yellow crystals: mp 233−235 °C; IR (Nujol mull) ν 3273 (NH stretch), 1657 cm^{-1} (C=O stretch); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.47 (3H, t, J = 7.1 Hz), 4.50 (2H, q, J = 7.1 Hz), 7.90−7.98 (4H, two overlapping AB quartets), 7.99 (1H, d, J = 8.8 Hz), 8.02 (1H, d, J = 8.6 Hz), 8.19 (1H, d,

J = 8.6 Hz), 8.32 (1H, d, J = 3.2 Hz), 8.90 (1H, d, J = 8.8 Hz), 13.02 (1H, br s); ^{13}C NMR (DMSO-d_6) δ 14.7, 60.4, 116.6, 119.2, 122.9, 125.0, 125.3, 125.9, 126.5, 126.6, 126.96, 126.98, 127.4, 127.5, 128.09, 128.10, 129.2, 130.1, 130.3, 133.1, 134.43, 134.46, 134.9, 136.0, 160.7; EIMS (70 eV) m/z (relative intensity) 362 (15), 361 (55, M^+), 316 (18, $[M - OEt]^+$), 315 (59, $[M - EtOH]^+$), 290 (24), 289 (100, $[M - EtOH - CN]^+$), 288 (27), 287 (31, $[M - EtOH - CO]^+$), 286 (27), 261 (37, $[M - EtOH - CN - CO]^+$); HRMS (EI) m/z calcd for $C_{25}H_{15}NO_2$ 361.1103, found 361.1102. Anal. Calcd for $C_{25}H_{15}NO_2$: C, 83.09; H, 4.18; N, 3.87. Found: C, 83.52; H, 4.02; N, 3.85.

Corannuleno[1,2-*c*]pyrrole (9). Potassium hydroxide (1.10 g) and 5 drops of hydrazine were added to a mixture of ethyl ester **8** (400 mg, 1.14 mmol) and ethylene glycol (50 mL), and nitrogen was bubbled through the mixture for 5 min. The stirred mixture was heated at 180−190 °C for 1 h under nitrogen and the resulting mixture poured into ice−water. The precipitate was suction filtered, washed well with water, and dried in vacuo to give the unsubstituted corannulenopyrrole (314 mg, 1.09 mmol, 96%) as an off-white solid: mp 185−188 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (2H, d, J = 2.8 Hz), 7.75 (2H, d, J = 8.7 Hz), 7.81 (2H, d, J = 8.7 Hz), 7.85 (2H, d, J = 8.5 Hz), 7.90 (2H, d, J = 8.5 Hz), 9.00 (1H, br s); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.84 (2H, d, J = 8.7 Hz), 7.90 (2H, d, J = 8.7 Hz), 7.93 (2H, d, J = 2.8 Hz), 7.94 (2H, d, J = 8.5 Hz), 8.04 (2H, d, J = 8.5 Hz), 12.10 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 112.0, 122.4, 124.9, 126.1, 127.26, 127.28, 127.4, 129.4, 130.6, 134.8, 135.8, 137.1; ^{13}C NMR (DMSO-d_6) δ 113.1, 120.9, 125.4, 125.9, 127.4, 127.5, 127.9, 128.6, 130.3, 133.3, 135.0, 136.0; EIMS (70 eV) m/z (relative intensity) 290 (23), 289 (100, M^+), 288 (15, $[M - H]^+$), 261 (21, $[M - H - HCN]^+$), 144.6 (20, M^{2+}), 130.7 (22); HRMS (EI) m/z calcd for $C_{22}H_{11}N$ 289.0892, found 289.0891. Anal. Calcd for $C_{22}H_{11}N \cdot {}^1/_2H_2O$: C, 88.57; H, 4.05; N, 4.69. Found: C, 88.80; H, 3.85; N, 5.01.

1,3-Bis(5-benzyloxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)corannuleno[1,2-*c*]pyrrole (13a). Nitrogen was bubbled through a stirred mixture of acetoxymethylpyrrole **12a**[41] (109 mg, 0.346 mmol) and corannulenopyrrole **9** (50.0 mg, 0.173 mmol) in ethanol (4 mL) and acetic acid (0.5 mL), and the stirred mixture was then refluxed under nitrogen for 16 h. The mixture was cooled in an ice bath, and the precipitate was filtered, washed with ethanol, and dried in vacuo overnight. The tripyrrane (101.5 mg, 0.127 mmol, 73%) was obtained as an off-white solid: mp 238 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (6H, t, J = 7.5 Hz), 2.31 (6H, s), 2.47 (4H, br), 3.63 (2H, v br), 4.10−4.70 (6H, v br), 6.64 (4H, br d, J = 7.2 Hz), 6.93 (4H, t, J = 7.6 Hz), 7.06 (2H, t, J = 7.4 Hz), 7.83 (2H, d, J = 8.7 Hz), 7.90 (2H, d, J = 8.7 Hz), 7.96 (2H, d, J = 8.5 Hz), 8.12 (2H, d, J = 8.5 Hz), 10.16 (1H, br s), 11.70 (2H, br s); ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.61 (6H, t, J = 7.5 Hz), 2.14 (6H, s), 2.16 (4H, q, J = 7.5 Hz), 4.55 (4H, s), 5.27 (4H, s), 7.32 (2H, m), 7.37 (4H, m), 7.43 (4H, m), 7.85 (2H, d, J = 8.7 Hz), 7.90 (2H, d, J = 8.6 Hz), 7.92 (2H, d, J = 8.7 Hz), 8.10 (2H, d, J = 8.6 Hz), 11.28 (2H, br s), 11.29 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 11.3, 16.0, 17.7, 24.0, 65.4, 117.5, 117.7, 123.9, 124.3, 124.4, 125.6, 126.0, 127.20, 127.23, 127.3, 127.4, 128.2, 128.4, 129.0, 130.7, 132.6, 134.7, 135.4, 136.7, 137.1, 163.4; ^{13}C NMR (DMSO-d_6) δ 10.4, 15.1, 16.8, 24.5, 64.6, 116.2, 117.3, 123.4, 123.6, 125.0, 125.9, 126.6, 127.3, 127.4, 127.84, 127.88, 128.0, 128.5, 128.6, 130.3, 131.3, 133.2, 134.4, 135.9, 137.2, 160.8; HRMS (ESI) m/z calcd for $C_{54}H_{45}N_3O_4$ 799.3410, found 799.3391. Anal. Calcd for $C_{54}H_{45}N_3O_4$: C, 81.08; H, 5.67; N, 5.25. Found: C, 81.12; H, 5.55; N, 5.32.

1,3-Bis(5-*tert*-butoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)corannuleno[1,2-*c*]pyrrole (13b). A mixture of acetoxymethylpyrrole **12b**[42] (195 mg, 0.694 mmol) and corannulenopyrrole **9** (100 mg, 0.346 mmol) in 2-propanol (5 mL) and acetic acid (0.5 mL) was refluxed under nitrogen for 16 h. The mixture was cooled to room temperature and poured into ice−water. The resulting precipitate was suction filtered, washed well with water, and dried overnight in vacuo to give the tripyrrane (218 mg, 0.298 mmol, 86%) as a light brown powder: mp 138 °C dec This material was used without further purification: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (6H, t, J = 7.5 Hz), 1.47 (18H, s), 2.28 (6H, s), 2.41 (4H, q, J = 7.5 Hz), 4.53 (4H, s), 7.78 (2H, d, J = 8.7 Hz), 7.82 (2H, d, J = 8.7 Hz), 7.84−7.87 (4H, AB quartet, J = 8.5 Hz), 8.11 (1H, br s), 8.50 (2H, br s); ^{13}C NMR ($CDCl_3$) δ 10.7, 15.6, 17.5, 25.2, 28.6, 80.6, 119.2, 119.6, 121.6, 124.4, 124.7, 126.2, 126.4, 127.2, 127.3, 127.58, 127.65, 129.2, 130.6, 134.8, 135.4, 137.0, 161.3; HRMS (EI) m/z calcd for $C_{48}H_{49}N_3O_4$ 731.3723, found 731.3727.

8,12,13,17-Tetraethyl-7,18-dimethylcorannuleno[1,2-*b*]porphyrin (11). In a 100 mL pear-shaped flask, crude tripyrrane di-*tert*-butyl ester **13b** (120 mg, 0.164 mmol) was stirred with TFA (2 mL) under nitrogen for 10 min. The mixture was diluted with dichloromethane (98 mL), pyrrole dialdehyde **14**[53] (29 mg, 0.16 mmol) was added, and the resulting mixture was stirred for 16 h. The mixture was neutralized by the dropwise addition of triethylamine, DDQ (38 mg) was added, and the resulting mixture was stirred for a further 1 h. The solution was washed with water and evaporated under reduced pressure. The residue was purified by column chromatography on grade 3 alumina, eluting with dichloromethane, and the product eluted as a dark red band. Recrystallization from chloroform−methanol gave the corannulenoporphyrin (74 mg, 0.11 mmol, 68%) as dark purple crystals: mp > 300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} ($\log_{10}$ ε) 370 (sh, 4.64), 407 (sh, 4.95), 429 (5.38), 523 (3.86), 562 (4.66), 578 (4.39), 631 (3.03), 644 nm (3.19); UV−vis (1% TFA-$CHCl_3$) λ_{max} ($\log_{10}$ ε) 427 (5.22), 446 (5.16), 569 (4.25), 618 nm (4.60); ^{1}H NMR (500 MHz, $CDCl_3$) δ −3.40 (2H, br s), 1.94 (6H, t, J = 7.7 Hz), 2.08 (6H, t, J = 7.7 Hz), 3.75 (6H, s), 4.05 (4H, q, J = 7.7 Hz), 4.37 (4H, q, J = 7.7 Hz), 7.96 (2H, d, J = 8.6 Hz), 8.03 (2H, d, J = 8.6 Hz), 8.37 (2H, d, J = 8.7 Hz), 9.57 (2H, d, J = 8.7 Hz), 10.10 (2H, s), 11.26 (2H, s); ^{1}H NMR (500 MHz, TFA-$CDCl_3$) δ −3.47 (1H, br s), −2.99 (3H, br s), 1.72 (6H, t, J = 7.7 Hz), 1.85 (6H, t, J = 7.7 Hz), 3.69 (6H, s), 4.13 (4H, q, J = 7.7 Hz), 4.31 (4H, q, J = 7.7 Hz), 7.97−8.02 (4H, AB quartet, J = 8.6 Hz), 8.44 (2H, d, J = 8.7 Hz), 9.32 (2H, d, J = 8.7 Hz), 10.63 (2H, s), 11.68 (2H, s); ^{13}C NMR (TFA-$CDCl_3$) δ 12.0, 16.7, 17.4, 20.1, 20.6, 98.9, 99.3, 126.3, 127.7, 128.1, 129.1, 130.7, 131.9, 133.8, 135.5, 137.2, 138.2, 138.6, 139.1, 142.0, 142.2, 143.0, 144.1, 144.5; HRMS (EI) m/z calcd for $C_{48}H_{40}N_4$ 672.3253, found 672.3254. Anal. Calcd for $C_{48}H_{40}N_4 \cdot {}^1/_{10}CHCl_3$: C, 84.36; H, 5.90; N, 8.18. Found: C, 84.26; H, 5.84; N, 8.22.

[8,12,13,17-Tetraethyl-7,18-dimethylcorannuleno[1,2-*b*]porphyrinato]nickel(II) (15a). A mixture of corannulenoporphyrin **11** (10.0 mg, 0.015 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (9.4 mg) in DMF (10 mL) was stirred under reflux for 1 h. The solution was cooled to room temperature, diluted with chloroform, and then washed with water. The organic layer was separated and evaporated under reduced pressure. The residue was purified by column chromatography on grade 3 neutral alumina, eluting with dichloromethane, and the product fraction was evaporated and then recrystallized from chloroform−methanol to give the nickel chelate (8.6 mg, 0.012 mmol, 80%) as a purple solid: mp > 300 °C; UV−vis ($CHCl_3$) λ_{max} ($\log_{10}$ ε) 420 (5.14), 528 (3.89), 562 (4.15), 587 nm (4.73); UV−vis (toluene): λ_{max} ($\log_{10}$ ε) 422 (5.15), 524 (sh, 3.93), 565 (4.21), 589 nm (4.82); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.80 (6H, t, J = 7.6 Hz), 1.85 (6H, t, J = 7.6 Hz), 3.42 (6H, s), 3.88 (4H, q, J = 7.6 Hz), 3.92 (4H, q, J = 7.6 Hz), 7.89 (2H, d, J = 8.5 Hz), 7.95 (2H, d, J = 8.5 Hz), 8.23 (2H, d, J = 8.5 Hz), 9.17 (2H, d, J = 8.5 Hz), 9.63 (2H, s), 10.63 (2H, s); ^{13}C NMR ($CDCl_3$) δ 11.7, 17.9, 18.5, 19.9, 20.2, 97.1, 99.8, 126.9, 127.0, 127.2, 127.5, 129.0, 129.6, 131.2, 135.4, 136.0, 136.4, 136.6, 136.9, 137.8, 140.8, 141.5, 142.4, 143.2, 144.0; EIMS (70 eV) m/z (relative intensity) 732 (11), 731 (23), 730 (50), 729 (48), 728 (100, M^+), 713 (8.7, $[M - CH_3]^+$), 364.9 (15),

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364.1 (15, M^{2+}); HRMS (EI), *m*/*z* calcd for $C_{48}H_{38}N_4Ni$ 728.2450, found 728.2454.

[8,12,13,17-Tetraethyl-7,18-dimethylcorannuleno[1,2-*b*]porphyrinato]copper(II) (15b). The title compound was prepared by the foregoing conditions from **11** (10.0 mg, 0.015 mmol) and copper(II) acetate (11.8 mg). Following chromatography on grade 3 neutral alumina and recrystallization from chloroform−methanol, the metal complex (8.7 mg; 0.012 mmol, 80%) was isolated as a purple solid: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} ($\log_{10}\varepsilon$) 426 (5.33), 552 (4.03), 595 nm (4.77); EIMS (70 eV) *m*/*z* (relative intensity) 736 (19), 735 (45), 734 (36), 733 (75, M^+), 718 (6.3, $[M - CH_3]^+$), 368 (24), 367 (27, M^{2+}); HRMS (EI) *m*/*z* calcd for $C_{48}H_{38}N_4Cu$ 733.2392, found 733.2392.

[8,12,13,17-Tetraethyl-7,18-dimethylcorannuleno[1,2-*b*]porphyrinato]zinc(II) (15c). The zinc complex was prepared by the foregoing conditions from **11** (10.4 mg, 0.0155 mmol) and zinc acetate (11.8 mg). Following chromatography on grade 3 neutral alumina and recrystallization from chloroform−methanol, the zinc derivative (9.1 mg; 0.0124 mmol, 80%) was isolated as a purple solid: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} ($\log_{10}\varepsilon$) 431 (5.23), 554 (4.01), 601 (4.65), 780 (3.40), 854 nm (3.48); UV−vis (1% pyrrolidine-$CHCl_3$) λ_{max} ($\log_{10}\varepsilon$) 383 (4.51), 420 (sh, 4.72), 446 (5.32), 562 (4.14), 610 (4.71), 669 nm (3.80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82−1.95 (12H, br), 3.32−3.70 (6H, br), 3.81−4.21 (8H, br), 7.83 (2H, br), 7.94 (2H, br), 8.21 (2H, br), 9.26 (2H, br), 9.67 (2H, v br), 10.53 (2H, v br); ^{1}H NMR (500 MHz, pyrrolidine-$CDCl_3$) δ 1.80 (6H, t, J = 7.7 Hz), 1.93 (6H, t, J = 7.7 Hz), 3.56 (6H, s), 3.97 (4H, q, J = 7.7 Hz), 4.18 (4H, q, J = 7.7 Hz), 7.82 (2H, d, J = 8.6 Hz), 7.90 (2H, d, J = 8.6 Hz), 8.28 (2H, d, J = 8.6 Hz), 9.55 (2H, d, J = 8.6 Hz), 9.90 (2H, s), 11.07 (2H, s); ^{13}C NMR (pyrrolidine-$CDCl_3$) δ 18.1, 18.7, 19.8, 20.2, 96.8, 99.6, 126.9, 127.0, 127.26, 127.33, 128.2, 128.7, 129.3, 131.0, 135.4, 135.6, 136.1, 136.6, 137.2, 142.5, 143.3, 143.8, 147.8, 148.7, 149.6; EIMS (70 eV) *m*/*z* (relative intensity) 739 (18), 738 (43), 737 (37), 736 (68), 735 (59), 734 (100, M^+), 733 (23), 719 (12, $[M - CH_3]^+$), 369 (15), 368 (21), 367 (22, M^{2+}); HRMS (EI) *m*/*z* calcd for $C_{48}H_{38}N_4Zn$ 734.2375, found 734.2378.

7,18-Diethyl-8,17-dimethylacenaphtho[1,2-*b*]corannuleno[1,2-*l*]porphyrin (16). Tripyrrane **13b** (106 mg, 0.145) was stirred with TFA (2 mL) for 10 min under nitrogen. The mixture was diluted with dichloromethane (38 mL), followed by the addition of acenaphthopyrrole dialdehyde **17**[22c] (35.7 mg, 0.144 mmol), and the resulting solution was stirred for 3 h. The mixture was washed with water, and the aqueous layer was back-extracted with chloroform. The combined organic solutions were shaken vigorously with 0.1% aqueous ferric chloride solution for 10 min, and the organic phase was separated and washed with water, saturated sodium bicarbonate solution, and water. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on grade 3 neutral alumina eluting initially with dichloromethane, then with chloroform and finally with 10% methanol−chloroform. The porphyrin-containing fractions were rechromatographed on silica, eluting with the same sequence of solvents, and the product was collected as a dark green band. Recrystallization from chloroform−methanol gave the acenaphthoporphyrin (35.6 mg, 0.048 mmol, 33%) as shiny purple crystals: mp >300 °C; UV−vis (1% Et_3N-$CHCl_3$) λ_{max} ($\log_{10}\varepsilon$) 410 (sh, 4.56), 438 (5.00), 540 (3.70), 564 (sh, 3.90), 587 (sh, 4.39), 601 (sh, 4.30), 618 (4.54), 683 nm (3.67); UV−vis (1% TFA-$CHCl_3$) λ_{max} ($\log_{10}\varepsilon$) 379 (4.39), 449 (5.00), 470 (5.25), 554 (3.78), 579 (4.06), 598 (4.02), 626 (sh, 3.92), 656 nm (4.84); ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C, aromatic region only) δ 7.85−8.05 (8H, m), 8.37 (2H, d, J = 8.6 Hz), 8.85 (2H, d, J = 7.5 Hz), 9.52 (2H, d, J = 8.6 Hz), 10.37 (2H, s), 11.14 (2H, s); ^{1}H NMR (500 MHz, TFA-$CDCl_3$) δ −3.04 (2H, br s), −2.50 (2H, v br, 1.92 (6H, br t, J = 7.7 Hz), 3.78 (6H, s), 4.33 (4H, q, J = 7.7 Hz), 7.99−8.03 (4H, AB quartet, J = 8.7 Hz), 8.11 (2H, dd, J = 7.0, 8.0 Hz), 8.30 (2H, d, J = 8.0 Hz), 8.44 (2H, d, J = 8.8 Hz), 9.13 (2H, br d, J = 7.0 Hz), 9.31 (2H, d, J = 8.8 Hz), 11.08 (2H, s), 11.65 (2H, s); ^{13}C NMR (TFA-$CDCl_3$) δ 12.1, 16.8, 20.6, 99.4, 101.1, 126.3, 127.0, 127.6, 128.1, 129.1, 129.3, 130.7, 131.0, 131.1, 131.3, 131.4, 131.9, 133.9, 135.5, 135.9, 136.7, 137.2, 138.6, 139.1, 139.5, 143.0, 143.3, 143.9, 144.5; HRMS (FAB) *m*/*z* calcd for $C_{54}H_{36}N_4$+H 741.3016, Found 741.3018.

Crystallographic Experimental Details of 15a. X-ray quality crystals of **15a** were obtained by vapor diffusion of hexanes into a $CDCl_3$ solution. The crystals were quickly suspended in mineral oil at ambient temperature, and a suitable crystal was selected. A mineral oil coated red block thereby obtained of approximate dimensions 0.15 × 0.13 × 0.11 mm^3 was mounted and transferred to a CCD equipped diffractometer. The X-ray diffraction data were collected at −173 °C using Mo Kα (λ = 0.71073 Å) radiation. Data collection and cell refinement were performed using SMART and SAINT+, respectively.[54] The unit cell parameters were obtained from a least-squares refinement of 1026 centered reflections. Compound **15a** was found to crystallize as the chloroform solvate in the monoclinic crystal system with the following unit cell parameters: a = 32.288(11) Å, b = 13.621(4) Å, c = 20.774(7) Å, β = 122.411(6)°, Z = 8. The systematic absences indicated the space group to be *Cc* (no. 9) or *C*2/*c* (no. 15);[55] the latter was chosen on the basis of centricity and led to a quality solution. A total of 19 337 reflections were collected, of which 7237 were unique, and 3684 were observed $F_o^2 > 2\sigma(F_o^2)$. Limiting indicies were as follows: $-39 \le h \le 38$, $-16 \le k \le 11$, $-25 \le l \le 25$. Data reduction was accomplished using SAINT.[54] The data were corrected for absorption using the SADABS procedure.[54]

Solution and data analysis were performed using the WinGX software package.[56] The structure of **15a** was solved by charge flipping methods using the program SUPERFLIP,[57] and the refinement was completed using the program SHELX-97.[58] All non-hydrogen atoms were refined anisotropically. All H atoms were included in the refinement in the riding-model approximation (C−H = 0.95, 0.98, 0.99, and 1.00 Å for Ar−H, CH_3, CH_2, and CH; U_{iso}(H) = 1.2Ueq(C) except for methyl groups, where U_{iso}(H) = 1.5U_{eq}(C)). Full-matrix least-squares refinement on F^2 led to convergence, $(\Delta/\sigma)_{max}$ = 0.001, $(\Delta/\sigma)_{mean}$ = 0.0000, with R_1 = 0.0791 and wR_2 = 0.1424 for 3684 data with $F_o^2 > 2\sigma(F_o^2)$ using 0 restraints and 516 parameters. A final difference Fourier synthesis showed features in the range of $\Delta\rho_{max}$ = 0.524 e$^-$/Å^3 to $\Delta\rho_{min}$ = −0.825 e$^-$/Å^3, which were deemed of no chemical significance. The structure validation program Mogul[59] indicated that most bond distances and angles were within expected norms. The two organic bond distances and 19 angles outside "normal" ranges appear to be reasonable and explainable by the nature of the macrocycle. All involved the corannulene moiety, and in fact, these parameters were similarly flagged as unusual for other corannulene derivatives.[60−62] Molecular diagrams were generated using ORTEP-3[63] and POV-Ray.[64]

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Supporting Information Available: ORTEP-3 and POV-Ray figures for the X-ray crystal structure of **15a**, and selected UV−vis spectra, proton, NOE difference, COSY, HMQC, HMBC, DEPT-135 and carbon-13 NMR spectra, and MS data are provided. This material is available free of charge via the Internet at http://pubs.acs.org.