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Further Observations on Conformational and Substituent Effects in Acid-Catalyzed "3 + 1" Cyclizations of Tripyrranes with Aromatic Dialdehydes†

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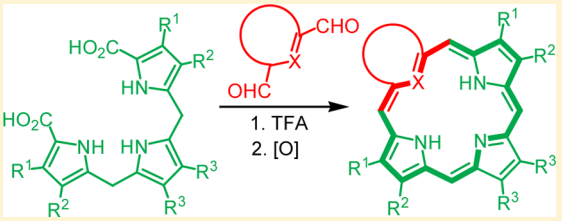
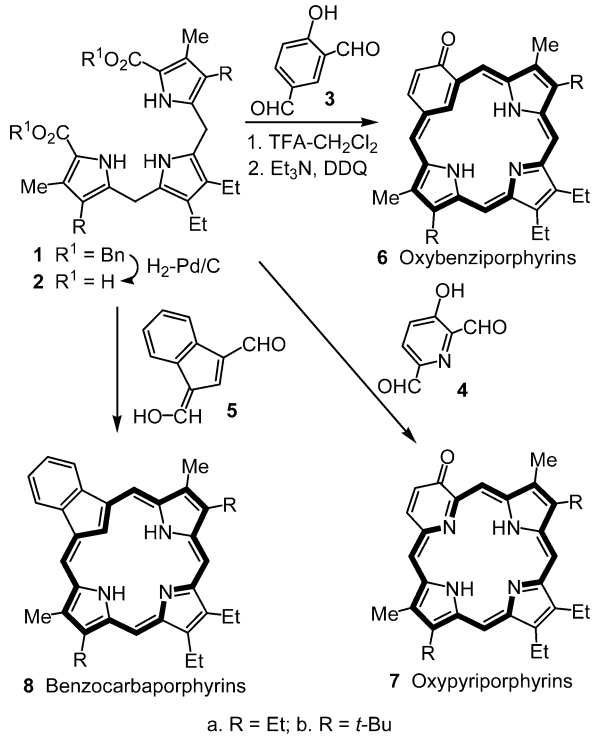
ABSTRACT: Tripyrranes with *tert*-butyl and phenyl substituents have been prepared and used to synthesize oxybenziporphyrins, oxypyriporphyrins, benzocarbaporphyrins, and azuliporphyrins with phenyl and *tert*-butyl substituents via a "3 + 1" methodology. The proton NMR spectra for the tripyrrane dibenzyl esters indicate that these tripyrrolic systems take on a helical conformation that favors macrocycle formation, and the NMR data can be a useful predictor on the efficiency of the "3 + 1" synthesis. Nevertheless, a tetraphenyltripyrrane proved to be susceptible to acidolytic cleavage under the usual reaction conditions and gave poor yields of porphyrinoid products. This problem could be overcome to a certain extent by carrying out the reactions in neat TFA. The presence of these substituents led to significant changes in the spectroscopic properties and diatropic character of the new porphyrinoid structures.



INTRODUCTION

The "3 + 1" variant of the MacDonald condensation,[1] which involves the acid-catalyzed reaction of a tripyrrane with an aromatic dialdehyde, has proven to be a very valuable methodology for synthesizing structurally diverse porphyrins[2−5] and porphyrin analogue systems[6−17] (Scheme 1). Commonly, the tripyrrane (e.g., **1a**), which consists of three pyrrole units linked by single carbon bridges, is reacted with a dialdehyde in the presence of trifluoroacetic acid.[9,10] Following oxidation with the electron-deficient quinone DDQ, or in some cases with aqueous ferric chloride,[15,16] porphyinoid products are commonly obtained in good to excellent yields. The versatility of this approach has allowed the synthesis of many carbaporphyrinoid structures that incorporate benzene,[9,10] azulene,[12] indene,[13] cyclopentadiene,[13] cycloheptatriene,[14] inverted pyrrole units,[15] and pyrazole rings.[16] Nevertheless, the efficiency of these cyclizations may be affected by the substituents attached to the tripyrrane precursor, which in turn can alter the conformation of this intermediate.[18] Proton NMR spectroscopy has been shown to give useful insights into the geometry of tripyrrane structures. The proton NMR spectra of tripyrranes with terminal benzyl ester groups (e.g., **1a**) are unusual because the ester methylene groups commonly show up at abnormally high field values as broad singlets near 4.5 ppm, and the *ortho*-protons of the associated phenyl groups are also shifted upfield to 6.5−7.0 ppm.[18] This compares to expectations that the OCH_2 resonance would give a sharp singlet at 5.2 ppm, while the *ortho*-protons would be expected to show up at 7.2 ppm. In addition, the bridging methylene units commonly give broadened resonances, and further resolution can be observed at lower temperatures.[5a] These observations suggest that tripyrranes favor a helical geometry in solution that undergoes an interconversion between the left-hand and right-hand helical forms at a moderate rate on the NMR time scale.[18] In this conformation, the terminal benzyl esters overlie the π-system

Scheme 1



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on the opposite end of this tripyrrolic unit, and this leads to the observed shielding effects. The helical conformation favors porphyrinoid ring formation, and indeed these data suggest that tripyrranes are predisposed for ring formation rather than intermolecular condensations leading to oligomer or polymer production. Tripyrranes with terminal *tert*-butyl ester units do not show these effects in their NMR spectra,[3,4] presumably due to steric repulsion, but in the "3 + 1" methodology the esters are cleaved and the deprotected tripyrrane can then take on the necessary conformation for macrocycle formation.

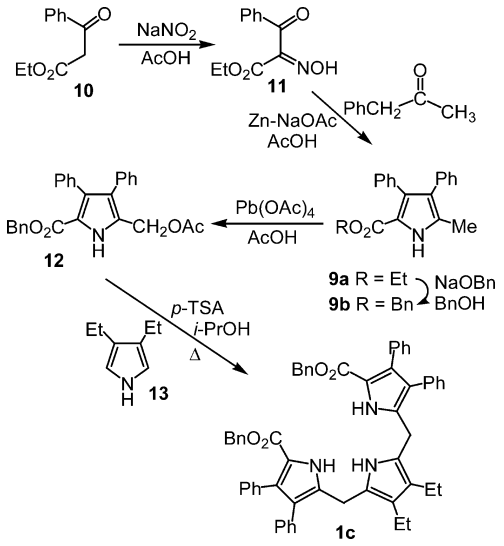
During the course of our studies into conjugated macrocycles related to the porphyrins, we synthesized a tripyrrane **1b** with two *tert*-butyl substituents.[18] The presence of compact substituents such as *tert*-butyl or phenyl groups has been shown to be beneficial in improving the solubility of the porphyrinoid systems and may aid in the formation of X-ray quality crystals for analysis.[13b,19,20] However, it was noted that the proton NMR spectrum for tripyrrane **1b** in $CDCl_3$ did not show the features exhibited by tripyrrane **1a** in that the benzyl ester OCH_2 units appeared as a sharp 4H singlet at 5.2 ppm, the protons on the adjacent phenyl unit gave a multiplet at 7.2−7.3 ppm with no upfield resonance for the *ortho*-protons, and the methylene bridges connecting the pyrrolic subunits gave a sharp resonance at 3.5 ppm.[18] These results strongly imply that tripyrrane **1b** does not favor a helical conformation. The dibenzyl ester was deprotected with hydrogen over 10% palladium−charcoal to give the related dicarboxylic acid **2b** and then further condensed with dialdehydes **3**−**5** under standard conditions to give the related porphyrin analogues **6b**, **7b**, and **8b**, respectively (Scheme 1).[18] The yields for these syntheses were all substandard compared to reactions using tripyrrane **1a**. Tripyrrane **1a** has been reported to react with 5-formylsalicylaldehyde (**3**) in the presence of TFA in dichloromethane to give, following oxidation with DDQ, oxybenziporphyrin **6a** in 35−44% yield,[9a,10] but reaction of **1b** with **3** gave the related di-*tert*-butyl porphyrinoid **6b** in only 4.9% yield.[18] Similarly, **1a** reacted with 3-hydroxy-2,6-pyridinedicarbaldehyde to give oxypyriporphyrin **7a** in 67% yield,[11] while condensation of **1b** with **4** gave **7b** in 25% yield.[18] In addition, although tripyrrane **1a** condensed with indene dialdehyde **5** to give benzocarbaporphyrin **8a** in 43% yield,[13] reaction of **1b** with **5** gave the related carbaporphyrin **8b** in only 18% yield.[18] It was concluded that the *tert*-butyl tripyrrane intermediate, like the dibenzyl ester precursor **1b**, does not favor the helical geometry that facilitates macrocycle formation and that this is responsible for the low yields. Furthermore, the proton NMR spectra for the dibenzyl esters **1a** and **1b** appear to be useful predictors for the efficiency of porphyrinoid macrocycle formation.[18]

In this study, tripyrranes with phenyl and *tert*-butyl substituents have been further investigated, and useful trends for porphyrinoid synthesis have been identified.

RESULTS AND DISCUSSION

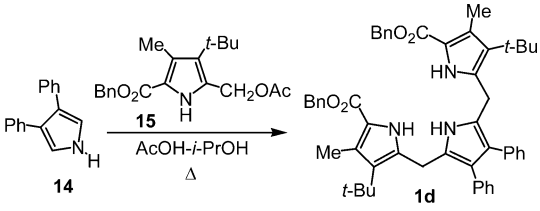
In order to more efficiently introduce phenyl and/or *tert*-butyl units into porphyrinoid structures, new tripyrranes were targeted for study. A tetraphenyltripyrrane **1c** was prepared in three steps from 3,4-diphenylpyrrole ethyl ester **9a** (Scheme 2). The pyrrole precursor was prepared from ethyl benzoylacetate (**10**) under Knorr condensation conditions. Although this methodology dates back to the nineteenth century,[21] the conditions that we used to prepare **9a** gave vastly improved results compared to previous reports for this compound.[22] Keto ester **10** was nitrosated with sodium nitrite and acetic acid to

Scheme 2



give oxime **11**, and this reacted with phenylacetone in the presence of zinc dust and sodium acetate in acetic acid to give the required pyrrole **9a** in up to 50% yield. Transesterification with benzyl alcohol containing a small amount of sodium benzyloxide afforded the corresponding benzyl ester **9b**, and this was selectively oxidized with lead tetraacetate in acetic acid to give the acetoxymethylpyrrole **12** (Scheme 2). Two equivalents of **12** were condensed with 1 equiv of 3,4-diethylpyrrole (**13**) under nitrogen in refluxing isopropyl alcohol containing *p*-toluenesulfonic acid as a catalyst to give tripyrrane **1c** in 75% yield. As is often the case for tripyrrane syntheses,[2,23] the product precipitated out and could be isolated in pure form by suction filtration. Tripyrrane **1d**, which has two phenyl and two *tert*-butyl substituents, was prepared similarly by reacting 3,4-diphenylpyrrole (**14**) with acetoxymethylpyrrole **15** in refluxing acetic acid−isopropyl alcohol (Scheme 3). The tripyrrane product could again be isolated by suction filtration in 77% yield.

Scheme 3



Tetraphenyltripyrrane **1c** in $CDCl_3$ gave a proton NMR spectrum that was consistent with a helical conformation (Figure 1a). The *ortho*-protons of the benzyl ester gave a comparatively upfield resonance near 6.5 ppm, while the OCH_2 units afforded two peaks near 4.0 and 4.8 ppm. The latter resonances are not only shifted upfield but have resolved into two separate peaks due to the diastereotopic nature of the methylene protons. This reflects the chiral nature of the helical conformation, which can only be interconverting relatively slowly with the enantiomeric conformer on the NMR time scale. The methylene protons for the bridges between the pyrrolic subunits are also diastereotopic, giving rise to peaks at 3.6 and 4.0 ppm (the latter resonance overlaps with one of the

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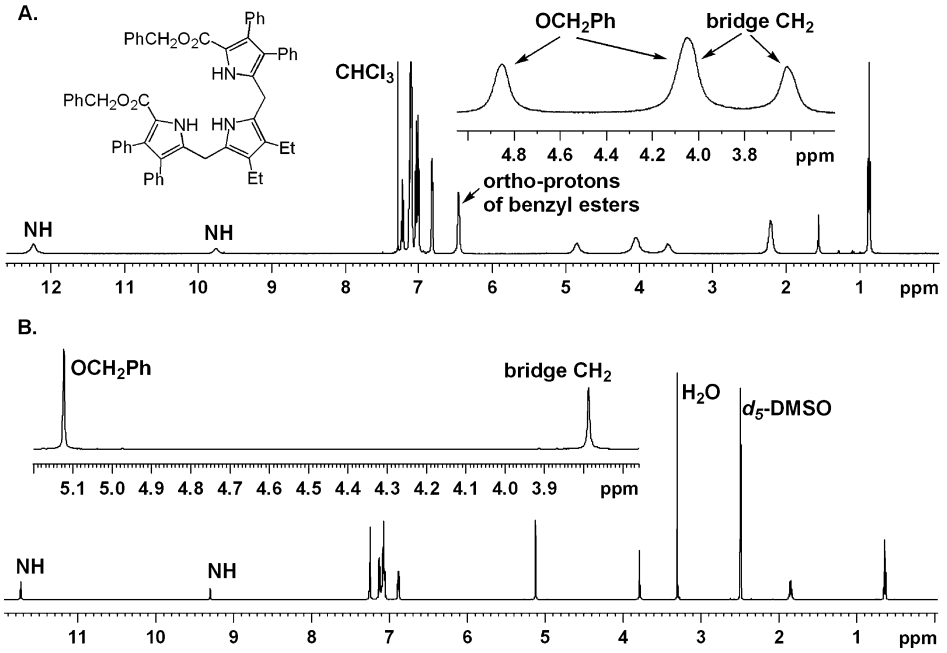

Figure 1. 500 MHz proton NMR spectra of tetraphenyltripyrrane **1c**. (A) NMR spectrum in $CDCl_3$ at 25 °C showing relatively upfield diastereotopic resonances for the benzyl ester CH_2s between 4 and 5 ppm. The *ortho*-protons for the benzyl group are shifted upfield to 6.5 ppm, and these data are consistent with the proposed helical geometry for tripyrranes in solution. The bridge methylenes are also highly diastereotopic, showing peaks at 3.6 and 4.0 ppm. (B) NMR spectrum in DMSO-d_6. The benzyl ester and bridge methylenes now give rise to two sharp 4H singlets at 5.1 and 3.8 ppm, respectively, indicating that the tripyrrane no longer favors a helical conformation.

peaks for the benzyl ester methylene group; see Figure 1a). Interestingly, when the spectrum for **1c** is run in DMSO-d_6, these features are no longer seen. The benzyl ester OCH_2 gave a 4H singlet at 5.1 ppm, while the methylene bridges gave a sharp singlet at 3.8 ppm. DMSO strongly hydrogen bonds with pyrrolic NHs,[24] and this undoubtedly leads to a disruption of the helical structure. Hence, the conformation is solvent-dependent, and the tripyrrane takes on an open structure in DMSO. The proton NMR spectra for **1c** are also temperature-dependent (Figure 2). At 25 °C, the ester and bridge methylenes are highly diastereotopic and the CH_2 units for the ethyl substituents give a broad peak at 2.2 ppm. At 40 °C, the ethyl methylene resonance shows some fine structure while the resonances for the OCH_2 and bridge CH_2 units have broadened out. At 50 °C, the ethyl CH_2 affords a recognizable quartet, while the bridge CH_2's gave a broad singlet, and the ester methylenes produce a very broad peak centered on 4.6 ppm (Figure 2). As expected, these results demonstrate that helix-to-helix interconversion occurs more rapidly at increased temperatures.

Dibenzyl ester **1c** was hydrogenolyzed over 10% Pd/C to give the corresponding dicarboxylic acid **2c**. As this system favors a helical conformation in solution, it was anticipated that **1c** would give good yields of porphyrinoid products using MacDonald-type "3 + 1" condensations. However, this did not prove to be the case. Reaction of **2c** with 5-formylsalicylaldehyde in TFA−CH_2Cl_2, followed by oxidation with 1 equiv of DDQ, gave oxybenziporphyrin in 14% yield (Scheme 4). Attempts to react **2c** with indene dialdehyde **5** gave even worse results, and only trace amounts of impure benzocarbaporphyrin **8c** could be isolated from these reactions. We noted that these were messy reactions that resulted in the formation of tarry materials and porphyrin byproducts. These results were attributed to the tripyrrane being prone to acidolytic cleavage,[10] a common problem for pyrrolic species of this type. Treatment of **2c** with TFA initially results in decarboxylation of the terminal carboxylic acid groups to give **16** (Scheme 5). The individual pyrrole units are prone to α-protonation to afford cationic species such as **17**, which can undergo a carbon−carbon bond cleavage to give dipyrrylmethane **18** and cation **19**. The latter species is resonance-stabilized as the azafulvene structure **19′**. Fragments **18** and **19** can recombine or further react to give oligomeric or other macrocyclic products. Once the porphyrinoid macrocycle has been generated, the product is immune to these types of processes. However, the more favorable the acidolytic cleavage process the faster it is likely to occur, and this will compete with macrocycle formation. The phenyl substituents in these structures are likely to stabilize the azafulvene fragment by introducing canonical forms such as **19″**. Hence, while the conformation of tripyrrane **16** is conducive to the formation of the porphyrinoid ring, enhanced acidolysis leads to the poor results that are observed. We speculated that the cyclization reactions would occur more rapidly in more concentrated solutions as the tripyrrane is preorganized for cyclization and this would speed up the initial condensation with the dialdehyde. With this in mind, tripyrrane **2c** was condensed with **3** in neat TFA for 1 h, diluted with dichloromethane, and oxidized with 0.1% aqueous ferric chloride solution. Following purification by column chromatography and recrystallization from chloroform−methanol, oxybenziporphyrin **6c** was isolated in 20% yield. Reaction of **2c** with indene dialdehyde **5** under these conditions gave benzocarbaporphyrin **8c** in 8% yield (Scheme 4). Hence, this concept appears to be valid, although the yields are relatively low compared to most reactions of this type. Condensation of **2c** with pyridine dialdehyde **4** in neat TFA gave oxypyriporphyrin in 25% yield. Azulene dialdehyde **20** was also

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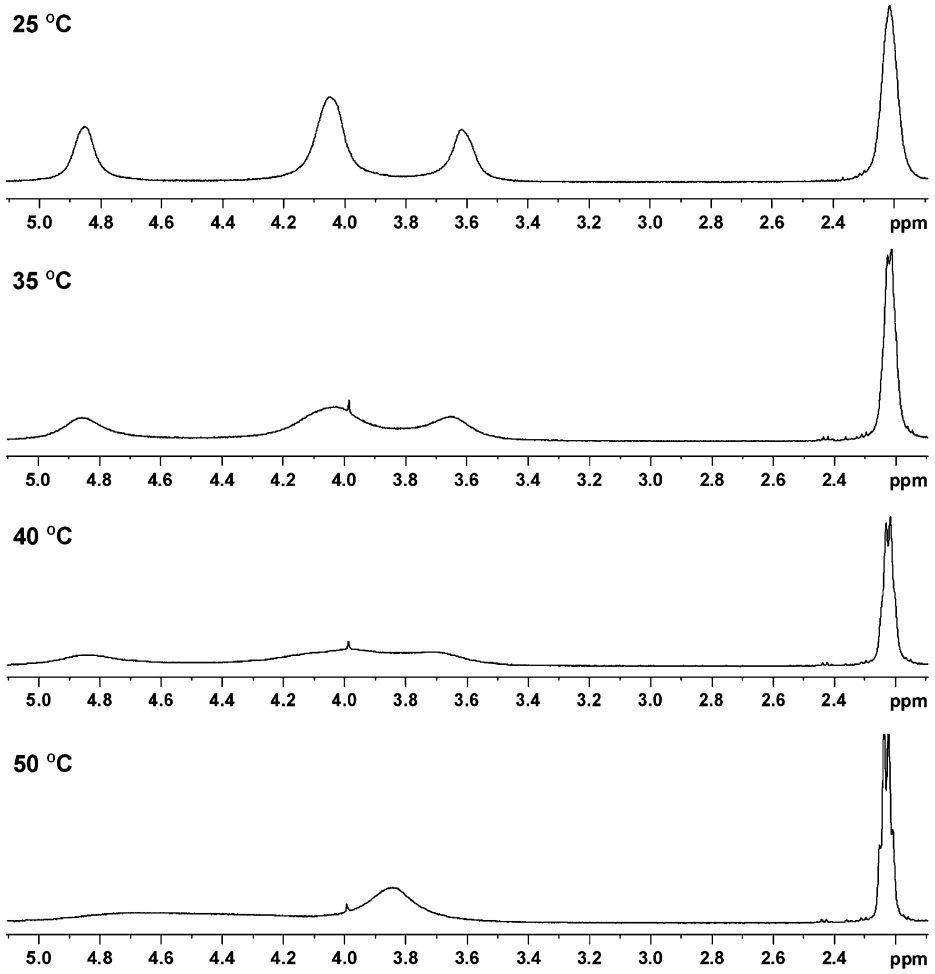

Figure 2. Partial 500 MHz proton NMR spectra of tetraphenyltripyrrane **1c** in $CDCl_3$ at 25, 35, 40, and 50 °C showing the region corresponding to the ethyl (2.2 ppm), bridge (3.6–4.0 ppm), and benzyl ester (4.0–4.9 ppm) methylene resonances. As the temperature increases, the ethyl CH_2 peak resolves as a quartet, while the diastereotopic protons for the bridging and benzyl ester methylenes are replaced by two broad peaks. These results are consistent with an increased rate of interconversion between two enantiomeric helical conformations.

reacted with **2c** under these conditions and afforded the corresponding azuliporphyrin **21c** in 15% yield.

Tripyrrane **1d** is structurally similar to **1b**, both of which possess two *tert*-butyl substituents. The apparent inhibition of the helical conformer for **1b** was attributed to the presence of these bulky substituents, and the low yields for porphyrinoids derived from **1b** also appeared to be due to this factor. For this reason, we had anticipated that tripyrrane **1d** would give poor results in "3 + 1" syntheses. However, the proton NMR spectrum for **1d** indicated that this tripyrrolic compound actually favors the helical conformation. The proton NMR spectrum for **1d** in $CDCl_3$ gave a broad singlet at 4.9 ppm for the benzyl ester methylenes, while the *ortho*-protons gave a slightly upfield resonance at 7.0 ppm. The bridging methylenes also produced a broad singlet at 4.0 ppm. In DMSO-d_6, the spectrum showed the loss of this conformation, but this is observed for all tripyrrane structures. Cleavage of the benzyl esters by hydrogenolysis over 10% Pd/C gave the related dicarboxylic acid **2d** in quantitative yield. This was reacted with dialdehydes **3**–**5** and **20** in the presence of TFA in dichloromethane, followed by neutralization of the solution with triethylamine and oxidation with 1 equiv of DDQ (Scheme 4). Using 100 mg of tripyrrane **1d** and 1 equiv of dialdehyde, two sets of conditions were used: 1 mL of TFA and 99 mL CH_2Cl_2 for 16 h (dilute conditions), and 1 mL of TFA in 19 mL CH_2Cl_2 for 2 h (concentrated conditions). All of the "3 + 1" reactions conducted with tripyrrane **2d** gave excellent results. Reaction of **1d** with **3** gave oxybenziporphyrin **6d** in 52% yield under the more concentrated conditions and 62% under the more dilute conditions. Condensation of **1d** with **4** gave oxypyriporphyrin **7d** in 80% yield under both sets of conditions, while **5** reacted with **1d** to give benzocarbaporphyrin **8d** in 43% and 44% yields for the concentrated and dilute conditions, respectively. Azulene dialdehyde **20** reacted with **2d** to give azuliporphyrin **21d** in 59% and 65% yield, respectively. Therefore, against expectations tripyrrane **2d** is an exceptionally good precursor for porphyrinoid synthesis. The difference between tripyrranes **1b** and **1d** are relatively subtle, but it is clear that the presence of two *tert*-butyl substituents in and of itself does not inhibit macrocycle formation. There appears to be a tipping point in terms of the favored conformation between tripyrranes **1b** and **1d**, and only the latter structure affords good yields of porphyrinoid products.

The porphyrinoids obtained from tripyrrane **1d** gave spectroscopic properties comparable to those obtained from **1a**, and oxybenziporphyrin **6d**, oxypyriporphyrin **7d**, benzocarbaporphyrin **8d**, and azuliporphyrin **21d** all showed UV–vis spectra similar to those previously reported for **6a**, **7a**, **8a**, and

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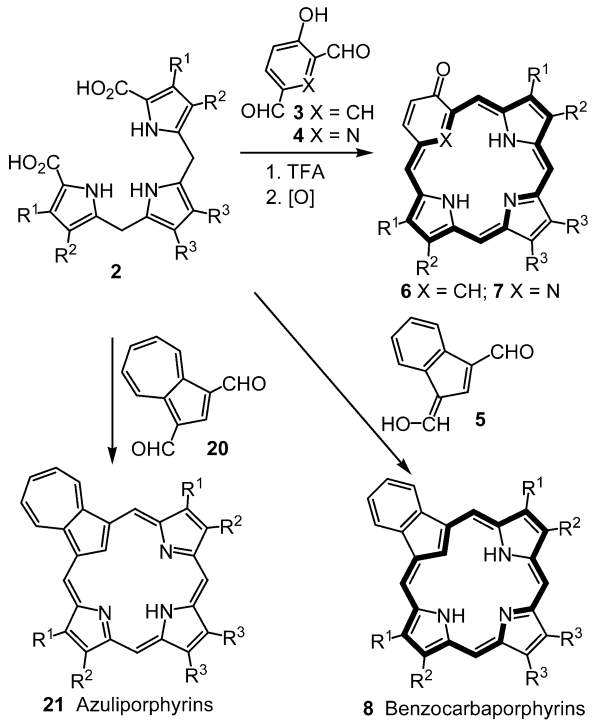
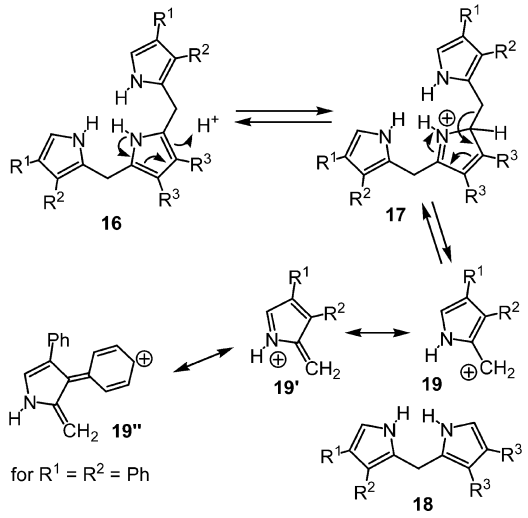
Scheme 4

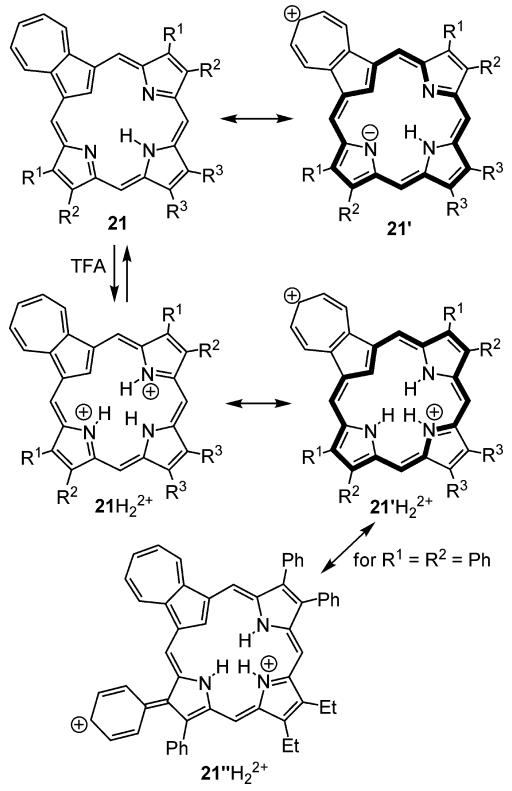


Scheme 5



21a where R^1 = Me and R^2 = R^3 = Et. However, the proton NMR spectra for the "d series" indicated that the diatropic character had been slightly enhanced. For instance, the external *meso*-protons for benzocarbaporphyrin **8a** were reported to give two 2H singlets at 9.82 and 10.10 ppm,[13] whereas these resonances appeared at 10.17 and 10.37 ppm for **8d**. Even taking into account proximity to *tert*-butyl or phenyl substituents, the downfield shifts are significant. Azuliporphyrins are often rather insoluble in organic solvents unless the azulene ring has been substituted with a phenyl or *tert*-butyl unit.[19,20] However, **21d** was reasonably soluble, and this enabled the internal CH and NH resonances to be identified at 2.53 and 2.88 ppm, respectively. Azuliporphyrins do not exhibit the very large diamagnetic ring currents seen for **6**, **7**, and **8** due to the presence of a cross-conjugated azulene subunit.[12] Nevertheless, these porphyrinoids do show a degree of diatropic character, which has been rationalized as being due to dipolar canonical forms such as **21′** that possess 18π electron delocalization pathways (Scheme 6). The internal protons in

Scheme 6



21a cannot be identified with confidence due to the low solubility of this compound,[12] although the external *meso*-protons were observed near 8.0 and 8.9 ppm for proton NMR spectra of **21a** in $CDCl_3$. As the *meso*-protons for **21d** appear as two 2H singlets at 8.61 and 8.95 ppm, the data suggest that the diatropicity has been slightly enhanced. Addition of TFA to solutions of azuliporphyrins leads to the formation of the corresponding dications $\mathbf{21}H_2^{2+}$ (Scheme 6).[12] The NMR spectra for the diprotonated species show a more substantial diamagnetic ring current due to the greater favorability of resonance contributors such as $\mathbf{21}'H_2^{2+}$ with 18π electron delocalization pathways that aid in charge delocalization. The NMR data for dications $\mathbf{21a}H_2^{2+}$ and $\mathbf{21d}H_2^{2+}$ showed similar chemical shifts when the proximity to *tert*-butyl and phenyl substituents was taken into account, indicating that the aromatic character of these two species are similar. In contrast to the observations for the "d series", porphyrinoids derived from tripyrrane **1c** gave somewhat altered UV–vis spectra and reduced diatropic character. The UV–vis spectra for the "c series" all showed small bathochromic shifts in the Soret band region and broadened absorptions for the Soret and Q bands. Benzocarbaporphyrin **8d** gave a Soret band at 432 nm, a smaller peak at 386 nm, and Q absorptions at 521, 556, 604, and 664 nm, but these peaks appeared at 434, 383, 517, 549, 616, and 677 nm, respectively, for **8c** (Figure 3a). Oxypyriporphyrin **7d** gave a Soret band at 429 nm with a shoulder at 442 nm and Q bands at 546, 592, and 614 nm, but these

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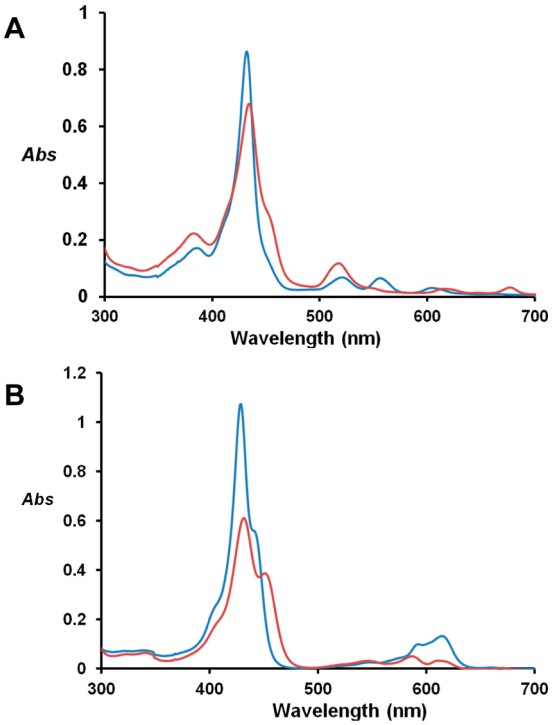
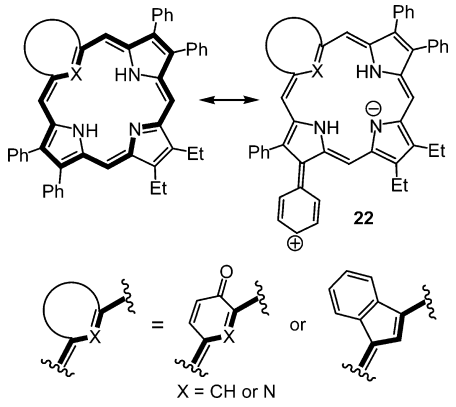


Figure 3. UV−vis spectra of selected porphyrinoids. (A) Comparison of the UV−vis spectra of benzocarbaporphyrins **8c** (red line) and **8d** in 1% Et_3N−$CHCl_3$. (B) Comparison of the UV−vis spectra of oxypyriporphyrins **7c** (red line) and **7d** in 1% Et_3N−$CHCl_3$.

absorptions appeared at 432, 451, 546, 587, and 610 nm for **7c** (Figure 3b). Similarly, oxybenziporphyrin **1d** gave Soret bands at 436 and 456 nm and Q bands at 552, 596, 639, and 700 nm, while **1c** gave Soret bands at 438 and 465 nm and Q absorptions at 545, 586, 639, and 709 nm. The electronic absorption spectra for azuliporphyrins **21** were also noticeably different, and **21d** showed four absorptions in the Soret region at 368, 404, 451, and 479 nm compared to values of 373, 392, 462, and 489 nm for **21c**. The proton NMR spectra for the "c series" oxybenziporphyrin **6c**, oxypyriporphyrin **7c**, and benzocarbaporphyrin **8c** all showed reduced diatropic character compared to the "d series", and the observed resonances gave values that were closer to those obtained for the original "a series" porphyrinoids. Nevertheless, the diatropicity appeared to be higher for the "c series" compared to the "a series", particularly for oxybenziporphyrin **6c**. The differences observed for the "c series" are unlikely to be due to steric interactions, and there is little reason to suppose that the planarity of these macrocycles has been compromised. The changes are instead attributed to conjugation with the four phenyl substituents. Although these units cannot lie coplanar with the macrocycle, there must be sufficient interactions to affect the UV−vis spectra. This type of conjugation interaction can be represented by dipolar canonical forms such as **22** (Scheme 7) that would not possess the 18π electron delocalization pathway necessary for porphyrinoid aromaticity, and this may be responsible for the observed reduction in diatopic character compared to the "d series". Azuliporphyrin **21c** proved to have excellent solubility characteristics, and the proton NMR spectrum for **21c** in $CDCl_3$ showed the internal CH resonance as a sharp singlet at 2.79 ppm and the NH as a broader peak at 2.65 ppm (Figure 4). The *meso*-protons showed up as two 2H singlets at 8.35 and 9.16 ppm, while the azulene protons closest to the

Scheme 7



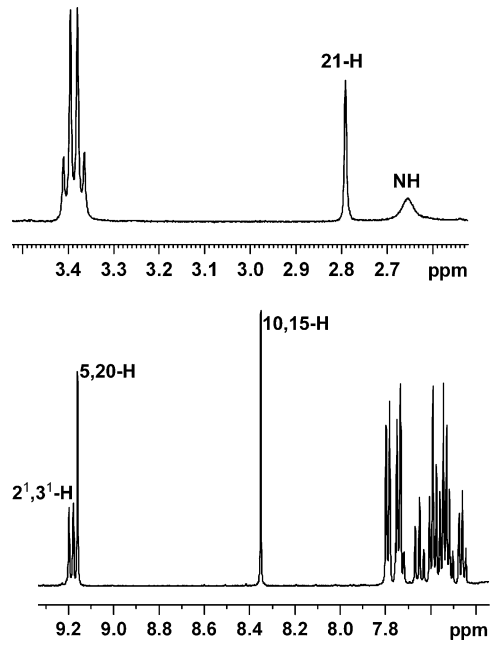


Figure 4. Partial 500 MHz proton NMR spectrum of tetraphenylazuliporphyrin **21c** showing the internal CH and NH resonances and the region corresponding to the external aromatic protons.

macrocycle gave rise to a doublet at 9.19 ppm. These results indicate that **21c** is at least as diatropic as **21d** and has significantly increased diatropicity compared to **21a**. However, addition of TFA gave rise to a dication $\mathbf{21c}H_2^{2+}$ that had reduced diatropicity compared to $\mathbf{21a}H_2^{2+}$ or $\mathbf{21d}H_2^{2+}$. In the proton NMR spectrum for $\mathbf{21c}H_2^{2+}$ in TFA−$CDCl_3$, the internal CH gave a resonance at −2.65 ppm compared to values of −2.91 and −2.98 ppm for $\mathbf{21d}H_2^{2+}$ and $\mathbf{21a}H_2^{2+}$, respectively. In addition, $\mathbf{21c}H_2^{2+}$ gave two 2H singlets for the *meso*-protons at 9.60 and 10.39 ppm, compared to values of 10.08 and 10.47 ppm for $\mathbf{21d}H_2^{2+}$ and 9.60 and 10.45 ppm for $\mathbf{21a}H_2^{2+}$.[12] The small reduction in the diatropicity for $\mathbf{21c}H_2^{2+}$ is attributed to resonance contributors such as $\mathbf{21c''}H_2^{2+}$ (Scheme 6) that do not possess 18π electron delocalization pathways. In the free base form **21c**, the favorability of aromatic dipolar canonical forms such as **21′** (Scheme 6) may be increased due to the reduced electron-donating character of phenyl moieties compared to alkyl substituents, and this could result in the slightly increased aromatic properties of this species.

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CONCLUSIONS

The "3 + 1" variant on the MacDonald condensation remains one of the most versatile routes to *meso*-unsubstituted porphyrinoid systems. Good yields are often obtained, in part due to the tripyrrane intermediates taking on a helical conformation that makes them predisposed to macrocycle formation. The presence of bulky substituents can disfavor the helical conformer and may lead to reduced yields of porphyrinoid products. However, this problem is rarely observed and can be predicted by analyzing the proton NMR spectra for the tripyrrane dibenzyl esters. A more challenging problem arises when the tripyrrolic intermediates are prone to acid-catalyzed cleavage, as this can greatly reduce the yields of the targeted porphyrinoids. It was demonstrated that a tetraphenyltripyrrane of this type that favors the helical conformation gave improved yields when reacted with dialdehydes in neat TFA, as this increased the rate of reaction with the dialdehydes and dilute conditions were not required due to the system being prearranged for cyclization. Although the yields in this case were modest, porphyrinoids with modified spectroscopic characteristics were identified.

EXPERIMENTAL SECTION

Melting points are uncorrected. NMR spectra were recorded using a 400 or 500 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm) relative to $CDCl_3$ (^{1}H residual $CHCl_3$ δ 7.26, ^{13}C $CDCl_3$ triplet δ 77.23) or DMSO-d_6 (^{1}H residual DMSO-d_5 δ 2.49, ^{13}C DMSO-d_6 septet δ 39.7). ^{1}H NMR values are reported as chemical shifts δ, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak) and coupling constant (J). Coupling constants were taken directly from the spectra. 2D experiments were performed by using standard software. High-resolution mass spectra (HRMS) were determined by using a double focusing magnetic sector instrument. ^{1}H and ^{13}C NMR spectra for all new compounds are reported in Supporting Information.

Ethyl 5-Methyl-3,4-diphenylpyrrole-2-carboxylate (9a). A solution of sodium nitrite (10.64 g) in water (16 mL) was added dropwise to a stirred solution of ethyl benzoylacetate (22.2 mL, 24.6 g, 0.128 mol) in acetic acid while maintaining the temperature of the reaction mixture below 15 °C with the aid of a salt−ice bath. The resulting oxime solution was allowed to stir at room temperature overnight. A solution of phenylacetone (17.25 g, 0.129 mol) in acetic acid (80 mL) was heated to 70 °C. The previously prepared oxime solution was added dropwise to the stirred mixture while simultaneously adding a mixture of zinc dust (18 g) and sodium acetate (36 g) in small portions, keeping the temperature of the reaction mixture between 70 and 75 °C throughout. Following completion of the addition, the stirred solution was heated at 120 °C for 30 min. The mixture was cooled to 70 °C and poured into 1000 mL of ice−water. The resulting precipitate was suction filtered and washed with water, followed by 2 × 100 mL of cold ethanol. The product was vacuum-dried overnight to give the pyrrole ester (19.4 g, 63.6 mmol, 50%) as pale pink crystals, mp 169−170 °C (lit. mp[22a] 168 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (3H, t, J = 7.6 Hz), 2.35 (3H, s), 4.19 (2H, q, J = 7.6 Hz), 7.02−7.05 (2H, m), 7.14−7.17 (1H, m), 7.19−7.23 (7H, m), 9.28 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 12.5, 14.3, 60.2, 117.4, 124.3, 126.1, 126.7, 127.4, 128.1, 130.2, 130.5, 131.04, 131.10, 134,7, 134.9, 161.6; EI MS m/z (% rel int) 305 (78, M^+), 259 (100, $[M - EtOH]^+$), 230 (26), 216 (27). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.28; H, 6.29; N, 4.74.

Benzyl 5-Methyl-3,4-diphenylpyrrole-2-carboxylate (9b). A solution of sodium benzyloxide was prepared by reacting sodium metal (0.20 g) with benzyl alcohol (10 mL). A stirred solution of ethyl 3,4-diphenylpyrrole-2-carboxylate (31.57 g, 0.103 mol) in benzyl alcohol (40 mL) was gradually heated in a 250 mL Erlenmeyer flask on an oil bath so that the temperature was raised from room temperature to 230 °C over a 90 min period while periodically adding small portions of the sodium benzyloxide solution. When the vapor temperature reached 190 °C, the last 1 mL of the sodium benzyloxide solution was added, and the reaction was allowed to continue for a further 5 min. The hot solution was poured into a chilled mixture of methanol (100 mL), water (62 mL), and acetic acid (1 mL) while stirring with a glass rod, and the resulting precipitate was collected by suction filtration. Recrystallization from ethanol gave the benzyl ester (30.90 g, 84.2 mmol, 82%) as pale pink crystals, mp 176−177 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (3H, s), 5.20 (2H, s), 7.00−7.03 (2H, m), 7.09−7.12 (2H, m), 7.13−7.17 (1H, m), 7.18−7.23 (7H, m), 7.26−7.29 (3H, m), 9.15 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 12.5, 65.9, 117.1, 124.6, 126.1, 126.8, 127.6, 128.03, 128.05, 128.1, 128.5, 130.4, 130.5, 131.0, 131.5, 134.7, 136.2, 161.2; EI MS m/z (% rel int) 367 (100, M^+), 259 (56, $[M - BnOH]^+$), 233 (43). Anal. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.79; H, 5.80; N, 4.03.

Benzyl 5-Acetoxymethyl-3,4-diphenylpyrrole-2-carboxylate (12). Benzyl 5-methyl-3,4-diphenylpyrrole-2-carboxylate (1.00 g, 2.72 mmol) was gently warmed with acetic acid (32 mL) and acetic anhydride (2 mL) until it was completely dissolved. Lead tetraacetate (95%, 1.27 g, 2.72 mmol) was then added, and the mixture was stirred at room temperature for 16 h. The mixture was poured into ice−water, and the resulting precipitate was suction filtered, washed with water, and dried *in vacuo* overnight. Recrystallization from chloroform−hexanes yielded the acetoxymethylpyrrole (0.951 g, 2.23 mmol, 82%) as a white solid, mp 187−188 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (3H, s), 5.05 (2H, s), 5.20 (2H, s), 7.03−7.06 (2H, m), 7.10−7.12 (2H, m), 7.15−7.24 (8H, m), 7.26−7.28 (3H, m), 9.55 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.2, 57.8, 66.1, 119.3, 126.8, 127.0, 127.4, 127.6, 127.7, 127.9, 128.0, 128.1, 128.3, 128.6, 130.4, 131.0, 133.4, 134.1, 136.0, 160.9, 172.2. Anal. Calcd for $C_{27}H_{23}NO_4$: C, 76.22; H, 5.45; N, 3.29. Found: C, 76.55; H, 5.48; N, 3.52.

2,5-Bis(5-benzyloxycarbonyl-3,4-diphenyl-2-pyrrolylmethyl)-3,4-diethylpyrrole (1c). 3,4-Diethylpyrrole[25] (0.26 g, 2.11 mol) and benzyl 5-acetoxymethyl-3,4-diphenylpyrrole-2-carboxylate[18] (1.80 g, 4.23 mmol) were dissolved in 2-propanol (45 mL), *p*-toluenesulfonic acid monohydrate (0.12 g) was added, and the resulting mixture was stirred under reflux for 16 h. The solution was allowed to cool to room temperature and further cooled in an ice bath. The resulting precipitate was suction filtered, washed with 2-propanol, and dried *in vacuo* overnight to give the tripyrrane dibenzyl ester (1.36 g, 1.59 mmol, 75%) as an off-white solid, mp 219 °C, dec; ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ 0.85 (6H, t, J = 7.4 Hz), 2.19 (4H, br), 3.59 (2H, br), 4.02 (4H, br), 4.83 (2H, br), 6.43 (4H, br d, J = 7.0 Hz), 6.78−6.81 (4H, m), 6.97−7.03 (8H, m), 7.05−7.11 (12H, m), 7.18−7.22 (2H, m), 9.74 (1H, br s), 12.22 (2H, br s); ^{1}H NMR (500 MHz, 50 °C, $CDCl_3$) δ 0.87 (6H, t, J = 7.4 Hz), 2.20 (4H, q, J = 7.4 Hz), 3.82 (4H, br s), 4.66 (4H, v br), 6.49 (4H, br d, J = 7.0 Hz), 6.81−6.84 (4H, m), 6.99−7.04 (8H, m), 7.06−7.12 (12H, m), 7.16−7.20 (2H, m), 9.58 (1H, br s), 12.01 (2H, br s); ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.63 (6H, t, J = 7.5 Hz), 1.85 (4H, q, J = 7.5 Hz), 3.79 (4H, s), 5.12 (4H, s), 6.87−6.89 (4H, m), 6.78−6.81 (4H, m), 7.05−7.14 (20H, m), 7.23−7.26 (6H, m), 9.30 (1H, s), 11.73 (2H, s); ^{13}C NMR ($CDCl_3$) δ 16.6, 17.7, 22.9, 66.0, 117.7, 119.7, 122.6, 124.5, 126.1, 126.4, 126.5, 127.2, 127.6, 128.02, 128.05, 130.4, 131.2, 131.4, 134.3, 134.4, 135.1, 135.9, 163.2; HR MS (FAB) calcd for $C_{58}H_{51}N_3O_4$ 853.3879, found 853.3871. Anal. Calcd for $C_{58}H_{51}N_3O_4$: C, 81.57; H, 6.02; N, 4.92. Found: C, 81.60; H, 5.99; N, 5.10.

2,5-Bis(5-benzyloxycarbonyl-3-*tert*-butyl-4-methyl-2-pyrrolylmethyl)-3,4-diphenylpyrrole (1d). 3,4-Diphenylpyrrole[26] (0.48 g, 2.19 mmol) and benzyl 5-acetoxymethyl-4-*tert*-butyl-3-methylpyrrole-2-carboxylate[18] (1.50 g, 4.37 mmol) were dissolved in 2-propanol (12.5 mL) and acetic acid (1.5 mL). The resulting solution was stirred and refluxed under an atmosphere of nitrogen for 16 h. The mixture was allowed to cool to room temperature and further cooled in an ice bath. The resulting precipitate was filtered, washed with cold ethanol, and dried *in vacuo* overnight to give the tripyrrane (1.34 g, 1.69 mmol, 77%) as an off-white powder, mp 236−237 °C; ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ 1.04 (18H, br s), 2.49 (6H, s), 4.02 (4H, br s), 4.88 (4H, br s), 6.99−7.02 (4H, m), 7.13−7.24 (10H, m), 7.27−7.35 (6H,

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m), 8.89 (2H, v br), 11.29 (1H, v br); ^{1}H NMR (500 MHz, 50 °C, $CDCl_3$) δ 1.15 (18H, s), 2.49 (6H, s), 4.05 (4H, s), 5.04 (4H, br s), 7.01−7.04 (4H, m), 7.13−7.16 (2H, m), 7.18−7.22 (4H, m), 7.27−7.34 (10H, m), 7.96 (1H, v br), 9.16 (2H, v br); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.02 (18H, br s), 2.33 (6H, s), 4.06 (4H, s), 5.20 (4H, s), 6.96−6.98 (4H, m), 7.07−7.11 (2H, m), 7.16−7.20 (4H, m), 7.29−7.33 (2H, m), 7.34−7.37 (4H, m), 7.38−7.41 (4H, m), 8.34 (1H, s), 10.62 (2H, s); ^{13}C NMR (50 °C, $CDCl_3$) δ 14.0, 26.7, 31.9, 33.1, 65.7, 118.4, 121.7, 124.9, 125.9, 127.8, 128.1, 128.2, 128.8, 129.6, 130.5, 135.9, 137.0, 161.7; ^{13}C NMR (500 MHz, DMSO-d_6) δ 13.4, 25.9, 31.2, 32.4, 64.5, 117.3, 119.4, 124.9, 125.3, 127.0, 127.95, 127.96, 127.98, 128.3, 128.5, 128.7, 129.7, 136.0, 136.9, 160.4; HR MS (ESI) calcd for $C_{52}H_{55}N_3O_4$ + H 786.4271, found 786.4272. Anal. Calcd for $C_{52}H_{55}N_3O_4$: C, 79.46; H, 7.05; N, 5.35. Found: C, 79.40; H, 7.08; N, 5.47.

13,14-Diethyl-8,9,18,19-tetraphenyl-2-oxybenziporphyrin (6c). Method A. Tetraphenyltripyrrane dibenzyl ester **1c** (0.600 g, 0.703 mmol) was placed in a hydrogenation vessel and dissolved in freshly distilled THF (150 mL), methanol (50 mL), and triethylamine (20 drops). After flushing the solution with nitrogen, 10% palladium on activated carbon (100 mg) was added, and the resulting mixture was shaken under hydrogen (40 psi) at room temperature overnight. The catalyst was removed by suction filtration, and the solvent was removed under reduced pressure. The residue was dissolved in 5% aqueous ammonia (50 mL), and the solution was neutralized with acetic acid to a litmus end point while maintaining the temperature at 0−5 °C using an ice−salt bath. The resulting precipitate was suction filtered and washed repeatedly with water to remove all traces of acid. After drying overnight in a vacuum desiccator, tripyrrane dicarboxylic acid **2c** (0.472 g, 0.701 mmol, quantitative) was obtained as a reddish powder. This was used for porphyrinoid synthesis without further purification. ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.62 (6H, t, J = 7.4 Hz), 1.83 (4H, q, J = 7.4 Hz), 3.77 (4H, s), 6.87−6.90 (4H, m), 7.06−7.15 (16H, m), 9.47 (1H, br s), 10.88 (2H, v br), 11.54 (2H, br s); ^{13}C NMR (500 MHz, DMSO-d_6) δ 16.3, 16.8, 22.4, 118.0, 118.9, 122.3, 123.2, 125.8, 126.0, 127.1, 127.3, 127.8, 128.1, 129.3, 130.4, 130.9, 132.2, 135.0, 135.3, 162.3.

The foregoing tripyrrane dicarboxylic acid (101.4 mg, 0.150 mmol) was dissolved in TFA (1 mL) and stirred under nitrogen for 5 min. The solution was diluted with dichloromethane (99 mL), 5-formylsalicylaldehyde (22.7 mg, 0.151 mmol) was added, and the mixture was stirred for 16 h at room temperature in the dark under a nitrogen atmosphere. The solution was neutralized by the dropwise addition of triethylamine, DDQ (36.5 mg) was added, and the resulting solution stirred for an additional 1 h. The solution was washed with water, and the solvent was removed on a rotary evaporator. The residue was purified by column chromatography on grade 3 neutral alumina, eluting with dichloromethane. The product was collected as a dark green band. Recrystallization from chloroform−methanol gave the oxybenziporphyrin (14.4 mg, 0.021 mmol, 14%) as shiny purple crystals, mp 288−290 °C, dec; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} ($\log_{10}$ ε) 438 (5.21), 465 (5.02), 545 (4.03), 586 (4.21), 639 (3.77), 709 nm (3.55); UV−vis (1% TFA−$CHCl_3$) λ_{max} ($\log_{10}$ ε) 328 (4.56), 440 (5.21), 479 (4.95), 563 (4.01), 613 (4.10), 634 nm (4.14); ^{1}H NMR (500 MHz, $CDCl_3$) δ −5.86 (1H, br d, J = 2.0 Hz), 1.70 (6H, t, J = 7.6 Hz), 3.63−3.68 (4H, two overlapping quartets), 7.37 (1H, d, J = 9.4 Hz), 7.59−7.70 (12H, m), 7.87−7.94 (8H, m), 8.66 (1H, dd, J = 2.2, 9.6 Hz), 9.45 (1H, s), 9.51 (1H, s), 9.59 (1H, s), 10.55 (1H, s); ^{13}C NMR ($CDCl_3$) δ 17.97, 18.05, 19.8, 96.8, 98.6, 110.0, 113.4, 115.5, 123.4, 127.6, 128.07, 128.14, 128.40, 128.45, 128.90, 128.92, 128.94, 130.8, 132.0, 132.49, 132.51, 132.8, 132.9, 134.0, 134.27, 134.33, 134.35, 134.6, 135.5, 136.3, 138.2, 140.0, 141.1, 143.1, 145.4, 145.9, 147.8, 155.8, 157.3, 188.1; HRMS (EI) calcd for $C_{50}H_{39}N_3O$ 697.3093, found 697.3097. Anal. Calcd for $C_{50}H_{39}N_3O$·0.3$CHCl_3$: C, 82.34; H, 5.39; N, 5.73. Found: C, 82.50; H, 4.99; N, 5.93.

Method B. Tripyrrane **2c** (100 mg) and 5-formylsalicylaldehyde (22.4 mg, 0.149 mmol) were stirred with TFA (5 mL) for 1 h at room temperature under nitrogen. The solution was diluted with dichloromethane and shaken with a 0.1% aqueous ferric chloride solution for 7−8 min. The two layers were separated, and the aqueous solution was extracted with dichloromethane. The combined organic phases were washed with water and 5% sodium bicarbonate solution and then evaporated under reduced pressure. The residue was purified on a grade 3 neutral alumina column, eluting with dichloromethane, and a dark green product fraction was collected. The solvent was removed on a rotary evaporator, and the residue was recrystallized from chloroform−methanol to give the porphyrinoid product (20.4 mg, 0.0292 mmol, 20%) as purple crystals, mp 288−289 °C, dec.

13,14-Diethyl-8,9,18,19-tetraphenyl-2-oxypyriporphyrin (7c). Using method B, 3-hydroxy-2,6-pyridinedicarbaldehyde[11] (22.5 mg, 0.149 mmol) was reacted with tripyrrane **2c** (100 mg, 0.148 mmol). Recrystallization from chloroform−methanol gave the oxypyriporphyrin (26.2 mg, 0.0375 mmol, 25%) as purple crystals, mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} ($\log_{10}$ ε) 432 (5.28), 451 (5.09), 546 (4.09), 587 (4.25), 610 (4.10), 670 nm (3.55); UV−vis (1% TFA−$CHCl_3$) λ_{max} ($\log_{10}$ ε) 433 (5.21), 456 (5.11), 550 (3.95), 594 (4.29), 646 (3.91), 720 nm (3.72); ^{1}H NMR (500 MHz, $CDCl_3$) δ −2.92 (1H, br s), −2.75 (1H, br s), 1.75 (6H, t, J = 7.6 Hz), 3.74 (4H, q, J = 7.6 Hz), 7.62−7.73 (12H, m), 7.83−7.88 (1H, m), 7.94−8.00 (8H, m), 9.20 (1H, br d, J = 9.5 Hz), 9.68 (1H, s), 9.89 (1H, s), 9.90 (1H, s), 10.98 (1H, s); ^{1}H NMR (500 MHz, TFA−$CDCl_3$) δ −0.50 (2H, v br), 1.55−1.59 (6H, two overlapping triplets), 3.80−3.86 (4H, two overlapping quartets), 7.60−7.66 (12H, m), 7.67−7.73 (4H, m), 7.75−7.78 (4H, m), 8.43 (1H, d, J = 9.7 Hz), 9.54 (1H, d, J = 9.7 Hz), 9.95 (1H, s), 10.314 (1H, s), 10.316 (1H, s), 10.90 (1H, s); ^{13}C NMR ($CDCl_3$) δ 18.16, 18.19, 19.8, 100.1, 100.4, 107.1, 111.6, 128.2, 128.35, 128.38, 128.90, 128.93, 132.0, 132.71, 132.74, 132.8, 133.1, 134.4, 134.5, 134.7, 145.8, 146.4, 156.7, 185.7; ^{13}C NMR (TFA−$CDCl_3$) δ 17.28, 17.33, 20.1, 103.8, 104.0, 105.1, 108.5, 110.8, 113.1, 115.4, 117.6, 129.56, 129.58, 129.85, 129.88, 129.94, 131.5, 131.6, 131.7, 132.39, 132.44, 132.5, 132.6, 133.0, 135.2, 136.3, 141.5, 141.8, 142.1, 142.6, 143.0, 143.4, 143.6, 144.0, 144.1, 145.3, 145.5, 179.8; HRMS (EI) calcd for $C_{49}H_{38}N_4O$ 698.3045, found 698.3031.

12,13-Diethyl-7,8,17,18-tetraphenyl-21-carbabenzo[*b*]-porphyrin (8c). Using method B, indene dialdehyde **5**[27] (25.6 mg, 0.149 mmol) was reacted with **2c** (100 mg, 0.148 mmol). Recrystallization from chloroform−methanol gave the benzocarbaporphyrin (8.5 mg, 0.012 mmol, 8.0%) as purple crystals, mp >300 °C; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} ($\log_{10}$ ε) 383 (4.71), 434 (5.19), 453 (sh, 4.81), 517 (4.43), 549 (sh, 3.84), 616 (3.82), 677 nm (3.88); UV−vis (1% TFA−$CHCl_3$) λ_{max} ($\log_{10}$ ε) 315 (4.51), 408 (4.87), 447 (4.97), 483 (4.73), 560 (4.19), 626 nm (4.10); ^{1}H NMR (500 MHz, $CDCl_3$) δ −6.25 (1H, s), −3.25 (2H, v br), 1.78 (6H, t, J = 7.7 Hz), 3.81 (4H, q, J = 7.7 Hz), 7.61−7.75 (14H, m), 8.03−8.06 (8H, m), 8.62−8.66 (2H, m), 9.90 (2H, s), 10.12 (2H, s); ^{13}C NMR ($CDCl_3$) δ 18.4, 20.0, 98.6, 102.3, 110.3, 120.9, 126.9, 127.9, 128.0, 128.89, 128.91, 132.7, 133.0, 134.6, 135.0, 135.2, 135.37, 135.44, 135.9, 137.8, 141.4, 145.1, 154.2; HRMS (EI) calcd for $C_{53}H_{41}N_3$ 719.3301, found 719.3308.

12,13-Diethyl-7,8,17,18-tetraphenylazuliporphyrin (21c). Using method B, tripyrrane **2c** (100 mg, 0.148 mmol) was reacted with 1,3-azulenedicarbaldehyde[28] (27.4 mg, 0.149 mmol). The product was purified by column chromatography on basic grade 3 alumina, eluting initially with chloroform and then with 1−2% methanol−chloroform. Recrystallization from chloroform−hexanes gave then with azuliporphyrin (16.6 mg, 0.0227 mmol, 15%) as dark purple crystals, mp >300 °C, dec; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} ($\log_{10}$ ε) 373 (sh, 4.83), 392 (4.83), 462 (4.71), 489 (4.86), 668 nm (4.09); UV−vis (1% TFA−$CHCl_3$) λ_{max} ($\log_{10}$ ε) 380 (4.92), 478 (5.00), 646 nm (4.26); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57 (6H, t, J = 7.6 Hz), 2.65 (1H, br s), 2.79 (1H, s), 3.39 (4H, q, J = 7.6 Hz), 7.44−7.48 (2H, m), 7.50−7.61 (10H, m), 7.65 (2H, t, J = 9.5 Hz), 7.71−7.75 (5H, m), 7.77−7.80 (4H, m), 8.35 (2H, s), 9.16 (2H, s), 9.19 (2H, d, J = 9.6 Hz); ^{1}H NMR (500 MHz, TFA−$CDCl_3$) δ −2.65 (1H, s), −1.32 (2H, v br), 1.63 (6H, t, J = 7.7 Hz), 3.72 (4H, q, J = 7.7 Hz), 7.66−7.75 (12H, m), 7.78−7.81 (4H, m), 7.85−7.88 (4H, m), 8.53 (1H, t, J = 9.5 Hz), 8.61 (2H, t, J = 9.5 Hz), 9.60 (2H, s), 9.86 (2H, d, J = 9.6 Hz), 10.39 (2H, s); ^{13}C NMR ($CDCl_3$) δ 16.8, 18.8, 95.7, 112.6, 126.8, 127.0, 128.2, 128.3, 131.5, 131.7, 133.2, 135.6, 135.88, 135.91, 136.3,

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140.2, 140.6, 141.6, 142.7, 146.3, 150.3, 153.4, 159.5; ^{13}C NMR (TFA–$CDCl_3$) δ 16.8, 19.7, 98.2, 113.6, 124.4, 129.1, 129.5, 129.6, 129.9, 131.9, 132.0, 132.1, 132.2, 140.0, 140.7, 143.3, 145.1, 145.2, 145.5, 146.2, 146.7, 154.7; HRMS (ESI) calcd for $C_{54}H_{41}N_3$ + H 732.3379, found 732.3378.

9,18-Di-*tert*-butyl-8,19-dimethyl-13,14-diphenyl-2-oxybenziporphyrin (6d). Using method A, tripyrrane dicarboxylic acid **2d** (100 mg, 0.165 mmol) was condensed with 5-formylsalicylaldehyde (24.8 mg, 0.165 mmol). Recrystallization from chloroform–methanol gave oxybenziporphyrin **6d** (64.5 mg, 0.102 mmol, 62%) as purple crystals, mp >300 °C. When the reaction was performed on the same scale with 1 mL of TFA and 19 mL of CH_2Cl_2 for 2 h, 54.2 mg of the porphyrinoid product (0.0862 mmol, 52%) was obtained. UV–vis (1% Et_3N–$CHCl_3$) λ_{max} ($\log_{10}$ ε) 343 (4.43), 436 (5.29), 456 (4.94), 552 (3.86), 596 (4.44), 639 (3.94), 700 nm (3.75); UV–vis (1% TFA–$CHCl_3$) λ_{max} ($\log_{10}$ ε) 333 (4.44), 442 (5.17), 475 (4.72), 620 (4.11), 704 nm (3.69); ^{1}H NMR (500 MHz, $CDCl_3$) δ −6.35 (1H, s), −2.80 (1H, br s), −2.65 (1H, br s), 2.11 (9H, s), 2.12 (9H, s), 3.69 (3H, s), 3.77 (3H, s), 7.44 (1H, d, J = 9.4 Hz), 7.56–7.60 (2H, m), 7.64–7.67 (4H, m), 7.89–7.92 (4H, m), 8.74 (1H, dd, J = 1.4, 9.4 Hz), 9.39 (1H, s), 9.99 (1H, s), 10.07 (1H, s), 10.65 (1H, s); ^{13}C NMR ($CDCl_3$) δ 14.9, 15.1, 34.3, 34.4, 36.14, 36.16, 101.1, 103.0, 105.6, 111.2, 111.9, 122.3, 126.7, 127.7, 128.5, 130.4, 132.3, 132.7, 134.9, 135.4, 136.1, 137.8, 138.9, 140.8, 142.0, 142.6, 145.2, 145.7, 148.1, 153.5, 154.9, 188.4; HRMS (EI) calcd for $C_{44}H_{43}N_3O$ 629.3406, found 629.3394. Anal. Calcd for $C_{44}H_{43}N_3O$: C, 83.91; H, 6.88; N, 6.67. Found: C, 83.51; H, 6.83; N, 6.65.

9,18-Di-*tert*-butyl-8,19-dimethyl-13,14-diphenyl-2-oxypyriporphyrin (7d). Using method A, dialdehyde **4**[11] (25.0 mg, 0.165 mmol) was reacted with tripyrrane **2d** (100 mg, 0.165 mmol). Recrystallization from chloroform–methanol gave the diphenyloxypyriporphyrin (83.2 mg, 0.132 mmol, 80%) as lustrous purple crystals, mp >300 °C. When the reaction was performed on the same scale with 1 mL of TFA and 19 mL of CH_2Cl_2 for 2 h, 83.5 mg of product (0.132 mmol, 80%) was obtained. UV–vis (1% Et_3N–$CHCl_3$) λ_{max} ($\log_{10}$ ε) 403 (infl, 4.75), 429 (5.40), 442 (sh, 5.11), 546 (3.82), 592 (4.37), 614 nm (4.50); UV–vis (1% TFA–$CHCl_3$) λ_{max} ($\log_{10}$ ε) 430 (5.25), 445 (5.09), 548 (3.88), 598 (4.41), 627 (sh, 4.22), 702 nm (4.02); ^{1}H NMR (500 MHz, $CDCl_3$) δ −3.15 (1H, br s), −3.05 (1H, br s), 2.192 (9H, s), 2.195 (9H, s), 3.81 (3H, s), 3.89 (3H, s), 7.58–7.62 (2H, m), 7.68 (4H, t, J = 7.5 Hz), 7.92–7.96 (5H, m), 9.31 (1H, d, J = 9.4 Hz), 9.63 (1H, s), 10.37 (1H, s), 10.38 (1H, s), 11.09 (1H, s); ^{1}H NMR (500 MHz, TFA–$CDCl_3$) δ −1.23 (1H, br s), −1.10 (1H, br s), 2.064 (9H, s), 2.067 (9H, s), 3.63 (3H, s), 3.68 (3H, s), 7.70–7.75 (6H, m), 7.77–7.81 (4H, m), 8.63 (1H, d, J = 9.6 Hz), 9.76 (1H, d, J = 9.6 Hz), 10.08 (1H, s), 10.81 (1H, s), 10.83 (1H, s), 11.01 (1H, s); ^{13}C NMR ($CDCl_3$) δ 14.9, 15.2, 34.7, 36.41, 36.43, 103.2, 103.5, 104.0, 107.7, 127.7, 128.6, 131.7, 132.4, 134.5, 134.9, 136.0, 136.4, 137.0, 138.8, 139.5, 144.4, 144.8, 145.0, 145.2, 145.3, 146.8, 153.2, 153.6, 186.1; ^{13}C NMR (TFA–$CDCl_3$) δ 14.9, 15.2, 33.3, 36.40, 36.43, 101.2, 104.9, 106.1, 106.4, 129.41, 129.45, 129.8, 131.24, 131.28, 131.8, 131.9, 134.2, 135.1, 138.6, 139.8, 141.8, 142.0, 142.4, 142.5, 143.3, 144.2, 144.6, 144.9, 148.5, 148.8, 179.8; HRMS (EI) calcd for $C_{43}H_{42}N_4O$ 630.3358, found 630.3343. Anal. Calcd for $C_{43}H_{42}N_4O$: C, 81.87; H, 6.71; N, 8.88. Found: C, 82.15; H, 6.78; N, 8.79.

8,17-Di-*tert*-butyl-7,18-dimethyl-12,13-diphenyl-21-carbabenzo[*b*]porphyrin (8d). Using method A, tripyrrane **2d** (100 mg, 0.165 mmol) was reacted with indene dialdehyde **5**[27] (28.5 mg, 0.165 mmol). Recrystallization from chloroform–methanol gave the diphenylcarbaporphyrin (48.9 mg, 44%) as purple crystals, mp >300 °C. When the reaction was performed on the same scale with 1 mL of TFA and 19 mL of CH_2Cl_2 for 2 h, 46.3 mg of product (0.0711 mmol, 43%) was obtained. UV–vis (1% Et_3N–$CHCl_3$) λ_{max} ($\log_{10}$ ε) 386 (4.61), 432 (5.32), 521 (4.21), 556 (4.19), 604 (3.87), 664 nm (3.31); UV–vis (1% TFA–$CHCl_3$) λ_{max} ($\log_{10}$ ε) 315 (4.44), 404 (sh, 4.74), 448 (5.13), 480 (4.61), 561 (4.09), 618 nm (4.03); ^{1}H NMR (500 MHz, $CDCl_3$) δ −6.75 (1H, s), −3.76 (2H, br s), 2.19 (18H, s), 3.86 (6H, s), 7.56–7.60 (2H, m), 7.65–7.68 (4H, m), 7.74–7.77 (2H, m), 7.96–7.98 (4H, m), 8.83–8.87 (2H, m), 10.17 (2H, s), 10.37 (2H, s); ^{13}C NMR ($CDCl_3$) δ 14.9, 34.5, 36.4, 98.1, 103.0, 108.6, 120.6, 126.8, 127.3, 128.4, 132.2, 132.7, 134.5, 135.9, 136.1, 137.1, 141.8, 143.1, 144.7, 151.1; HRMS (EI) calcd for $C_{47}H_{45}N_3$ 651.3614, found 651.3621. Anal. Calcd for $C_{47}H_{45}N_3$: C, 86.60; H, 6.96; N, 6.45. Found: C, 86.52; H, 7.00; N, 6.30.

8,17-Di-*tert*-butyl-7,18-dimethyl-12,13-diphenylazuliporphyrin (21d). 1,3-Azulenedicarbaldehyde[28] (29.6 mmol, 0.165 mmol) was reacted with tripyrrane **2d** (100 mg, 0.165 mmol) using the foregoing procedure. The product was purified by column chromatography on basic grade 3 alumina, eluting initially with chloroform and then with 1–2% methanol–chloroform. Recrystallization from chloroform–hexanes gave diphenylazuliporphyrin **21d** (71.2 mg, 0.07 mmol, 65%) as dark green crystals, mp >300 °C. When the reaction was performed on the same scale with 1 mL of TFA and 19 mL of CH_2Cl_2 for 2 h, 64.9 mg of product (0.0979 mmol, 59%) was obtained. UV–vis (1% Et_3N–$CHCl_3$) λ_{max} ($\log_{10}$ ε) 368 (4.79), 404 (4.75), 451 (4.73), 479 (4.80), 640 nm (4.17); UV–vis (1% TFA–$CHCl_3$) λ_{max} ($\log_{10}$ ε) 374 (4.89), 476 (5.01), 655 nm (4.36); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85 (18H, s), 2.53 (1H, br s), 2.88 (1H, br s), 3.21 (6H, s), 7.42 (2H, t, J = 9.5 Hz), 7.48–7.52 (3H, m), 7.53–7.57 (4H, m), 7.73–7.75 (4H, m), 8.61 (2H, s), 8.95 (2H, s), 9.08 (2H, d, J = 9.5 Hz); ^{1}H NMR (500 MHz, TFA–$CDCl_3$) δ −2.91 (1H, s), −1.60 (1H, v br), −0.72 (2H, s), 2.02 (18H, s), 3.67 (6H, s), 7.68–7.72 (6H, m), 7.76–7.79 (4H, m), 8.57 (1H, t, J = 9.6 Hz), 8.68 (2H, t, J = 9.7 Hz), 10.04 (2H, d, J = 9.6 Hz), 10.08 (2H, s), 10.47 (2H, s); ^{13}C NMR (50 °C, $CDCl_3$) δ 13.9, 33.9, 34.9, 100.9, 107.8, 126.5, 127.9, 128.4, 131.8, 132.1, 134.87, 134.94, 138.1, 140.0, 146.6, 149.0, 155.7, 162.8; ^{13}C NMR (TFA–$CDCl_3$) δ 14.9, 33.3, 36.4, 101.3, 109.6, 122.8, 125.2, 128.4, 129.6, 130.0, 131.8, 131.9, 140.7, 141.8, 142.1, 143.0, 143.09, 143.12, 146.86, 146.90, 147.6, 154.4; HRMS (ESI) calcd for $C_{48}H_{45}N_3$ + H 664.3692, found 664.3692. Anal. Calcd for $C_{48}H_{45}N_3 \cdot {}^1/_3H_2O$: C, 86.06; H, 6.87; N, 6.27. Found: C, 85.98; H, 6.88; N, 6.27.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected ^{1}H NMR, ^{1}H–^{1}H COSY, HMQC, ^{13}C NMR, MS, and UV–vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

Ⓡ Related Articles

Part 63 in the series "Conjugated Macrocycles Related to the Porphyrins". For part 62, see: Lash, T. D.; Lammer, A. D.; Ferrence, G. M. *Angew. Chem., Int. Ed.* **2012**, in press; DOI: 10.1002/anie.201206385.

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Notes

The authors declare no competing financial interest.

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