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Naphthiporphyrins†

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Supporting Information

ABSTRACT: Benziporphyrins, cross-conjugated porphyrin analogues with a benzene ring in place of one of the usual pyrrole units, have varying degrees of macrocyclic aromaticity because the 6π electron arene needs to give up its aromatic characteristics to facilitate conjugation over the entire system. As naphthalene would lose less resonance stabilization energy in giving up one of its benzene units, it was proposed that naphthiporphyrins would exhibit enhanced diatropicity compared to the related benziporphyrins. A naphthiporphyrin was prepared using the "3 + 1" variant of the MacDonald condensation by reacting 1,3-naphthalenedicarbaldehyde with a tripyrrane in the presence of TFA, followed by oxidation with DDQ. Although the free base form of naphthiporphyrin showed no overall diatropicity, the corresponding dication in TFA-$CDCl_3$ demonstrated a significant diatropic ring current where the internal CH shifted upfield to between 4.0 and 4.6 ppm. Naphthiporphyrin was converted to the corresponding palladium(II) complexes by reaction with $Pd(OAc)_2$ in acetonitrile, and the complex was further characterized by X-ray crystallography. Oxynaphthiporphyrins were similarly prepared by the "3 + 1" methodology from 4-methoxy-1,3-naphthalene-dicarbaldehyde, and these showed slightly enhanced diatropic character compared to oxybenziporphyrins. Reaction of oxybenziporphyrins or oxynaphthiporphyrins with silver(I) acetate afforded the corresponding silver(III) organometallic derivatives. A *meso*-tetraphenyl naphthiporphyrin was also synthesized in 4% yield by reacting a 1,4-naphthalene dicarbinol with 2 equiv of benzaldehyde and 3 equiv of pyrrole in the presence of $BF_3.Et_2O$, followed by oxidation with DDQ. However, this 1,4-naphthiporphyrin showed reduced diatropic character compared to the corresponding *p*-benziporphyrin system. The NMR spectra for the 1,4-naphthiporphyrin show that the naphthalene unit pivots over the macrocycle and this presumably leads to further steric interactions that reduce the planarity of the macrocycle. These results demonstrate that while naphthiporphyrins can show enhanced aromatic properties as predicted, other factors may overwhelm this effect.

INTRODUCTION

Carbaporphyrinoid systems, where one of the usual pyrrole units in the porphyrin macrocycle has been replaced with a carbocyclic ring, show diverse spectroscopic properties and chemical reactivity.[1−5] While some carbaporphyrins (e.g., **1** and **2**) show strong diatropic ring currents,[6,7] azuliporphyrins **3** have much reduced aromatic properties[8] and benziporphyrins **4** exhibit virtually no macrocyclic aromaticity.[9−11] In benzocarbaporphyrins **1**[6] and tropiporphyrins **2**,[7] the macrocycles possess 18π electron delocalization pathways that are analogous to those found in true porphyrins, and this provides an explanation for their porphyrin-like aromatic properties.[12,13] Azuliporphyrins, on the other hand, are cross-conjugated and this interrupts any potential aromatic delocalization pathway.[8] Nevertheless, the internal CH in azuliporphyrins shows up near 3 ppm in their proton NMR spectra, and this result demonstrates that a significant albeit weakened ring current is present in this system as well.[8] This observation can be rationalized with dipolar resonance contributors (e.g., **5**) that possess both an 18π electron delocalization pathway as well as tropylium character.[8] However, cross-conjugation in benziporphyrins appears to prevent any macrocyclic delocalization, and **4** shows its internal CH resonance at a typical benzene chemical shift of 7.9 ppm.[11] The *meso*-protons gave two 2H resonances at 6.57 (11, 16-CH) and 7.27 ppm (6,21-CH), values that are considerably upfield compared to those given by **1**-**3** and that are consistent with a nonaromatic porphyrinoid.[11] Benziporphyrins would have to give up the favorable 6π-electron arene aromaticity of the benzene unit to gain an [18]annulene type conjugation pathway, and dipolar canonical forms like **6** would not be expected to contribute significantly to the properties of this system. However, addition of TFA to NMR solutions of benziporphyrin **4** afforded a dication $\mathbf{4}H_2^{2+}$ which showed an upfield shift to the interior CH to 5 ppm, while the external *meso*-protons shifted downfield by approximately 1 ppm.[11] This result suggests that the dication has a small diamagnetic ring current, presumably due to resonance contributors like **7** which aid in charge delocalization. Tetraarylbenziporphyrins **8** have also been synthesized,[14−18] and these too exhibit small diagmagnetic

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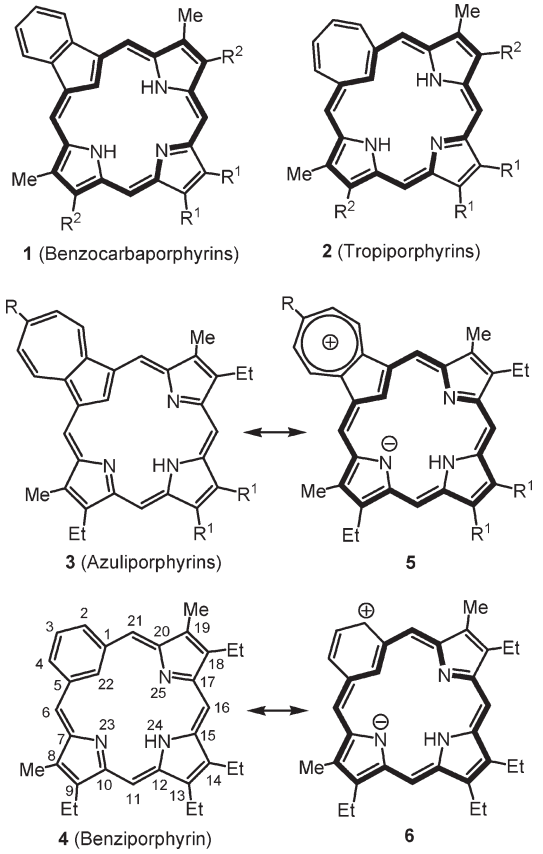
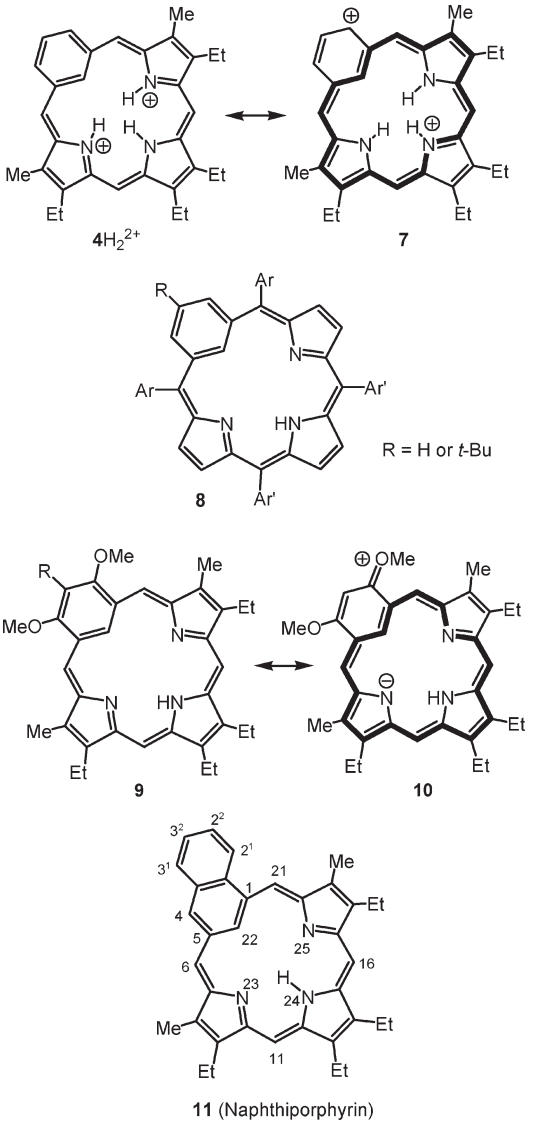
ring currents for the protonated species that are enhanced when an electron-donating *tert*-butyl moiety is attached to the benzene subunit.[18] Dimethoxybenziporphyrins **9** have also been reported, and these show some diatropic character even for the free base forms and substantially increased diatropicity for the corresponding dications.[16,17,19] These improved aromatic characteristics have been attributed to the influence of the electron-donating methoxy substituents which stabilize resonance contributors with 18π electron delocalization pathways (e.g., **10**).[19]



Benziporphyrins not only provide insights into porphyrinoid aromaticity but they also exhibit interesting and unusual reactivity, undergoing regioselective oxidation reactions[15,17,20] and readily forming organometallic derivatives.[14−18,21] Given the significance of these porphyrin analogues, we wanted to extend these studies to the synthesis of naphthiporphyrins (e.g., **11**) where a naphthalene moiety is introduced in place of a benzene unit. As the resonance stabilization of an individual benzene ring within the naphthalene framework is far less than that for benzene itself,[22] it was anticipated that naphthiporphyrins could take on increased diatropic characteristics. In essence, we postulated that the penalty for losing 6π electron arene aromaticity in canonical forms such as **12** (Scheme 1) should be somewhat reduced and that this should result in increased diatropic character in naphthiporphyrins compared to benziporphyrins. To test this hypothesis, syntheses of naphthalene-containing porphyrinoids were developed.[23] The results from these investigations, together with the spectroscopic properties of naphthiporphyrins and their metallo-derivatives, are presented below.



RESULTS AND DISCUSSION

Synthesis, Metalation, and Spectroscopic Properties of a Naphthiporphyrin. Benziporphyrin had previously been synthesized by reacting tripyrrane **13a**[24,25] with isophthalaldehyde in the presence of TFA in dichloromethane, followed by neutralization with triethylamine and oxidation with DDQ.[11] In this work, improved results were obtained when the oxidation was carried out without first neutralizing the solution and benziporphyrin **4** was isolated in 29% yield (Scheme 1). Similarly, 1,3-naphthalenedicarbaldehyde[26] reacted with tripyrrane **13a** under these conditions to give naphthiporphyrin **11** in 24% yield (Scheme 1). Much poorer results were obtained if the solution was neutralized with triethylamine prior to oxidation and the product was contaminated with an aromatic oxidation product oxynaphthiporphyrin (see later). Naphthiporphyrin was isolated as a stable dark-green-colored compound but showed no significant aromatic character. The UV−vis spectrum of naphthiporphyrin **11** showed two moderately strong bands at 329 and

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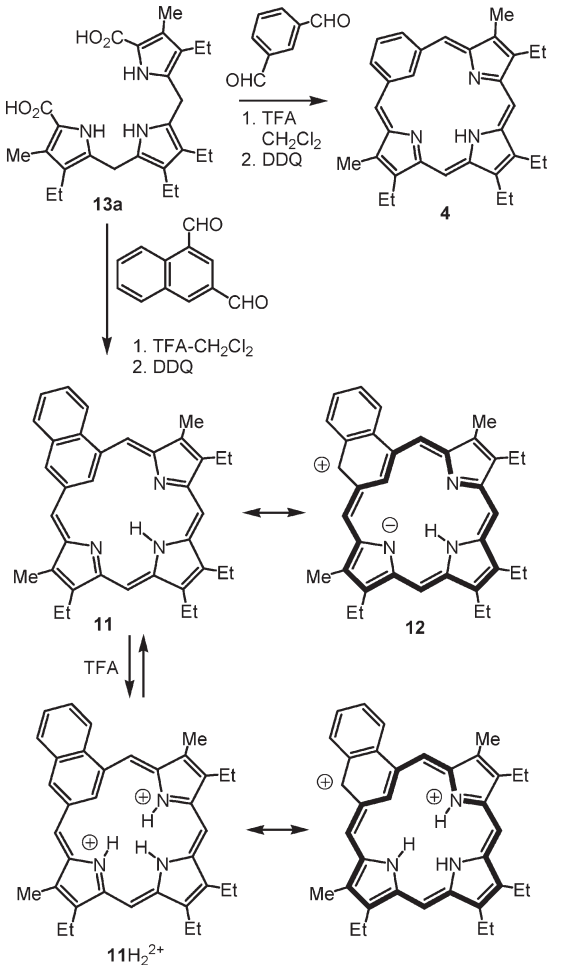
Scheme 1



410 nm and weaker poorly defined absorptions that extended beyond 800 nm (Figure 1). The spectrum was bathochromically shifted but otherwise similar to the UV−vis spectrum for benziporphyrin, which shows two peaks at 316 and 383 nm and smaller broad absorptions in the visible region (Figure 1). The proton NMR spectrum for **11** in $CDCl_3$ also gave no indication of a macrocyclic ring current (Figure 2). Aromatic character could have resulted from contributions from dipolar canonical forms such as **12** (Scheme 1) or from the existence of a tautomeric species **14** that has an 18π-electron delocalization pathway. However, neither of these options appears to be viable for naphthiporphyrin. The *meso*-protons at positions 11 and 16, which are furthest removed from the naphthalene unit, gave rise to two 1H singlets at 6.54 and 6.56 ppm, while benziporphyrin gives a 2H resonance for these protons at 6.57 ppm (Figure 2, Table 1). The *meso*-protons in fully aromatic porphyrinoids show up near 10 ppm, and the observed values clearly fall into the nonaromatic region. The *meso*-protons at positions 6 and 21 gave 1H singlets at 7.37 and 8.21 ppm, respectively, but these are affected by their proximity to the naphthalene unit. The corresponding protons in benziporphyrin resonate at 7.27 ppm (Table 1). The internal CH for **11** shows up at 8.08 ppm, compared to a value of 7.90 ppm for **4**, and again shows no sign of the upfield shift expected in an aromatic system. The resonances for the methyl substituents may also be used as a guide as these peaks are commonly observed downfield at 3.6 ppm for porphyrins. The values of 2.45 and

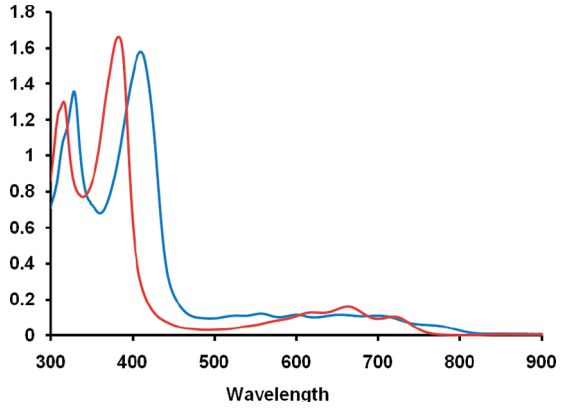


Figure 1. UV−vis spectra of benziporphyrin **4** (red line) and naphthiporphyrin **11** (blue line) in chloroform.

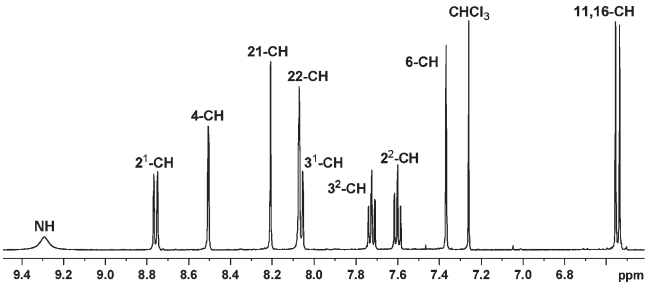
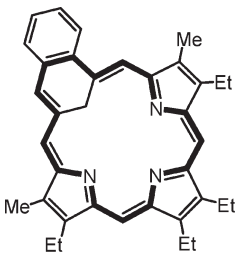


Figure 2. Partial 500 MHz proton NMR spectrum of naphthiporphyrin **11** in $CDCl_3$ showing details of the aromatic region.

Table 1. Selected Proton NMR Data (ppm) for Benziporphyrin 4, Naphthiporphyrin 11, and the Related Diprotonated Dications

	6-CH	11-CH	16-CH	21-CH	22-CH	8-Me	19-Me
4	7.27	6.57	6.57	7.27	7.90	2.43	2.43
11	7.37	6.54/6.56	6.54/6.56	8.21	8.08	8.45	2.54
$\mathbf{4}H_2^{2+}$	8.15	7.15	7.15	8.15	4.97	2.70	2.70
$\mathbf{11}H_2^{2+}$	8.29	7.17/7.20	7.17/7.20	8.81	4.50	2.73	2.77

2.54 ppm for **11**, and 2.43 ppm observed for **4**, are again consistent with structures that have no overall aromatic character (Table 1). The identity of **11** was further confirmed by $^1H-^1H$ COSY, HSQC, NOE difference ^1H NMR and carbon-13 NMR spectroscopy, and mass spectrometry.



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Addition of TFA to solutions of benziporphyrin or naphthiporphyrin shows the initial formation of a monoprotonated species using UV−vis spectroscopy, followed by the formation

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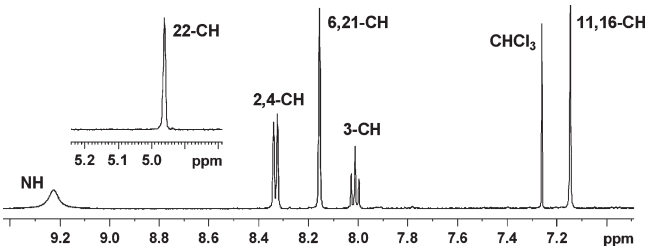


Figure 3. Partial 500 MHz proton NMR spectrum of benziporphyrin **4** in TFA-$CDCl_3$. The internal CH shows up near 5 ppm.

of a diprotonated dication (see Supporting Information). The monocation for naphthiporphyrin ($\mathbf{11}H^+$) shows a strong broad band at 708 nm, but this disappears in the presence of higher quantities of TFA. The dication $\mathbf{11}H_2^{2+}$ in 10% TFA-$CHCl_3$ gave two weak Soret-like bands at 330 and 400 nm and minor bands at 571 and 617 nm. The proton NMR spectrum of $\mathbf{11}H_2^{2+}$ in TFA-$CDCl_3$ showed the presence of a significant diatropic ring current, although this is also observed for the benziporphyrin dication $\mathbf{4}H_2^{2+}$. The proton NMR spectrum of **4** in TFA-$CDCl_3$ (Figure 3) shows the *meso*-protons downfield at 7.15 and 8.15 ppm, while the internal CH shifts upfield to approximately 5 ppm. The latter resonance is somewhat sensitive to the concentration of **4** and the quantity of TFA, but consistently fell into a range of 4.9−5.5 ppm. The data are clearly consistent with the presence of a weak diatropic ring current, although the positive charges on the macrocycle presumably contribute to the downfield shifts for the external protons. The latter factor should be less significant for the methyl substituents, but the 6H singlet corresponding to the two equivalent methyls is still shifted downfield to 2.70 ppm (Table 1). The proton NMR spectrum for the diprotonated naphthiporphyrin dication $\mathbf{11}H_2^{2+}$ in TFA-$CDCl_3$ shows many of the same trends (Figure 4). The *meso*-protons are observed at 7.17, 7.20, 8.29, and 8.81 ppm, values that are substantially downfield shifted compared to the free base, and the methyl substituents give rise to two 3H singlets at 2.73 and 2.77 ppm. The *meso*-protons furthest removed from the naphthalene unit (11,16-CH) are only slightly further downfield than the values seen for $\mathbf{4}H_2^{2+}$, as is also the case for the methyl resonances, but the data are consistent with a slightly increased diatropic character in $\mathbf{11}H_2^{2+}$. Support for this interpretation comes from the resonance for the internal CH. As was the case for benziporphyrin, this resonance varied somewhat with concentration and quantity of TFA added, but nevertheless fell into the range of 4.0−4.6 ppm. Not only is the resonance for the 22-CH shifted upfield, but it is also consistently upfield from the values observed for $\mathbf{4}H_2^{2+}$. Three NH resonances were also noted at 6.6, 8.7, and 9.2 ppm. Overall, our results support our conjecture that naphthalene units would enhance the diatropic properties of borderline aromatic benziporphyrin systems.

Although tetraarylbenziporphyrins have been shown to form metallo-derivatives previously,[14−18] no examples of metalated species have been reported for *meso*-unsubstituted benziporphyrins. Benziporphyrin **4** was reacted with nickel(II) acetate in refluxing DMF for 30 min and the corresponding nickel(II) organometallic derivative **15a** was generated in 42% yield (Scheme 2). The corresponding palladium(II) complex **15b** was also formed by reacting **4** with palladium(II) acetate in refluxing acetonitrile. The UV−vis spectrum for the nickel complex showed two weak Soret-like bands at 343 and

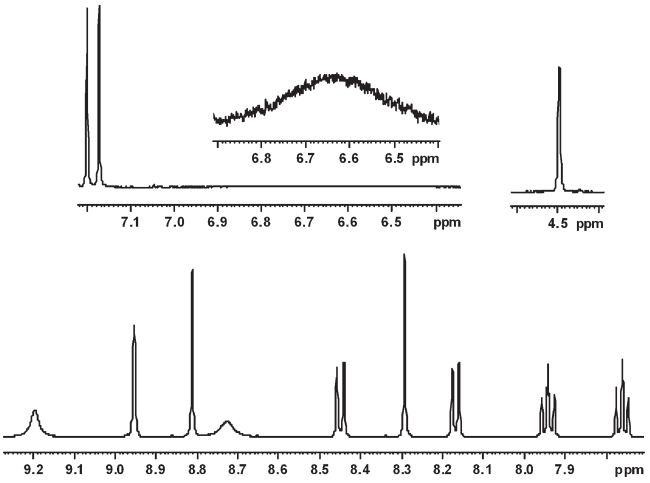
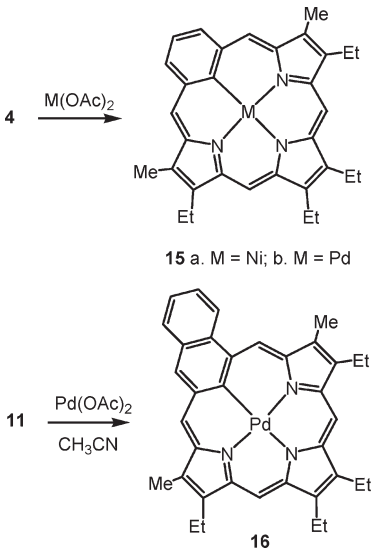


Figure 4. Partial 500 MHz proton NMR spectrum of naphthiporphyrin **11** in TFA-$CDCl_3$. In this case the internal CH is apparent at 4.5 ppm.

Scheme 2



408 nm, and a broad absorption centered on 652 nm. In contrast, the palladium complex gave a stronger Soret band at 406 nm, and a series of small absorptions between 450 and 800 nm. The proton NMR spectrum of **15a** gave resonances for the *meso*-protons at 7.16 and 7.48 ppm, while the methyl substituents gave a 6H singlet at 2.45 ppm. These values are all shifted downfield compared to the free base benziporphyrin, and suggest that the metalated derivative has a small diatropic ring current. The palladium complex gives two 2H resonances for the *meso*-protons at 7.35 and 7.72 ppm and a 6H singlet for the methyl groups at 2.63 ppm, indicating that the diatropicity of **15b** is enhanced compared to the nickel complex. This is consistent with results for other nickel(II) and palladium(II) carbaporphyrinoid complexes[21b] and is attributable to the palladium complex taking on a more planar conformation compared to **4** where the macrocycle is likely to be distorted or ruffled to accommodate the smaller nickel cation. Attempts to prepare the nickel(II) complex of naphthiporphyrin were

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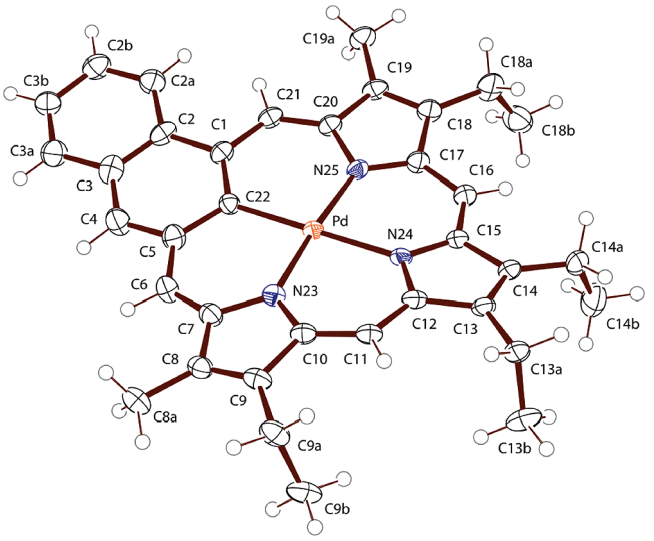


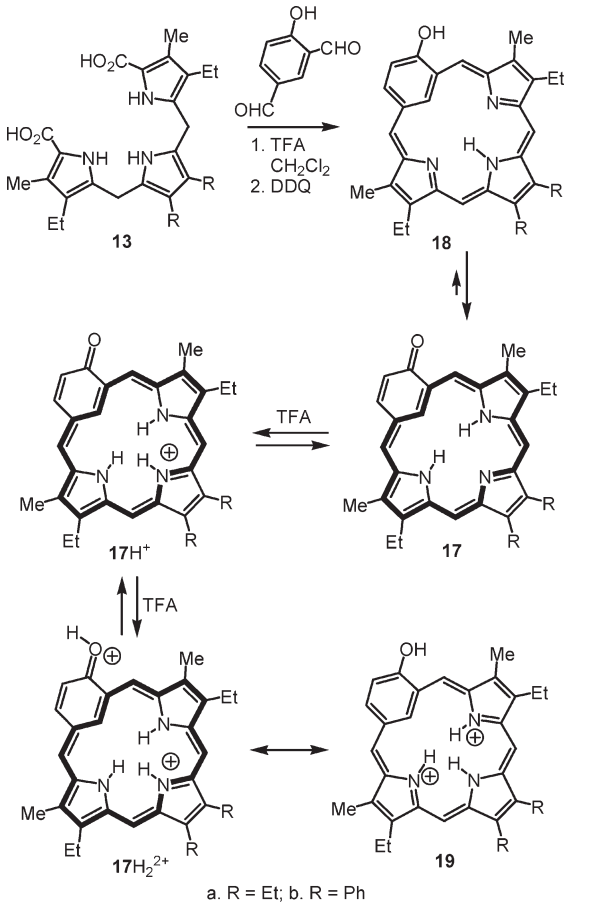
Figure 5. Color ORTEP III drawing (50% probability level, hydrogens drawn arbitrarily small) of palladium(II) naphthiporphyrin **16**.

unsuccessful, but **11** reacted with palladium(II) acetate in refluxing acetonitrile to give the palladium derivative **16** in 37% yield (Scheme 2). In this case, the *meso*-protons were observed at 7.27, 7.39, 7.64, and 8.50 ppm while the methyl groups gave two 3H singlets at 2.58 and 2.72 ppm. Taking into account the effect of the naphthalene moiety on the nearby *meso*-protons, these data suggest that the naphthiporphyrin complex has similar diatropic character to the benziporphyrin derivative.

The X-ray crystal structure of palladium complex **16** has also been obtained (Figure 5), and this not only confirms the presence of a naphthalene moiety but also demonstrates that the macrocycle is a little saddled as evidenced by the 0.180 Å rms distance the framework atoms lie from the plane defined by Pd, C(22), N(23), N(24), and N(25). The largest deviations from the plane are C(21) (0.325(4) Å), C(6) (−0.320(4) Å), C(2) (0.303(4) Å), and C(19) (0.280(4) Å). Of the 25 framework atoms, 13 deviate more than 0.15 Å from this plane. The structure exhibits framework bond distances consistent with a generally localized π-bonding model. The metal coordination environment of **16** is essentially the typical 4-coordinate square planar geometry characteristic of Pd(II) complexes. This is similar to related and quite planar palladium(II) N-confused porphyrins[27−29] and a related palladium(II) pyrazoloporphyrin,[21d] with no particular significance being attributed to the small observed deviation from planarity in **16**. The 2.055(4) Å Pd−C distance of **16** is longer than the 1.946(5) Å distance observed in the previously characterized palladium(II) pyrazoloporphyrin[21d] but is still consistent with the 2.00(5) Å distances observed for nearly 3000 crystallographically measured complexes containing Pd−C(phenyl) σ-bonds.[30]

Synthesis, Metalation, and Spectroscopic Properties of Oxynaphthiporphyrins. Some time ago, we reported that 4-hydroxy-1,3-benzenedicarbaldehyde reacted with tripyrrane **13a** using the "3 + 1" variant of the MacDonald condensation[31] to give an aromatic porphyrinoid **17a** (Scheme 3).[10] Although this reaction could have given the hydroxybenziporphyrin **18a**, this species tautomerizes to produce oxybenziporphyrin **17a**.[10,11,19,32,33] The reaction has also been carried out with

Scheme 3



tripyrrane **13b** to give the diphenyloxybenziporphyrin **17b** (Scheme 3). Oxybenziporphyrins give porphyrin-like UV−vis spectra with a strong Soret band near 430 nm and a series of Q bands extending to >700 nm. The NMR spectra of oxybenziporphyrins confirm that these carbaporphyrinoids are highly diatropic in nature, showing the internal CH upfield near −7 ppm, while the *meso*-protons are shifted downfield to give resonances between 8.8 and 10.3 ppm. Unlike benziporphyrins, addition of TFA to solutions of oxybenziporphyrins leads to a decrease in the aromatic properties for the system.[11] In the presence of trace amounts of TFA, a monocation **17**H^+ is formed, but further addition of TFA leads to the formation of a dicationic species **17**H_2^{2+}. The second protonation takes place on the carbonyl unit, but this leads to a species with substantial phenolic character (resonance contributor **19**) that interrupts the 18π electron delocalization pathway.[11] The loss of aromatic character is particularly evident in the proton NMR spectra where the internal CH shifts from −7 ppm to +1 ppm upon addition of TFA. Given the beneficial effect of a naphthalene unit on the aromatic properties of naphthiporphyrin dication **11**H_2^{2+}, we were interested to see how the properties of naphthalene analogues of oxybenziporphyrins would be effected.[34] To pursue this study, an α-naphthol dialdehyde **20** was required (Scheme 4).

1-Methoxynaphthalene was reacted with 2 equiv of bromine in acetic acid to give the corresponding 2,4-dibromo derivative **21** in 94% yield. Metalation at room temperature with excess *n*-butyllithium, followed by the addition of DMF and hydrolysis

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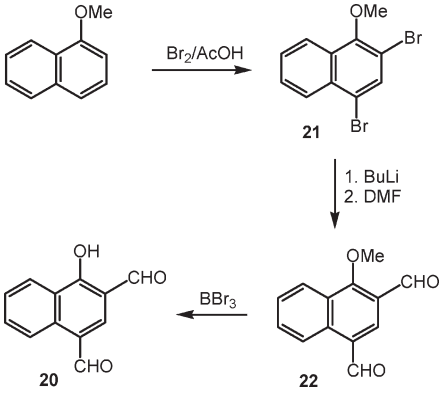
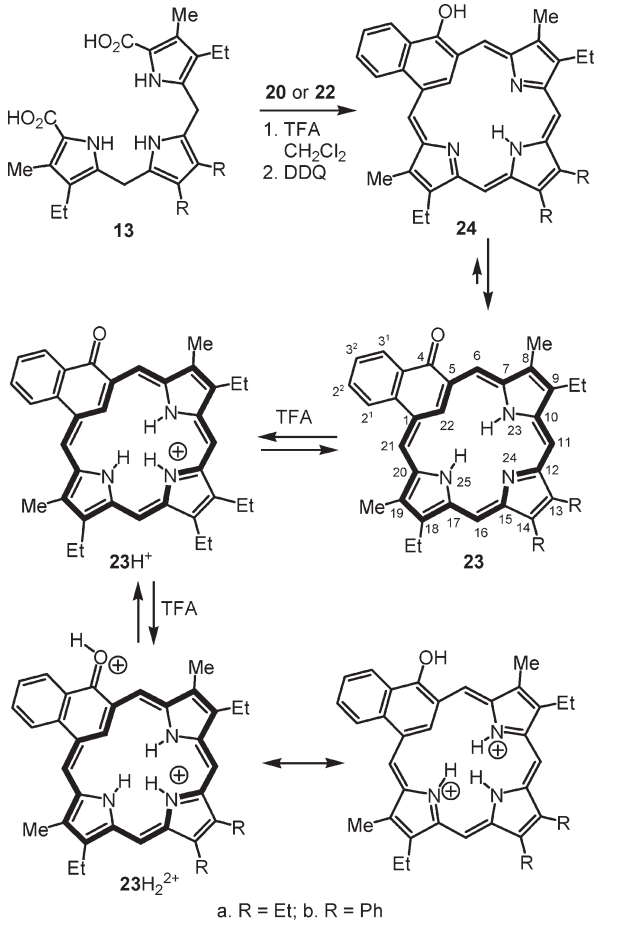
Scheme 4



Scheme 5



with hydrochloric acid gave the corresponding dialdehyde **22**. Treatment with boron tribromide in dichloromethane at room temperature then gave the required dialdehyde **20**. Naphthol dialdehyde **20** was reacted with tripyrrane **13a** in the presence of TFA to give, following neutralization with triethylamine and oxidation with DDQ, oxynaphthiporphyrin **23a** in approximately 20% yield. Surprisingly, reaction of 4-methoxy-1,3-naphthalenedicarbaldehyde (**22**) with tripyrrane **13a** under the same conditions gave superior results affording the oxynaphthiporphyrin in 35% yield. The methyl ether appears to undergo spontaneous cleavage under the reaction conditions and no methoxynaphthiporphyrin could be isolated. This stands in contrast with earlier studies, where dimethoxybenzene dialdehydes reacted with tripyrrane **13a** using the same "3 + 1" methodology to give dimethoxybenziporphyrins with no cleavage of the methyl ethers occurring under these mild conditions.[19] Although this result was unexpected, the use of the methoxy derivative **22** is convenient as it cuts out one step in the synthesis. Dialdehyde **22** also reacted with tripyrrane **13b** to give the related diphenyloxynaphthiporphyrin **23b** in comparable yields (Scheme 5). Again, hydroxynaphthiporphyrins **24** might arise in this chemistry but this species apparently strongly favors the aromatic seminaphthoquinone tautomers. The formation of this tautomer is confirmed by the presence of an absorption for C═O stretching at 1630 cm^{-1} and the presence of a C═O resonance in the carbon-13 NMR spectra near 190 ppm.

As is the case for oxybenziporphyrin,[10,11] oxynaphthiporphyrin shows some shifts in its proton NMR spectra due to concentration. Nevertheless, under comparable conditions, oxynaphthiporphyrin **23a** shows slightly enhanced diatropic character compared to oxybenziporphyrin **17a**. The internal CH was observed at −7.4 ppm, while the *meso*-protons were shifted downfield to give resonances at 9.27, 9.33, 9.94, and 10.65 ppm. The UV−vis spectrum of **23a** was similar to **17a**, showing a strong Soret band at 429 nm and a secondary absorption at 447 nm, followed by a series of four Q bands between 500 and 700 nm. The related diphenyl compound gave similar spectroscopic results. Both oxynaphthiporphyrins were further characterized by $^1H-^1H$ COSY, HSQC, NOE difference proton NMR and carbon-13 NMR spectroscopy and mass spectrometry (see Supporting Information).

Addition of TFA to solutions of oxynaphthiporphyrins **23** in chloroform lead to reduced aromatic character, but far higher quantities of acid were required to see the same effects as for oxybenziporphyrins. These effects are easily monitored using UV−vis spectroscopy. Figure 6 shows the formation of monocation **17a**H^+ by adding small increments of TFA to a cuvette containing a solution of oxybenziporphyrin **17a** in chloroform. The Soret band and the secondary peak shift to slightly higher wavelength (427 and 467 nm) and the Q bands show significant shifts as well. Addition of 20 equiv of TFA takes the first protonation to completion. Similar results were obtained with oxynaphthiporphyrin **23a**, where the Soret and the associated secondary absorption shift to 431 and 460 nm, respectively (Figure 7). Further protonation requires a large excess of TFA. However, in 1% TFA-$CHCl_3$ oxybenziporphyrin shows a greatly reduced intensity of the Soret band, and in 5% TFA the monocation **17a**H^+ has been completely converted into a new species **17a**H_2^{2+} (Figure 8). The dication gives a weak Soret band at 431 nm and Q bands at 552, 596, 693, and 764 nm. Although similar changes were observed for oxynaphthiporphyrin **23a**, 1% TFA only slightly reduced the intensity of the Soret band and it was necessary to use a 50% TFA-chloroform solution to fully form the new species **23a**H_2^{2+} (Figure 9). This gave a weak split Soret band at 441 and 460 nm, and Q bands at 635, 689, and 760 nm. The presence of the naphthalene unit appears to inhibit the second protonation rather than enhance the aromatic characteristics of the dicationic species but the differences between the two porphyrinoid systems are substantial. Addition of one drop of TFA to a solution of **23a** in $CDCl_3$ gave a

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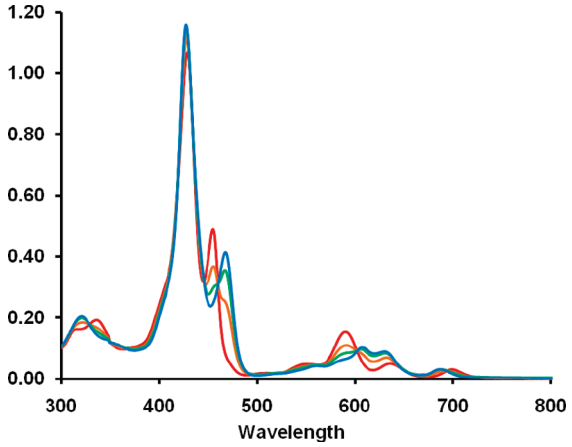

Figure 6. UV−vis spectra of oxybenziporphyrin **17a** in chloroform with 0 (red), 2 (orange), 5 (green), and 20 equiv (blue) of trifluoroacetic acid showing the formation of monocation **17a**H^+.

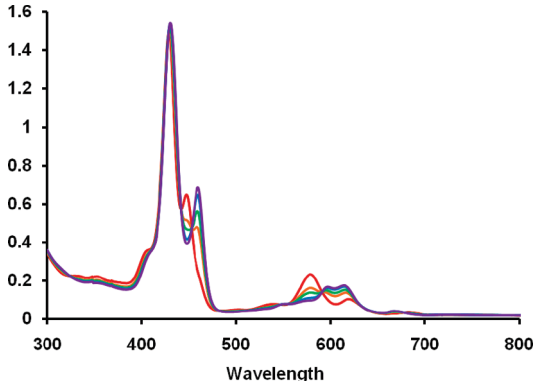

Figure 7. UV−vis spectra of oxynaphthiporphyrin **23a** in chloroform with 0 (red), 1 (orange), 2 (green), 5 (blue), and 10 equiv (purple) of trifluoroacetic acid showing the formation of monocation **23a**H^+.

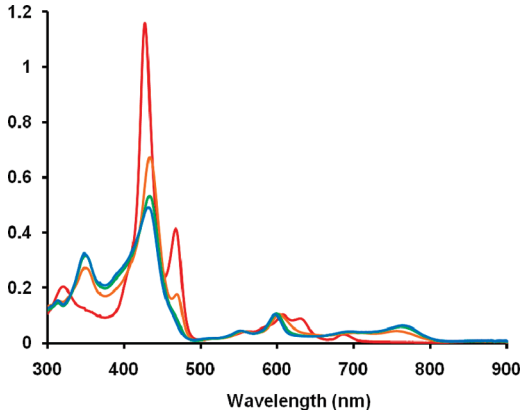

Figure 8. UV−vis spectra of oxybenziporphyrin **17a** in chloroform with 20 equiv of TFA (monocation, red), and in 1% TFA-$CHCl_3$ (orange), 2% TFA-chloroform (green), and 5% TFA-chloroform (blue) showing the formation of dication **17a**H_2^{2+}.

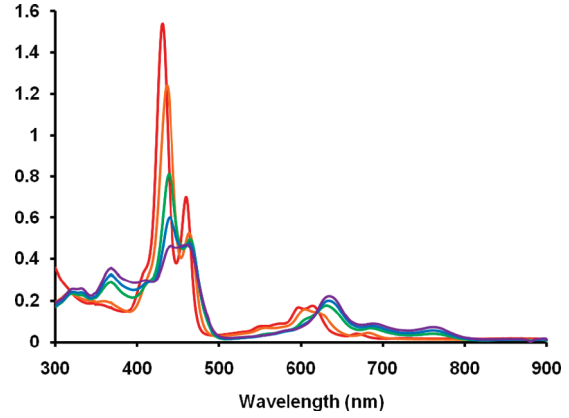

Figure 9. UV−vis spectra of oxynaphthiporphyrin **23a** in chloroform with 10 equiv of TFA (monocation, red), and in 1% TFA-$CHCl_3$ (orange), 10% TFA-chloroform (green), 20% TFA-chloroform (blue), and 50% TFA-chloroform (purple) showing the formation of dication **23a**H_2^{2+}.

clean proton NMR spectrum of the monocation **23a**H^+. This showed the internal CH at −5.69 ppm and three broad NH resonances at −4.41, −1.42, and −0.98 ppm. The *meso*-protons were shifted downfield to 9.71, 9.78, 10.55, and 10.86 ppm. The methyl groups gave two 3H singlets at 3.46 and 3.47 ppm. The results indicate that the monocation has a similar diamagnetic ring current to the free base form of oxynaphthiporphyrin. Addition of further quantities of TFA to the NMR solution resulted in small downfield shifts to the internal protons, indicating that dication **23a**H_2^{2+} is present in equilibrium with **23a**H^+, but the results confirm that the monocation predominates in solution at higher acid concentrations (see Supporting Information). Similar spectroscopic data were obtained for the diphenyl substituted porphyrinoids **17b** and **23b**.

There are three hydrogens present in the internal cavity of oxybenziporphyrins and oxynaphthiporphyrins, and in principle these porphyrinoids could act as trianionic ligands. However, oxybenziporphyrin reacts with palladium(II) chloride in the presence of potassium carbonate to form the palladium(II) organometallic species **25** (Scheme 6).[35] In this instance, the system is acting as a dianionic ligand in much the same way as benziporphyrins **4** (see previous section). Nevertheless, many carbaporphyrinoid systems including benzocarbaporphyrins, tropiporphyrins and N-confused porphyrins form silver(III) derivatives upon reaction with silver(I) salts.[7b,36,37] Oxybenziporphyrin **17a** was reacted with silver acetate in chloroform−methanol at room temperature and the silver(III) complex **26a** was isolated in 96% yield (Scheme 6). Diphenyl oxybenziporphyrin reacted similarly to give the related complex **26b** in 95% yield. Unfortunately, **26a** and **26b** were fairly insoluble in organic solvents. Silver(III) complex **26a** gave a poor quality NMR spectra in $CDCl_3$, or a mixture of methanol-d_4 and $CDCl_3$, which showed the *meso*-protons in the downfield region and confirmed the diatropic character of this species. Improved spectroscopic data could be obtained for the diphenyl substituted silver complex **26b**, and in this case the proton NMR spectrum for a dilute sample in $CDCl_3$ showed the *meso*-protons as four 1H singlets at 8.87, 9.69, 9.71, and 10.32 ppm, while the methyl groups gave 3H singlets at 3.30 and 3.43 ppm. The solubility of **26b** was improved by adding some methanol-d_4 to the NMR solution, but it was only possible to obtain a low quality carbon-13 NMR spectrum for this silver(III) complex. The UV−vis spectrum of **26a** showed a Soret band at 456 nm and

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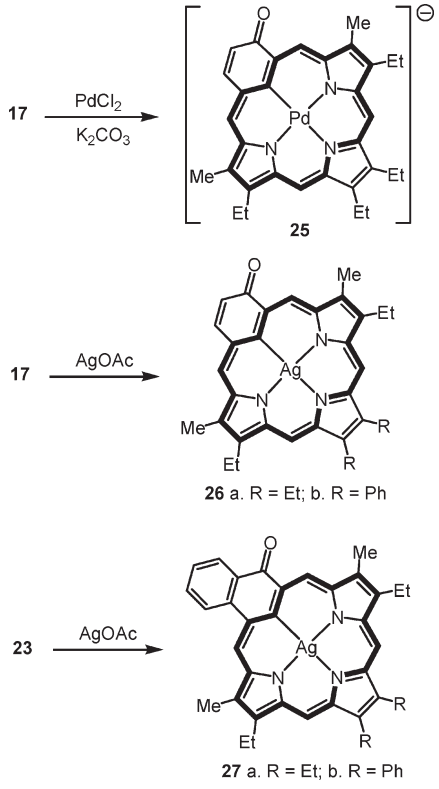
Scheme 6



broadened Q bands between 550 and 650 nm. The IR spectrum for **26a** showed two strong peaks for the carbonyl group at 1619 and 1641 cm^{-1}, while **26b** showed these two bands at 1618 and 1639 cm^{-1}. The origin of the peak splitting is not clear, and we speculate that this is due to a Fermi resonance. Mass spectral data were also obtained for these complexes.

Oxynaphthiporphyrin **23a** and **23b** also reacted smoothly with silver(I) acetate to give the corresponding silver(III) complexes **27** in 68−87% yield (Scheme 6). These derivatives were far more soluble in organic solvents and this allowed the silver complexes to be characterized by ^{1}H NMR, ^{1}H−^{1}H COSY, HSQC, NOE difference proton NMR and carbon-13 NMR spectroscopy, as well as by IR and UV−vis spectroscopy and mass spectrometry. The UV−vis spectrum for **27a** in chloroform showed a strong Soret band at 456 nm and broad Q bands between 500 and 620 nm. Diphenyl complex **27b** gave a similar UV−vis spectrum with a Soret band at 458 nm. Carbon-13 NMR spectra for **27a** and **27b** showed resonances for the carbonyl moiety at 191.6 and 191.7 ppm, respectively. The proton NMR spectra for silver(III) oxynaphthiporphyrins **27a** and **27b** demonstrated that the complexes had retained highly diatropic characteristics. The data for **27b** will be discussed so that it can be compared to the results for oxybenziporphyrin complex **26b**. The proton NMR spectrum for **27b** showed the *meso*-protons as four 1H singlets at 9.29, 9.42, 9.52, and 9.85 ppm, while the methyl resonances appeared at 3.11 and 3.34 ppm. These values suggest that the diatropicity of the oxynaphthiporphyrin complexes is slightly decreased compared to the oxybenziporphyrin series. This is the opposite of our expectations but could be explained due to steric factors. Silver(III) carbaporphyrins are known to be quite planar,[37a] and this factor would draw the naphthalene unit into the same plane as the rest of the porphyrinoid framework. This would increase the interaction between the naphthalene 2^1-CH and the adjacent *meso*-hydrogen causing the naphthalene moiety to twist out of alignment. For the oxybenziporphyrins, the silver(III) cation would draw the macrocycle into a planar arrangement, but this is not possible for the oxynaphthiporphyrin series. Hence, other factors need to be taken into account when assessing the spectroscopic data. Similar arguments can be used to explain why palladium(II) naphthiporphyrin **16** showed no increased diatropicity compared to the benziporphyrin complex **15b** (see previous section).

Silver has two naturally occurring isotopes with natural abundances of 51.82% (^{107}Ag) and 48.18% (^{109}Ag).[38] The near equal abundances of two isotopes differing by two mass units gives the mass spectra of silver complexes **26a**, **26b**, **27a** and **27b** a superficial resemblance to bromine compounds. In addition, both isotopes have a spin $I = {}^1/_2$.[38] In most silver(III) carbaporphyrinoid complexes, it has not been possible to locate the carbon connected to the silver cation.[37] However, the silver(III) complex of tetraphenyl N-confused porphyrin showed the carbon as two overlapping doublets at 138.97 ppm with coupling constants of 75.7 and 83.0 Hz.[36] The gyromagnetic ratios for ^{107}Ag and ^{109}Ag are reported to be −1.0828 and −1.2448, respectively.[38] Therefore, the ratio of the *J* values should be 1.15. The values reported by Furuta and co-workers give a slightly lower ratio of 1.10.[36] The best resolved carbon-13 NMR spectrum for our silver complexes corresponded to the most soluble derivative **27a**. The carbon-13 NMR spectrum for this silver(III) oxynaphthiporphyrin showed some signs of long-range coupling but also gave two doublets at 163.2 ppm with *J* values of 50.1 and 56.4 Hz (see Supporting Information). The *J* values are smaller than the ones reported for the N-confused porphyrin complex, but the ratio for the two values of 1.125 is closer to the expected value.

Synthesis and Spectroscopic Properties of Tetraphenyl-1,4-naphthiporphyrin. In 2002, Stepien and Latos-Grazynski reported a low yielding synthesis of tetraaryl-*p*-benziporphyrins **28** (Scheme 7).[39] This was accomplished by reacting dicarbinols **29** with 3 equiv of pyrrole and 2 equiv of benzaldehyde or *p*-tolualdehyde in the presence of $BF_3.Et_2O$ in dichloromethane, followed by oxidation with DDQ, and the *p*-benziporphyrins were isolated in 1% yield.[39] The 1,4-connection to the benzene ring cannot accommodate a completely planar porphyrinoid structure and the *p*-phenylene unit is pivoted out of the mean macrocyclic plane for the system by 44−48° (Scheme 8).[39] The benzene ring is too large to pass through the macrocyclic cavity, but at room temperature the arene moiety undergoes a rapid teeter-tottering or see-sawing motion between two equivalent conformations A and B, where the environments of the two CH═CH components interconvert (Scheme 8). In spite of the nonplanar structure and conformational mobility of this system, the proton NMR data showed the presence of a significant diamagnetic ring current.[39] The pyrrolic protons were shifted downfield by approximately 1 ppm compared to the nonaromatic tetraphenylbenziporphyrin **8**, and gave resonances at 7.62, 7.74, and 8.20 ppm.[39] At 323 K, the four *p*-phenylene protons gave a single resonance at 5.24 ppm corresponding to the average environment for this teeter-tottering unit, but when the temperature was lowered to 168 K two distinct 2H resonances were observed at 7.68 and 2.32 ppm.[39] The upfield shift of the "inner" phenylene protons strongly supports the proposed diatropic properties for this system, and the aromatic character was further

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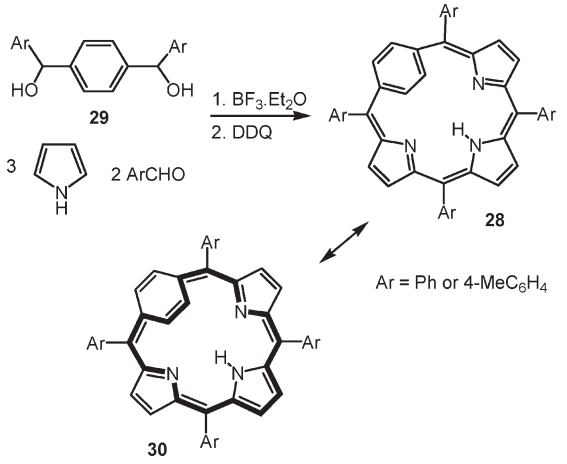
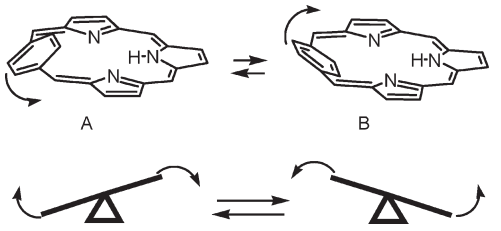
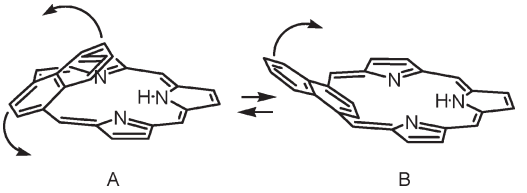
Scheme 7



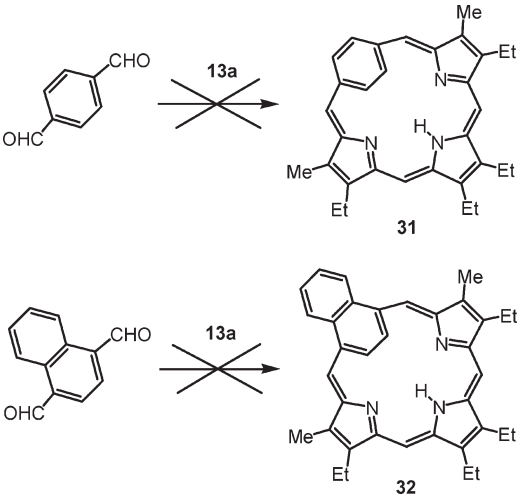
Scheme 8



Scheme 9



Scheme 10



supported by an analysis of bond lengths from X-ray crystallography.[39] The aromatic properties are believed to be due to resonance contributors like **30** which have the necessary 18π electron delocalization pathways.[39] Nickel(II) and cadmium complexes of **28** were also reported and these showed an interesting η^2-interaction with the *p*-phenylene unit.[15,39]

Given the intriguing properties of *p*-benziporphyrins, we were interested in seeing how the aromatic properties would be altered for a naphthalene analogue of this system. A similar teeter-tottering process might occur for a 1,4-naphthiporphyrin (Scheme 9), but in this case the two conformations would not be equivalent. We reasoned that conformation A would be less favorable due to steric interactions and that the proposed system would exist primarily as conformer B. This unit might be expected to be better suited to support a macrocyclic ring current and could thereby show an enhanced diamagnetic ring current. Some time ago, we had attempted to prepare *p*-benziporphyrin **31** using the "3 + 1" methodology from tripyrrane **13a** and terephthalaldehyde (Scheme 10), but no porphyrinoid products could be isolated.[40] Perhaps not surprisingly, reaction of **13a** with 1,4-naphthalenedicarbaldehyde[26] also failed to afford any of the desired naphthiporphyrin product **32** (Scheme 10). However, the synthesis of tetraphenyl-1,4-naphthiporphyrin **33** was easily carried out in three isolated steps from 1,4-naphthalenedicarboxylic acid (**34**, Scheme 11). Treatment of dicarboxylic acid **34** with thionyl chloride gave the corresponding diacyl chloride **35**, and this was used directly to carry out a double Friedel–Crafts acylation reaction with benzene and $AlCl_3$ to give excellent yields of 1,4-dibenzoylnaphthalene (**36**). Reduction with sodium borohydride then gave the corresponding dicarbinol **37** as a mixture of two diastereoisomers. The dialcohol was reacted with 3 equiv of pyrrole and 2 equiv of benzaldehyde in dichloromethane with a catalytic quantity of $BF_3.Et_2O$ to generate a naphthiporphyrinogen **38**, and this was oxidized *in situ* with DDQ to afford tetraphenyl-1,4-naphthiporphyrin **33**. The novel porphyrinoid was isolated in approximately 4% yield as a dark green solid and was easily separated from the tetraphenylporphyrin byproduct by column chromatography on grade 2 basic alumina.

The UV–vis spectrum of **33** in chloroform gave a moderately strong band at 466 nm and a broad absorption at 632 nm (Figure 10). Addition of 1 equiv of TFA gave rise to a new spectrum with an intensified band at 488 nm and a broad absorption centered on 757 nm, and this species was attributed to the corresponding monocation $\mathbf{33H}^+$. Further addition of TFA resulted in the formation of a new species, assigned to the dication $\mathbf{33H_2}^{2+}$, and this showed a hypsochromically shifted Soret band at 471 nm and a broad absorption at 731 nm. None of these spectra resembled those for porphyrin-type systems, and the Soret-like bands between 400 and 500 nm were weaker than the one reported for *p*-benziporphyrin **28**.[39] The proton NMR spectrum for **33** in $CDCl_3$ was particularly revealing, and against our expectations showed that the diatropicity was decreased compared to the corresponding *p*-benziporphyrin (Figure 11). The pyrrolic protons gave resonances at 7.14, 7.22, and 7.97 ppm, values that are between 0.23 and 0.52 ppm upfield from the corresponding resonances in **28**. The naphthalene protons were also anomalous. The 21,22-CH unit gave a singlet at 6.93 ppm, but the AA′XX′ system corresponding to the

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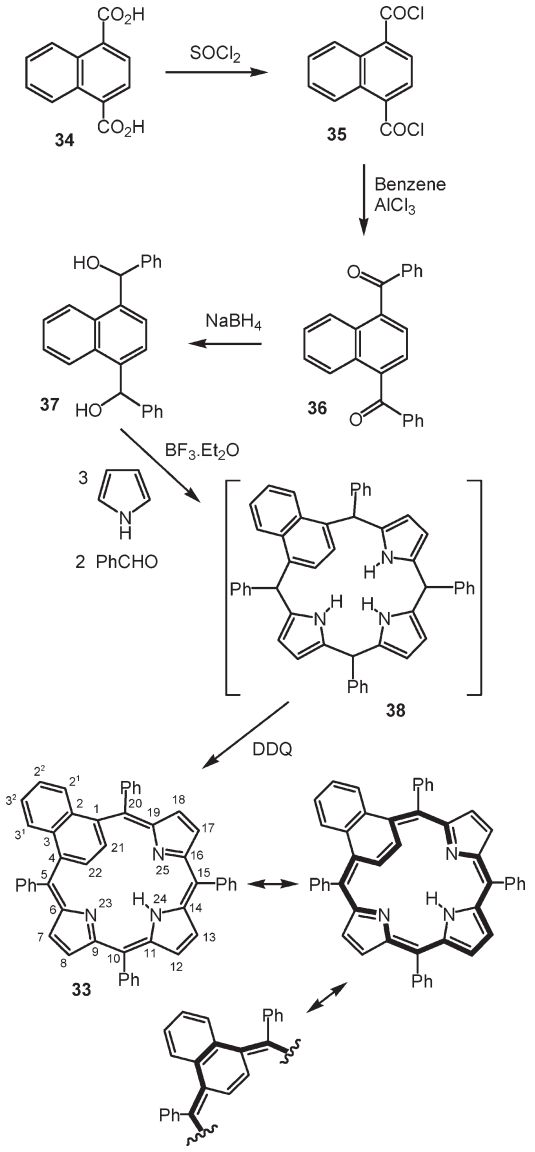
Scheme 11



supposedly external naphthalene protons gave two upfield multiplets at 6.01 and 6.28 ppm. The data indicate that it is conformer A, and not B, that is favored for this 1,4-naphthiporphyrin (Scheme 9). This form is presumably favored due to π-stacking interactions, but the bulky naphthalene unit is likely to increase the tilt angle and diminish the aromatic properties for the macrocycle. The proton NMR spectrum for naphthiporphyrin **33** was assigned using NOE difference proton NMR spectroscopy, and these results showed a correlation between both the 21,22- and the 2^1,3^1-naphthalene protons and the *o*-protons on the adjacent phenyl substituents. These correlations are consistent with conformation A, as only the protons at positions 2^1 and 3^1 would be expected to interact with the *o*-protons in conformer B (see Supporting Information). Unfortunately, we have not as yet been able to structurally characterize **33** by X-ray crystallography.

The NH resonance in the proton NMR spectrum of **33** could not be identified and in an attempt to identify this resonance, a D_2O shake was conducted. Two drops of D_2O were added to an

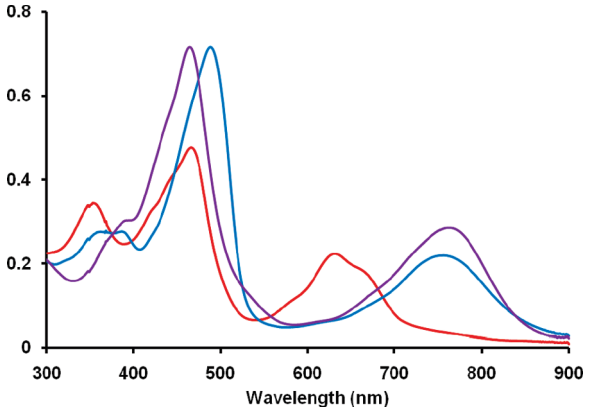


Figure 10. UV−vis spectra of tetraphenyl-1,4-naphthiporphyrin **33** in chloroform with 0 equiv (free base, red line), 1 equiv (monocation $\mathbf{33H}^+$, blue line) and 10 equiv TFA (dication $\mathbf{33H_2}^{2+}$, purple line).

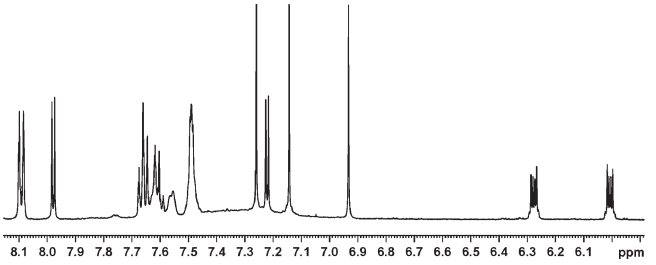


Figure 11. 500 MHz proton NMR spectrum of tetraphenyl-1,4-naphthiporphyrin **33** in $CDCl_3$.

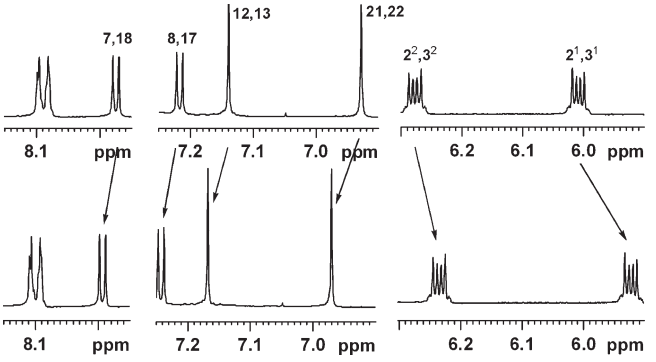


Figure 12. Partial 500 MHz proton NMR spectra of naphthiporphyrin **33** in $CDCl_3$ before and after carrying out a D_2O shake. The external protons are shifted downfield but the 2^1,2^2,3^1, and 3^2 protons overlying the system shift upfield.

NMR solution of **33** in $CDCl_3$ and the mixture shaken for several min. The proton NMR spectrum was then rerun but the NH peak could still not be identified. However, many of the peaks shifted following the deuteration (Figure 12). The pyrrolic protons and the 21,22-protons on the naphthalene subunit all shifted downfield but the 2^1,2^2,3^1,3^2 protons moved upfield. Even though the shifts were small (<0.1 ppm), these results are surprising as they indicate that the diatropic characteristics of 1,4-naphthiporphyrin **33** are enhanced upon deuteration. The changes could be attributed to the shorter N−D bond replacing the original N−H unit, which might allow the naphthalene unit in conformer A to tilt further

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toward the tripyrrolic component of the system and in so doing improve π-conjugation around the macrocycle. Deuteration of [18]annulene has been shown to have a similar effect, where the shorter C−D bonds apparently allow the 18-membered ring to flatten out, and this leads to leads to a small but measurable increase in the aromatic ring current.[41] Similar observations have also been made for the antiaromatic character of [16]annulene and the aromatic characteristics of the related dianion.[42] However, having such a large effect due to a single deuteration seemed unrealistic. Therefore, a control experiment was conducted using H_2O instead to D_2O. This resulted in slightly larger shifts than had been observed with D_2O and demonstrated that the increased diatropicity is not due to deuteration on the nitrogen atom. Presumably the conformational changes that are responsible for the observed changes in the NMR spectra result from hydrogen bonding to the core nitrogens.

Addition of TFA to NMR solutions of **33** generated the corresponding dication but this species gave poor quality NMR spectra. However, the data suggested that the macrocycle retains the same type of conformation. The 1,4-naphthiporphyrin was further characterized by ^{1}H−^{1}H COSY, HSQC, and carbon-13 NMR spectroscopy and electron impact mass spectrometry.

CONCLUSIONS

The incorporation of naphthalene units into a carbaporphyrinoid framework leads to significant changes compared to the analogous benziporphyrins. Naphthiporphyrin **11**, like benziporphyrin **4**, is nonaromatic, but protonation leads to the formation of a dication $\mathbf{11}H_2^{2+}$ with an increased diamagnetic ring current compared to the related benziporphyrin dication. Similarly, oxynaphthiporphyrins **23** show a slight increase in their diatropic character compared to oxybenziporphyrins **17**. Furthermore, although oxybenziporphyrins readily form dicationic species that have lost most of their aromatic characteristics, oxynaphthiporphyrins do not favor the second protonation step. These results are consistent with a valence bond theory interpretation of porphyrinoid aromaticity based on the presence of 18π electron delocalization pathways. In benziporphyrins, the competition between the 6π electron arene and the 18π electron delocalization pathways generally favors the former at the expense of the latter. As the loss of a benzene unit from a naphthalene system involves a smaller decrease in resonance stabilization energy, naphthiporphyrins were expected to better facilitate porphyrinoid aromaticity. Nevertheless, other factors may overwhelm this effect. Silver(III) complexes of oxynaphthiporphyrins are less diatropic than the corresponding silver(III) oxybenziporphyrins because the silver cation draws the macrocycle into a more planar conformation that increases steric interactions between the naphthalene unit and the adjacent *meso*-proton. This leads the carbocyclic moiety to twist away, decreasing the efficiency of π-conjugation. In tetraphenyl-1,4-naphthiporphyrin **33**, the porphyrinoid favors a conformation where the naphthalene folds over the rest of the macrocycle and steric interactions disrupt much of the π-conjugation. The 1,4-naphthiporphyrin is potentially of value in the formation of metallo-derivatives with unusual coordination properties as the extra fused benzene ring will lie over a metal cation that binds to the three nitrogen atoms. The results from our studies demonstrate that the introduction of a naphthalene unit in place of a benzene moiety can increase the aromatic character, but these modifications may lead to unexpected changes that extend our understanding of carbaporphyrinoid systems.

EXPERIMENTAL SECTION

1,3-Naphthalenedicarbaldehyde. The dialdehyde was prepared by the procedure described by Ried et al.[26] Recrystallization from ethanol gave an off-white powder, mp 120.5−122 °C (lit. mp[26] 124 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70−7.74 (1H, m), 7.84−7.88 (1H, m), 8.11 (1H, d, J = 8.2 Hz), 8.47 (1H, d, J = 1.6 Hz), 8.59 (1H, br s), 9.32 (1H, d, J = 8.6 Hz), 10.24 (1H, s), 10.45 (1H, s); ^{13}C NMR ($CDCl_3$): δ 125.8, 128.4, 130.4, 132.4, 132.6, 133.2, 133.3, 133.5, 133.7, 140.1, 191.0, 193.2.

9,13,14,18-Tetraethyl-8,19-dimethylbenziporphyrin (4). Tripyrrane dicarboxylic acid **13a**[24,25] (100 mg, 0.22 mmol) was stirred with TFA (1 mL) under nitrogen for 2 min. The mixture was diluted with dichloromethane (99 mL) and isophthalic dicarboxaldehyde (31 mg, 0.23 mmol) was immediately added in a single portion. The resulting solution was stirred overnight under nitrogen in the dark and then oxidized by stirring with DDQ (60 mg, 0.26 mmol) for 1 h. The mixture was then washed with water, followed by saturated aqueous sodium bicarbonate solution (the aqueous solutions were back-extracted with chloroform at each stage in the extractions). The solvent was removed under reduced pressure and the residue chromatographed on grade 3 basic alumina, eluting with dichloromethane to give a dark blue band. The solvent was removed under reduced pressure and recrystallized from chloroform−methanol to yield benziporphyrin (30 mg, 0.065 mmol, 29%) as dark-blue crystals, mp >300 °C (lit. mp[11] >300 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (6H, t, J = 7.6 Hz), 1.36 (6H, t, J = 7.6 Hz), 2.43 (6H, s), 2.77 (4H, q, J = 7.6 Hz), 2.86 (4H, q, J = 7.6 Hz), 6.57 (2H, s), 7.27 (2H, s), 7.75 (1H, t, J = 7.5 Hz), 7.90 (1H, br s), 7.98 (2H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz), 8.93 (1H, br s); ^{1}H NMR (500 MHz, trace TFA-$CDCl_3$): δ 1.28−1.34 (12H, 2 overlapping triplets), 2.62 (6H, s), 2.89 (8H, q, J = 7.7 Hz), 5.24 (1H, br s), 5.47 (1H, s), 6.91 (2H, s), 7.91 (1H, t, J = 7.7 Hz), 7.94 (2H, s), 8.19 (2H, d, J = 8.0 Hz); ^{1}H NMR (TFA-$CDCl_3$): δ 1.33 (6H, t, J = 7.7 Hz), 1.39 (6H, t, J = 7.7 Hz), 2.70 (6H, s), 2.96−3.01 (8H, 2 overlapping quartets), 4.97 (1H, s), 7.15 (2H, s), 8.01 (1H, t, J = 7.7 Hz), 8.15 (2H, s), 8.33 (2H, d, J = 7.7 Hz), 9.23 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 10.3, 15.2, 16.0, 18.1, 18.4, 93.1, 122.7, 125.2, 129.0, 134.3, 137.4, 140.7, 141.3, 141.5, 148.0, 157.3, 169.2; ^{13}C NMR (TFA-$CDCl_3$): δ 10.6, 14.2, 15.1, 18.1, 18.4, 94.4, 128.5, 132.1, 134.1, 140.6, 142.1, 143.9, 147.1, 149.0, 154.5, 162.8; HR MS (EI): Calcd for $C_{32}H_{35}N_3$: 461.2831. Found: 461.2832.

[9,13,14,18-Tetraethyl-8,19-dimethylbenziporphyrinato]-nickel(II) (15a). Nickel(II) acetate tetrahydrate (22 mg, 0.088 mmol) was added to a solution of benziporphyrin **25** (20 mg, 0.044 mmol) in DMF (40 mL), and the solution was stirred under reflux for 30 min. The solution was cooled, diluted with chloroform, and washed with water. The organic layer was separated, evaporated to dryness and chromatographed on grade 3 basic alumina, eluting with chloroform, to give a dark green band. The solvent was evaporated to dryness and the residue recrystallized from chloroform−methanol to yield the nickel(II) complex (10 mg, 0.019 mmol, 42%) as dark-green crystals, mp >300 °C; UV−vis ($CHCl_3$): λ_{max} (log ε) 343 (4.20), 408 (4.22), 529 (3.43), 652 nm (3.64); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (6H, t, J = 7.7 Hz), 1.39 (6H, t, J = 7.7 Hz), 2.45 (6H, s), 2.87 (4H, q, J = 7.7 Hz), 2.94 (4H, q, J = 7.7 Hz), 7.16 (2H, s), 7.48 (2H, s), 7.51 (1H, t, J = 7.3 Hz), 8.04 (2H, d, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$): δ 10.42, 15.37, 16.54, 18.52, 18.55, 29.92, 95.26, 123.41, 125.52, 135.95, 140.01, 141.32, 141.44, 144.76, 145.84, 153.14, 159.11; HR MS (EI): Calcd for $C_{32}H_{33}N_3Ni$: 517.2028. Found: 517.2022.

[9,13,14,18-Tetraethyl-8,19-dimethylbenziporphyrinato]-palladium(II) (15b). Palladium(II) acetate (20 mg, 0.089 mmol) was added to a solution of benziporphyrin **4** (20 mg, 0.043 mmol) in acetonitrile (40 mL), and the solution was stirred under reflux for

30 min. The solution was cooled, diluted with chloroform, washed with water, and the organic layer separated and then evaporated to dryness. The residue was chromatographed with grade 3 basic alumina, eluting with chloroform, and the product was collected as a reddish/brown band. The solvent was evaporated to dryness and the residue recrystallized from chloroform−methanol to yield the palladium(II) complex (8.5 mg, 0.015 mmol, 35%) as dark-purple crystals, mp >300 °C; UV−vis ($CHCl_3$): λ_{max} (log ε) 309 (4.38), 345 (4.19), 406 (4.58), 516 (3.54), 707 (3.47), 778 nm (3.38); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.40 (6H, t, J = 7.7 Hz), 1.45 (6H, t, J = 7.7 Hz), 2.63 (6H, s), 2.97−3.04 (8H, 4 overlapping quartets), 7.35 (2H, s), 7.71 (1H, t, J = 7.4 Hz), 7.72 (2H, s), 8.12 (2H, d, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ 10.5, 15.4, 16.7, 18.6, 18.9, 95.5, 125.7, 126.8, 132.4, 138.6, 141.2, 142.3, 144.0, 144.5, 153.4, 156.8; HR MS (EI): Calcd for $C_{32}H_{33}N_3Pd$: 565.1709. Found: 565.1699.

9,13,14,18-Tetraethyl-8,19-dimethylnaphthiporphyrin (11). Tripyrrane dicarboxylic acid **13a**[24,25] (100 mg, 0.22 mmol) was stirred with TFA (1 mL) under nitrogen for 2 min. The mixture was diluted with dichloromethane (99 mL) and naphthalene-1,3-dicarboxaldehyde[26] (44 mg, 0.24 mmol) was immediately added in a single portion. The resulting solution was stirred overnight under nitrogen in the dark and then oxidized by stirring with DDQ (100 mg, 0.44 mmol) for 1 h. The mixture was then washed with water, followed by saturated sodium bicarbonate (the aqueous solutions were back-extracted with chloroform at each stage in the extractions). The solvent was removed under reduced pressure and the residue chromatographed on grade 3 basic alumina, eluting with dichloromethane, to give a dark turquoise band. The solvent was removed under reduced pressure and recrystallized from chloroform−methanol to yield naphthiporphyrin (27 mg, 0.053 mmol, 24%) as dark-green crystals, mp >300 °C; UV−vis ($CHCl_3$): λ_{max} (log ε) 329 (4.73), 410 (4.80), 521 (sh, 3.64), 556 (3.69), 601 (3.66), 652 (3.66), 700 (3.63), 767 nm (3.36); UV−vis (50 eq TFA-$CHCl_3$): λ_{max} (log ε) 333 (4.51), 413 (4.55), 609 (3.99), 708 nm (4.27); UV−vis (10% TFA-$CHCl_3$): λ_{max} (log ε) 330 (4.62), 400 (4.75), 571 (4.08), 617 (4.27), 731 nm (3.77); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (6H, q, J = 7.7 Hz), 1.35 (6H, t, J = 7.6 Hz), 2.45 (3H, s), 2.54 (3H, s), 2.74−2.87 (8H, m), 6.54 (1H, s), 6.56 (1H, s), 7.37 (1H, s), 7.60 (1H, t, J = 7.6 Hz), 7.73 (1H, t, J = 7.6 Hz), 8.06 (1H, d, J = 7.7 Hz), 8.08 (1H, s), 8.21 (1H, s), 8.51 (1H, s), 8.76 (1H, d, J = 8.5 Hz), 9.30 (1H, br s); ^{1}H NMR (500 MHz, trace TFA-$CDCl_3$): δ 1.32−1.39 (12H, 4 overlapping triplets), 2.74 (3H, s), 2.78 (3H, s), 2.97−3.03 (8H, m), 4.44 (1H, s), 7.20 (1H, s), 7.22 (1H, s), 7.77 (1H, t, J = 7.5 Hz), 7.95 (1H, t, J = 7.7 Hz), 8.18 (1H, d, J = 8.0 Hz), 8.31 (1H, s), 8.46 (1H, d, J = 8.4 Hz), 8.62 (1H, br s), 8.73 (1H, br s), 8.83 (1H, s), 8.97 (1H, s), 9.09 (1H, s); ^{1}H NMR (500 MHz, TFA-$CDCl_3$): δ 1.31−1.39 (12H, 4 overlapping triplets), 2.73 (3H, s), 2.77 (3H, s), 2.96−3.02 (8H, m), 4.50 (1H, br d), 6.64 (1H, v br), 7.17 (1H, s), 7.20 (1H, s), 7.76 (1H, t, J = 7.5 Hz), 7.92−7.96 (1H, m), 8.17 (1H, s), 8.29 (1H, s), 8.45 (1H, d, J = 8.4 Hz), 8.73 (1H, br s), 8.81 (1H, s), 8.95 (1H, s), 9.20 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.6, 10.8, 15.4, 15.5, 16.16, 16.17, 18.2, 18.6, 95.1, 93.2, 115.7, 122.7, 123.3, 126.3, 128.5, 130.0, 130.3, 131.6, 134.8, 135.2, 139.3, 140.4, 140.5, 141.0, 141.2, 141.3, 141.9, 147.8, 148.1, 157.1, 157.2, 169.0, 169.5; ^{13}C NMR (TFA-$CDCl_3$): δ 10.8, 10.9, 14.5, 15.38, 15.40, 18.29, 18.34, 18.5, 93.9, 94.2, 107.0, 122.8, 126.4, 127.4, 128.8, 129.3, 129.7, 132.4, 133.4, 135.9, 136.0, 136.0, 141.4, 141.5, 143.1, 143.7, 145.3, 146.4, 146.6, 147.5, 148.1, 153.2, 153.3, 161.1, 161.2; HR MS (EI): Calcd for $C_{36}H_{37}N_3$ + 2H: 513.3144. Found: 513.3134. Anal. Calcd for $C_{36}H_{37}N_3.{}^1/_{20}CHCl_3$: C, 83.64; H, 7.21; N, 8.12. Found: C, 83.52; H, 7.19; N, 8.16.

[9,13,14,18-Tetraethyl-8,19-dimethylnaphthiporphyrinato]palladium(II) (16). Palladium(II) acetate (20 mg, 0.089 mmol) was added to a solution of naphthiporphyrin **11** (20 mg, 0.039 mmol) in acetonitrile (40 mL), and the solution was stirred under reflux for 30 min. The solution was cooled, diluted with chloroform, washed with water, and the organic layer separated and then evaporated to dryness. The residue was chromatographed with grade 3 basic alumina, eluting with chloroform, and the product was collected as a reddish/brown band. The solvent was evaporated to dryness and the residue recrystallized from chloroform−methanol to yield the palladium(II) complex (8.6 mg, 0.014 mmol, 37%) as dark-purple crystals, mp >300 °C; UV−vis ($CHCl_3$): λ_{max} (log ε) 273 (4.71), 319 (sh, 4.45), 421 (4.51), 518 (3.80), 562 (3.82), 599 (3.85), 680 (3.36), 740 nm (3.45); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37−1.47 (12H, 4 overlapping triplets), 2.58 (3H, s), 2.72 (3H, s), 2.94 (2H, q, J = 7.7 Hz), 2.98−3.05 (6H, 3 overlapping quartets), 7.27 (1H, s), 7.39 (1H, s), 7.55 (1H, t, J = 7.3 Hz), 7.64 (1H, s), 7.68 (1H, t, J = 7.6 Hz), 8.02 (1H, d, J = 7.5 Hz), 8.50 (1H, s), 8.82−8.84 (2H, overlapping singlet and doublet); ^{13}C NMR ($CDCl_3$): δ 10.4, 10.7, 15.3, 15.6, 16.7, 17.6, 18.6, 18.7, 18.9, 19.0, 95.5, 95.7, 118.3, 124.1, 125.5, 126.8, 128.3, 130.1, 130.7, 133.1, 138.3, 138.7, 139.3, 140.5, 141.5, 142.3, 143.2, 143.4, 144.1, 144.3, 145.6, 152.2, 153.3, 155.3, 157.0; HR MS (EI): Calcd for $C_{36}H_{35}N_3Pd$: 615.1866. Found: 615.1849

2,4-Dibromo-1-methoxynaphthalene (21). Bromine (20.9 g, 0.13 mol) in acetic acid (40 mL) was added dropwise over a period of 30 min to a stirred solution of 1-methoxynaphthalene (10.31 g, 65.2 mmol) in acetic acid and the resulting mixture was stirred for a further 1 h at room temperature and a further 2 h under reflux. The solution was poured into ice−water and the resulting precipitate suction filtered and washed well with water. Recrystallization from ethanol gave the dibromo derivative (19.45 g, 61.5 mmol, 94%) as an off-white solid, mp 51−52 °C (lit. mp[43] 54−55 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.00 (3H, s), 7.58−7.65 (2H, m), 7.91 (1H, s), 8.13−8.15 (1H, m), 8.17−8.19 (1H, m); ^{13}C NMR ($CDCl_3$): δ 61.8, 112.3, 118.3, 122.8, 127.8, 127.9, 128.1, 130.0, 132.4, 133.2, 153.4.

4-Methoxynaphthalene-1,3-dicarbaldehyde (22). *n*-Butyllithium in hexanes (24 mL, 1.6 M) was added dropwise over a period of 25 min to a stirred solution of dibromonaphthalene **21** (3.60 g, 11.4 mmol) in anhydrous ether (180 mL) at room temperature. The resulting mixture was stirred for a 3 h at ambient temperature, DMF (3.2 g, 44 mmol) was added dropwise and the mixture was stirred for a further 2 h. Hydrochloric acid (10%, 60 mL) was then added cautiously and the resulting mixture was extracted with ether, washed with 5% sodium bicarbonate and dried over magnesium sulfate. Recrystallization from ethanol gave the dialdehyde (1.32 g, 6.17 mmol, 54%) as fluffy yellow needles, mp 137−138 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.24 (3H, s), 7.67−7.72 (1H, m), 7.82−7.85 (1H, m), 8.34 (1H, d, J = 8.4 Hz), 8.41 (1H, s), 9.37 (1H, d, J = 8.5 Hz), 10.30 (1H, s), 10.60 (1H, s); ^{13}C NMR ($CDCl_3$): δ 66.4, 123.9, 124.1, 126.3, 128.2, 128.57, 128.65, 132.5, 134.8, 135.8, 167.1, 188.4, 192.7. Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.70. Found: C, 72.43; H, 4.61.

1-Hydroxynaphthalene-1,3-dicarbaldehyde (20). Boron tribromide in dichloromethane (1.0 M, 2 mL) was added to a stirred solution of dialdehyde **22** (214 mg, 1.00 mmol) in dichloromethane (10 mL) and the mixture was stirred for 1 h at room temperature. The solution was washed with 10% hydrochloric acid and water, and dried over sodium sulfate. Recrystallization from ethanol−water gave the naphthol (157 mg, 0.78 mmol, 78%) as small yellow needles, mp 148.5−149.5 °C (lit. mp[44] 137 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66−7.70 (1H, m), 7.86−7.89 (1H, m), 8.07 (1H, s), 8.54 (1H, d, J = 8.3 Hz), 9.31 (1H, d, J = 8.6 Hz), 10.07 (1H, s), 10.24 (1H, s), 13.25 (1H, s); ^{13}C NMR ($CDCl_3$): δ 113.5, 124.6, 124.7, 125.3, 127.4, 133.5, 134.4, 139.7, 166.5, 191.1, 195.6.

9,18-Diethyl-8,19-dimethyl-13,14-diphenyl-2-oxybenziporphyrin (17b). Tripyrrane dicarboxylic acid **13b**[6b] (100 mg, 0.18 mmol) was stirred under nitrogen with TFA (1 mL) in a 50 mL pear shaped flask at room temperature for 10 min. The solution was diluted with dichloromethane (39 mL), 5-formylsalicylaldehyde (27 mg, 0.18 mmol) was added and the resulting mixture stirred at room temperature for 2 h. The solution was neutralized by the dropwise addition of triethylamine, DDQ (98%, 42 mg, 0.18 mmol) was added, and the mixture was stirred for an additional 1 h. The solution was washed with water and the solvent

removed on a rotary evaporator. The residue was purified on a grade 3 neutral alumina column, eluting initially with dichloromethane. After a pink band had been collected, the solvent was switched to chloroform and the product eluted as a dark-green band. Recrystallization from chloroform−methanol gave the oxybenziporphyrin (47 mg, 0.082 mmol, 45%) as a dark-purple solid, mp >300 °C; UV−vis ($CHCl_3$): λ_{max} (log ε) 343 (4.42), 432 (5.25), 453 (4.87), 594 (4.47), 641 (3.96), 704 nm (3.82); UV−vis (80 equiv TFA-$CHCl_3$): λ_{max} (log ε) 328 (4.41), 433 (5.23), 470 (4.77) 613 (4.26), 696 nm (3.85); UV−vis (20% TFA-$CHCl_3$): λ_{max} (log ε) 355 (4.71), 437 (4.92), 560 (3.89), 607 (4.29), 707 (3.88), 778 nm (4.04); ^{1}H NMR (500 MHz, $CDCl_3$): δ −7.27 (1H, br d, J = 2.0 Hz), −3.67 (2H, br s), 1.62−1.68 (6H, 2 overlapping triplets), 3.30 (3H, s), 3.45 (3H, s), 3.68−3.75 (4H, 2 overlapping quartets), 7.27 (1H, d, J = 9.4 Hz), 7.59−7.63 (2H, m), 7.69 (4H, t, J = 7.5 Hz), 7.89−7.92 (4H, m), 8.42 (1H, dd, J = 2.0, 9.4 Hz), 8.91 (1H, s), 9.37 (1H, s), 9.41 (1H, s), 10.25 (1H, s); ^{1}H NMR (500 MHz, TFA-$CDCl_3$): δ 1.32−1.36 (6H, 2 overlapping triplets), 2.96 (3H, s), 2.97 (3H, s), 3.15−3.20 (4H, 2 overlapping quartets), 5.29 (1H, s), 5.48 (1H, br s), 5.51 (1H, br s), 7.54−7.57 (4H, m), 7.58−7.62 (7H, m), 8.09 (1H, s), 8.13 (1H, s), 8.61 (1H, dd, J = 1.8, 8.7 Hz), 8.87 (1H, s), 9.47 (1H, s); ^{13}C NMR ($CDCl_3$): δ 11.5, 11.8, 16.9, 17.0, 19.39, 19.43, 97.2, 99.1, 105.5, 110.9, 111.9, 122.0, 126.3, 127.61, 127.62, 128.7, 130.3, 132.2, 132,4, 134.5, 135.5, 136.0, 137.4, 138.01, 138.03, 138.2, 140.1, 144.7, 145.2, 147.0, 153.5, 154.8, 187.9; ^{13}C NMR (TFA-$CDCl_3$): δ 11.2, 14.9, 15.0, 18.8, 96.8, 98.0, 120.0, 120.5, 122.0, 124.4, 127.7, 129.6, 130.29, 130.32, 130.35, 131.0, 141.2, 141.8, 141.9, 142.2, 143.6, 144.1, 147.4, 148.3, 148.5, 149.3, 149.6, 155.3, 156.8, 171.2; HR MS (FAB): calcd for $C_{40}H_{35}N_3O$ + H: m/z 574.2858; found: 574.2860. Anal. Calcd for $C_{40}H_{35}N_3O.^1/_4CHCl_3$: C, 80.10; H, 5.89; N, 6.96. Found: C, 80.17; H, 5.89; N, 7.01.

9,13,14,18-Tetraethyl-8,19-dimethyl-2-oxynaphthiporphyrin (23a). Tripyrrane dicarboxylic acid **13a**[24,25] (100.2 mg) was stirred with TFA (1 mL) under an atmosphere of nitrogen for 5 min. The solution was diluted with dichloromethane (19 mL), followed immediately by the addition of 4-methoxynaphthalene-1,3-dicarbaldehyde (**22**; 44.5 mg), and the mixture was stirred under nitrogen, in the dark, for a further 3 h. After neutralization by the dropwise addition of triethylamine, DDQ (51 mg) was added and the resulting solution was stirred in the dark for an additional 1 h. The mixture was washed with water and chromatographed on grade 3 neutral alumina, eluting first with dichloromethane and then with chloroform. A deep green fraction was collected with chloroform and recrystallized from chloroform−methanol to give the porphyrin analogue (39.4 mg; 35%) as sparkling purple needles, mp 283−284 °C; IR (KBr): ν 3343 (w, NH str.), 1630 cm^{-1} (s, C=O str.); UV−vis ($CHCl_3$): λ_{max} (log ε) 404 (infl, 4.68), 429 (5.30), 447 (4.94), 537 (4.01), 579 (4.49), 619 (4.14), 683 nm (3.67); UV−vis (20 equiv TFA-$CHCl_3$): λ_{max} (log ε) 406 (infl, 4.65), 431 (5.31), 460 (4.97), 550 (sh, 4.01), 571 (sh, 4.08), 596 (4.36), 614 (4.38), 667 nm (3.75); UV−vis (50% TFA-$CHCl_3$): λ_{max} (log ε) 331 (4.54), 368 (4.68), 441 (4.79), 460 (4.79), 635 (4.47), 689 (4.08), 760 nm (3.99); ^{1}H NMR (400 MHz, $CDCl_3$): δ −7.42 (1H, s), 1.69 (3H, t, J = 7.6 Hz), 1.74−1.80 (9H, 3 overlapping triplets), 3.40 (3H, s), 3.57 (3H, s), 3.74−3.81 (4H, 2 overlapping quartets), 3.84 (2H, q, J = 7.6 Hz), 3.93 (2H, q, J = 7.7 Hz), 7.73 (1H, t, J = 7.5 Hz), 7.96−8.00 (1H, m), 8.92 (1H, dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz), 8.96 (1H, d, J = 8.1 Hz), 9.27 (1H, s), 9.33 (1H, s), 9.94 (1H, s), 10.65 (1H, s); ^{1}H NMR (400 MHz, 1 drop TFA-$CDCl_3$; monocation): δ −5.69 (1H, s), −4.41 (1H, br s), −1.42 (1H, br s), −0.98 (1H, br s), 1.54−1.60 (6H, 2 overlapping triplets), 1.78−1.85 (6H, 2 overlapping triplets), 3.46 (3H, s), 3.47 (3H, s), 3.89−4.01 (8H, m), 7.76 (1H, t, J = 7.6 Hz), 8.04−8.08 (1H, m), 8.82 (1H, d, J = 7.8 Hz), 8.94 (1H, d, J = 8.0 Hz), 9.71 (1H, s), 9.78 (1H, s), 10.55 (1H, s), 10.86 (1H, s); ^{13}C NMR ($CDCl_3$): δ 11.8, 11.9, 17.2, 18.4, 19.5, 19.6, 19.9, 94.2, 94.6, 103.0, 113.6, 120.1, 123.0, 124.9, 127.7, 128.8, 132.1, 132.7, 133.4, 134.0, 135.3, 136.6, 137.1, 137.8, 138.7, 140.6, 144.6, 144.7, 154.3, 154.8, 187.3; ^{13}C NMR (TFA-$CDCl_3$): δ 11.7, 16.1, 17.1, 19.67, 19.71, 92.8, 93.8, 113.2, 117.3, 122.1, 123.4, 127.5, 129.0, 129.3, 131.7, 135.3, 139.0, 140.0, 140.5, 140.7, 141.4, 142.1, 143.3, 143.7, 144.9, 186.7; HR MS (EI): calcd for $C_{36}H_{37}N_3O$: m/z 527.2937; found: 527.2932. Anal. Calcd for $C_{36}H_{37}N_3O.^1/_{10}CHCl_3$: C, 80.35; H, 6.93; N, 7.79. Found: C, 80.56; H, 6.99; N, 7.87.

9,18-Diethyl-8,19-dimethyl-13,14-diphenyl-2-oxynaphthiporphyrin (23b). Tripyrrane **13b**[6b] (212 mg, 0.38 mmol) and dialdehyde **22** (82.7 mg, 0.38 mmol) were reacted under the foregoing conditions. Recrystallization from chloroform−methanol gave the oxynaphthiporphyrin (88 mg, 0.14 mg, 36%) as purple crystals, mp 240 °C, dec; UV−vis ($CHCl_3$): λ_{max} (log ε) 406 (sh, 4.70), 431 (5.35), 446 (5.02), 540 (3.90), 584 (4.59), 625 (4.14), 686 nm (3.74); UV−vis (80 equiv TFA-$CHCl_3$): λ_{max} (log ε) 324 (4.47), 435 (5.32), 462 (4.94), 553 (sh, 3.88), 578 (sh, 4.07), 603 (4.35), 622 (4.39), 675 nm (3.87); UV−vis (50% TFA-$CHCl_3$): λ_{max} (log ε) 338 (4.46), 376 (4.66), 416 (sh, 4.65), 446 (4.89), 465 (4.85), 645 (4.48), 699 (4.10), 775 nm (3.93); ^{1}H NMR (500 MHz, $CDCl_3$): δ −7.26 (1H, s), −3.76 (2H, br s), 1.68 (3H, t, J = 7.7 Hz), 1.71 (3H, t, J = 7.7 Hz), 3.50 (3H, s), 3.58 (3H, s), 3.78−3.86 (4H, 2 overlapping quartets), 7.59−7.63 (2H, m), 7.67−7.71 (4H, m), 7.74 (1H, t, J = 7.5 Hz), 7.93−7.96 (4H, m), 7.95−7.99 (1H, m), 8.91 (1H, dd, J = 1.4, 7.7 Hz), 9.01 (1H, d, J = 8.2 Hz), 9.603 (1H, s), 9.605 (1H, s), 10.14 (1H, s), 10.73 (1H, s); ^{1}H NMR (500 MHz, TFA-$CDCl_3$): δ −5.69 (1H, s), −4.10 (1H, br s), −1.42 (1H, br s), −0.98 (1H, br s), 1.50 (3H, t, J = 7.7 Hz), 1.52 (3H, t, J = 7.7 Hz), 3.47 (6H, s), 3.82 (4H, q, J = 7.7 Hz), 7.67−7.75 (6H, m), 7.78 (1H, t, J = 7.5 Hz), 7.90−7.94 (4H, m), 8.07−8.10 (1H, m), 8.81 (1H, dd, J = 1.3, 7.8 Hz), 8.96 (1H, d, J = 8.1 Hz), 9.80 (1H, s), 9.86 (1H, s), 10.60 (1H, s), 10.88 (1H, s); ^{13}C NMR ($CDCl_3$): δ 12.0, 17.06, 17.11, 19.6, 98.0, 98.5, 103.0, 104.8, 113.4, 121.1, 123.5, 125.1, 127.5, 128.0, 128.7, 128.8, 132.5, 132.7, 133.0, 133.9, 135.6, 136.3, 137.3, 137.7, 137.9, 138.1, 138.7, 140.5, 144.5, 144.6, 152.9, 153.4, 187.5; ^{13}C NMR (TFA-$CDCl_3$): δ 12.0, 12.1, 16.3, 19.9, 95.6, 96.8, 111.2, 111.7, 120.1, 124.4, 127.6, 129.27, 129.29, 129.39, 129.40, 132.29, 132.34, 132.73, 132.77, 133.0, 135.0, 137.4, 138.2, 138.3, 139.4, 139.5, 140.0, 140.1, 140.5, 140.8, 141.0, 141.2, 142.5, 190.0; HR MS (EI): Calcd for $C_{44}H_{37}N_3O$: 623.2937. Found: 623.2921. Anal. Calcd for $C_{44}H_{37}N_3O.^1/_{20}CHCl_3$: C, 84.01; H, 5.93; N, 6.67. Found: C, 84.01; H, 5.93; N, 6.62.

[9,13,14,18-Tetraethyl-8,19-dimethyl-2-oxybenziporphyrinato]silver(III) (26a). A suspension of silver(I) acetate (40 mg) in methanol (10 mL) was added to a solution of 9,13,14,18-tetraethyl-8,19-dimethyl-2-oxybenziporphyrin (**17a**, 20.0 mg) in chloroform (20 mL) and the resulting mixture stirred at room temperature for 16 h. The mixture was washed with water and evaporated under reduced pressure. The residue was purified by column chromatography on grade 3 alumina, eluting with chloroform and then 1% methanol-chloroform. Evaporation of the green fractions afforded a dark residue. Recrystallization from chloroform−methanol gave the silver derivative (23.5 mg, 96%) as a dark-purple powder, mp >300 °C; IR (KBr): ν 1641 (s), 1619 cm^{-1} (s, C=O str.); UV−vis ($CHCl_3$): λ_{max} (log ε) 336 (4.51), 456 (4.94), 524 (3.55), 608 (4.40), 629 nm (4.20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (3H, t, J = 8 Hz), 1.64−1.73 (9H, 3 overlapping triplets), 3.10 (3H, s), 3.31 (3H, s), 3.62 (2H, q, J = 8 Hz), 3.67−3.75 (6H, 3 overlapping quartets), 7.32 (1H, d, J = 8.4 Hz), 8.44 (1H, d, J = 8.4 Hz), 8.69 (1H, s), 9.01 (1H, s), 9.13 (1H, s), 10.23 (1H, s); HRMS (EI): calcd for $C_{32}H_{32}N_3OAg$: 581.1610; found: 581.1608. Anal. Calcd for $C_{32}H_{32}N_3OAg.^1/_8CHCl_3$: C, 64.51; H, 5.37; N, 7.02. Found: C, 64.56; H, 5.38; N, 6.95.

[9,18-Diethyl-8,19-dimethyl-13,14-diphenyl-2-oxybenziporphyrinato]silver(III) (26b). A suspension of silver(I) acetate (40 mg) in methanol (10 mL) was added to a solution of **17b** (20.0 mg) in chloroform (20 mL) and the resulting mixture stirred at room temperature for 16 h. The mixture was washed with water and evaporated under reduced pressure. The residue was purified by column chromatography on grade 3 alumina,

eluting with chloroform and then 1% methanol-chloroform. Evaporation of the green fractions afforded a dark residue. Recrystallization from chloroform−methanol gave the silver complex (22.5 mg, 95%) as a dark-green powder, mp >300 °C; IR (KBr): ν 1639 (s), 1618 cm^{-1} (s, C═O str.); UV−vis ($CHCl_3$): λ_{max} (log ε) 344 (4.59), 458 (4.96), 526 (3.57), 614 (4.48), 638 nm (4.31); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67−1.74 (6H, 2 overlapping triplets), 3.30 (3H, s), 3.43 (3H, s), 3.72−3.79 (4H, 2 overlapping quartets), 7.31 (1H, d, J = 8.0 Hz), 7.65 (2H, t, J = 7.6 Hz), 7.73 (4H, t, J = 7.4 Hz), 7.99−8.02 (4H, m), 8.47 (1H, d, J = 8.0 Hz), 8.87 (1H, s), 9.69 (1H, s), 9.71 (1H, s), 10.32 (1H, s); ^{1}H NMR (400 MHz, d_4-MeOH-$CDCl_3$, 50 °C): δ 1.56 (3H, t, J = 7.6 Hz), 1.63 (3H, t, J = 7.6 Hz), 3.02 (3H, s), 3.24 (3H, s), 3.55 (2H, q, J = 7.6 Hz), 3.62 (2H, q, J = 7.6 Hz), 7.04 (1H, d, J = 8.4 Hz), 7.60 (2H, t, J = 7.6 Hz), 7.66−7.71 (4H, m), 7.92−7.96 (4H, m), 8.02 (1H, d, J = 8.8 Hz), 8.28 (1H, s), 9.43 (1H, s), 9.46 (1H, s), 9.92 (1H, s); ^{13}C NMR (d_4-MeOH-$CDCl_3$, 50 °C): δ 11.2, 11.6, 16.7, 16.8, 20.1, 20.3, 29.8, 99.9, 101.2, 113.5, 115.9, 113.5, 115.9, 125.7, 127.9, 128.8, 132.5, 135.3, 139.1 (due to the very low solubility of the silver complex, not all of the carbon-13 resonances could be identified); HRMS (EI): calcd for $C_{40}H_{32}N_3OAg$: 677.1596; found: 677.1592. Anal. Calcd for $C_{40}H_{32}N_3OAg$: C, 70.80; H, 4.75; N, 6.19. Found: C, 70.83; H, 4.65; N, 6.22.

[9,13,14,18-Tetraethyl-8,19-dimethyl-2-oxynaphthiporphyrinato]silver(III) (27a). A suspension of silver(I) acetate (40.5 mg) in methanol (10 mL) was added to a solution of **23a** (20.1 mg) in chloroform (20 mL) and the resulting mixture stirred at room temperature under nitrogen for 16 h. The mixture was washed with water (×2), dried over sodium sulfate, and evaporated under reduced pressure. The greenish-purple residue was purified by column chromatography on grade 3 alumina, eluting with dichloromethane and then chloroform. Evaporation of the green fractions and recrystallization from chloroform-hexanes gave the silver chelate (21.1 mg, 87%) as dark greyish-green crystals, mp 274−275 °C; IR (KBr): ν 1642 (s), 1619 cm^{-1} (s, C═O str.); UV−vis ($CHCl_3$): λ_{max} (log ε) 456 (4.975), 522 (3.70), 593 (4.39), 616 nm (4.075); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.58 (3H, t, J = 7.7 Hz), 1.68−1.75 (9H, 3 overlapping triplets), 3.07 (3H, s), 3.36 (3H, s), 3.56 (2H, q, J = 7.7 Hz), 3.66−3.75 (6H, 3 overlapping quartets), 7.72 (1H, t, J = 7.8 Hz), 7.85−7.88 (1H, m), 8.35 (1H, d, J = 7.9 Hz), 8.75 (1H, dd, J = 1.3, 7.7 Hz), 9.02 (1H, s), 9.16 (1H, s), 9.29 (1H, s), 9.95 (1H, s); ^{13}C NMR ($CDCl_3$): δ 11.4, 11.8, 17.2, 17.3, 18.2, 19.7 (2), 20.1, 20.3, 95.7, 95.8, 107.5 (d, J = 3.1 Hz), 109.9 (d, J = 3.4 Hz), 110.7, 113.5, 126.9, 127.7, 128.4, 131.6, 132.4, 132.8, 133.4 (m), 135.1 (d, J = 2.8 Hz), 136.8, 138.0, 138.4, 138.9, 141.1, 141.2 (d, J = 3.1 Hz), 141.4, 142.4 (d, J = 3.3 Hz), 142.9, 163.2 (dd, J = 50.1, 56.4 Hz), 191.6; FD MS: m/z (rel. int.) 635.2 (7.3), 634.2 (35), 633.2 (90), 632.1 (40), 631.2 (100, M^+). Anal. Calcd for $C_{36}H_{34}N_3OAg$: C, 68.36; H, 5.42; N, 6.64. Found: C, 68.30; H, 5.44; N, 6.57.

[9,18-Diethyl-8,19-dimethyl-13,14-diphenyl-2-oxynaphthiporphyrinato]silver(III) (27b). Oxynaphthiporphyrin **23b** (23.0 mg, 0.0369 mmol) was reacted with silver(I) acetate (40 mg) under the foregoing conditions. Recrystallization from chloroform-hexanes gave the silver derivative (18.4 mg, 0.0253 mmol, 68%) as green crystals, mp 275−276 °C; UV−vis ($CHCl_3$): λ_{max} (log ε) 332 (4.29), 386 (sh, 4.34), 430 (infl, 4.38), 458 (5.00), 521 (3.65), 599 (4.43), 622 nm (sh, 4.18); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.55 (3H, t, J = 7.7 Hz), 1.64 (3H, t, J = 7.7 Hz), 3.11 (3H, s), 3.34 (3H, s), 3.52 (2H, q, J = 7.7 Hz), 3.65 (2H, q, J = 7.7 Hz), 7.61−7.64 (2H, m), 7.67−7.71 (4H, m), 7.80−7.84 (1H, m), 7.86−7.91 (4H, m), 8.23 (1H, d, J = 8.0 Hz), 8.68 (1H, dd, J = 1.4, 7.7 Hz), 9.29 (1H, s), 9.42 (1H, s), 9.52 (1H, s), 9.85 (1H, s); ^{13}C NMR ($CDCl_3$): δ 11.5, 11.8, 17.06, 17.09, 20.2, 20.4, 99.5, 99.7, 107.30, 107.33, 109.22, 109.25, 111.8, 114.2, 127.1, 127.69, 127.71, 128.6, 128.77, 128.78, 131.4, 132.5, 132.6, 133.8, 134.0, 134.4, 135.44, 135.46, 135.55, 135.59, 137.7, 137.8, 138.4, 138.9, 140.3, 140.5, 142.5, 142.9, 143.6, 191.7. HR MS (EI): Calcd for $C_{44}H_{34}N_3OAg$: 727.1753. Found: 727.1737. Anal. Calcd for $C_{44}H_{34}N_3OAg$: C, 72.53; H, 4.70; N, 5.77. Found: C, 72.46; H, 4.64; N, 5.77.

1,4-Dibenzoylnaphthalene (36). Thionyl chloride (40 mL) was added to 1,4-naphthalenedicarboxylic acid (10.00 g, 46.3 mmol) in a 100 mL round-bottom flask. DMF (10 drops) was added and the stirred mixture was heated under reflux for 1 h. The excess thionyl chloride was removed on a rotary evaporator to give a pale yellow liquid that solidified on standing. The diacyl chloride was transferred to a 1 L round-bottom flask and dissolved in benzene (400 mL). Aluminum chloride (15 g) was added in several portions to the stirred solution, which initially turned dark brown but then lightened up to produce an orange solution. The mixture was stirred under reflux overnight, poured into a mixture of ice (400 g) and hydrochloric acid (46 mL) and extracted with ether (3 × 200 mL). The combined ether layers were dried over sodium sulfate and evaporated under reduced pressure. The residue was recrystallized from ethanol−water to give the diketone (13.45 g, 40.0 mmol, 86%) as white crystals, mp 101.5−102 °C (lit. mp[45] 106 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47−7.51 (4H, m), 7.52 (2H, AA′XX′ system), 7.60 (2H, s), 7.61−7.65 (2H, m), 7.89−7.92 (4H, m), 8.05 (2H, AA′XX′ system); ^{13}C NMR ($CDCl_3$): δ 125.5, 126.3, 127.9, 128.9, 130.6, 131.3, 133.9, 137.9, 139.4, 197.8.

1,4-Bis(phenylhydroxymethyl)naphthalene (37). 1,4-Dibenzoylnaphthalene (10.00 g, 29.7 mmol) was heated with ethanol (200 mL) in a 1 L Erlenmeyer flask until it had completely dissolved. The mixture was allowed to cool to 35 °C and sodium borohydride (2.25 g) was added. The mixture was stirred for 15 min, water (200 mL) was added and the mixture was heated on a boiling water bath for 20 min. The flask was removed from the heat and mixture diluted with water (400 mL). The flask was cooled in ice, the resulting precipitate was suction filtered, and the solid dried *in vacuo* to give the dicarbinol (9.91 g, 29.1 mmol, 98%) as a white powder, mp 169−171 °C. As expected, the NMR data were consistent with the presence of two diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.35−2.38 (2H, 2 overlapping doublets), 6.53 (d, J = 3.3 Hz), 6.54 (d, J = 3.3 Hz) (2H combined), 7.26−7.29 (2H, m), 7.31−7.35 (4H, m), 7.39−7.42 (6H, m), 7.62 (s), 7.65 (s) (2H combined), 8.05−8.10 (2H, m); ^{13}C NMR ($CDCl_3$): δ 73.6, 73.8, 124.1, 124.3, 124.6, 124.8, 125.9, 127.0, 127.1, 127.7, 127.8, 128.57, 128.60, 131.1, 131.2, 138.95, 139.02, 143.02, 143.04. Anal. Calcd for $C_{24}H_{16}O_2.{}^1/_{10}H_2O$: C, 84.23; H, 5.95. Found: C, 84.08; H, 5.91.

5,10,15,20-Tetraphenyl-1,4-naphthiporphyrin (33). Dicarbinol **37** (340 mg, 1.00 mmol), pyrrole (208 μL, 201 mg, 3.00 mmol) and benzaldehyde (204 μL, 212 mg, 2.00 mmol) were dissolved in dichloromethane (900 mL). $BF_3.Et_2O$ in dichloromethane (10% v/v, 1 mL) was added and the mixture was stirred under nitrogen at room temperature for 2 h. DDQ (680 mg, 3 mmol) was added and the mixture stirred for a further 10 min. The solvent was removed on a rotary evaporator, and the residue purified on a grade 2 basic alumina column eluting initially with dichloromethane and then with chloroform. An impure porphyrin fraction eluted initially, followed by a green band corresponding to the product. Recrystallization from chloroform−methanol gave the tetraphenylnaphthiporphyrin (24−31 mg, 0.035−0.046 mmol, 3.5−4.6%) as a dark-green solid, mp >300 °C, darkens at 200 °C; UV−vis ($CHCl_3$): λ_{max} (log ε) 353 (4.45), 466 (4.59), 632 (4.26), 663 nm (infl, 4.18); UV−vis (1 equiv TFA-$CHCl_3$): λ_{max} (log ε) 368 (4.35), 488 (4.77), 757 nm (4.25); UV−vis (10% TFA-$CHCl_3$): λ_{max} (log ε) 384 (4.43), 471 (4.82), 731 nm (4.45); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.01 (2H, AA′XX′ system), 6.28 (2H, AA′XX′ system), 6.93 (2H, s), 7.14 (2H, s), 7.22 (2H, d, J = 4.7 Hz), 7.47−7.50 (6H, m), 7.54−7.57 (2H, m), 7.58−7.63 (4H, m), 7.64−7.68 (4H, m), 7.97 (2H, d, J = 4.7 Hz), 8.08−8.10 (4H, m); ^{1}H NMR (500 MHz, TFA-$CDCl_3$): δ 6.14 (4H, br), 7.26−7.66 (2H, v br), 7.77 (4H, t, J = 7.5 Hz), 7.81−7.88 (6H, m), 7.98−8.06 (8H, m), 8.18 (2H, br), 8.46 (2H, d, J = 7.3 Hz), 8.92 (2H, br); ^{13}C NMR ($CDCl_3$): δ 116.0, 124.1, 124.3, 124.5, 127.46, 127.50, 128.6, 128.9, 130.4, 132.8, 133.3, 133.5, 134.0, 135.1, 136.7, 141.3, 142.1, 144.7, 146.4, 148.6, 159.0, 164.6; ^{13}C NMR (TFA-$CDCl_3$): δ 119.1, 128.7,

128.8, 130.71, 130.75, 131.6, 134.1, 134.3, 134.5, 135.2, 135.3, 137.8, 138.3, 140.4, 147.4, 148.3, 151.5; HR MS (EI): Calcd for $C_{50}H_{33}N_3$: 675.2674. Found: 675.2661. HR MS (EI): Calcd for $C_{50}H_{33}N_3$ + 2H: 677.2831. Found: 677.2815.

Crystallographic Experimental Details of 16. X-ray quality crystals of **16** were obtained by slow evaporation of a $CDCl_3$ solution. The crystals were suspended in mineral oil at ambient temperature and a suitable crystal was selected. A mineral oil coated black needle thereby obtained of approximate dimensions 0.55 × 0.13 × 0.09 mm^3 was mounted on a 50 μm polyimide micromount and transferred to a CCD equipped X-ray diffractometer. The X-ray diffraction data were collected at −173 °C using Mo−K_α (λ = 0.71073 Å) radiation. Data collection and cell refinement were performed using SMART and SAINT+, respectively.[46] The unit cell parameters were obtained from a least-squares refinement of 7528 centered reflections. Compound **16** was found to crystallize in the monoclinic crystal system with the following unit cell parameters: a = 8.7176(18) Å, b = 10.561(2) Å, c = 17.629(4) Å, β = 104.079(3)°, Z = 2. The systematic absences indicated the space group to be $P2_1/n$ (no. 14).[47] A total of 23309 reflections were collected, of which 5044 were unique, and 4316 were observed $F_o^2 > 2\sigma(F_o^2)$. Limiting indicies were as follows: $-15 \le h \le 15$, $-16 \le k \le 16$, $-19 \le l \le 19$. Data reduction were accomplished using SAINT.[46] The data were corrected for absorption using the SADABS procedure.[46]

Solution and data analysis were performed using the WinGX software package.[48] The structure of **16** was solved by charge-flipping methods using the program SUPERFLIP[49] and the refinement was completed using the program SHELX-97.[50] All non-H atoms were refined anisotropically. With the exception of H atoms internal to the macrocycle, all H atoms were included in the refinement in the riding-model approximation (C−H = 0.95, 0.98, 0.99 Å for Ar−H, CH_3, and CH_2; $U_{iso}(H)$ = 1.2Ueq(C) except for methyl groups, where $U_{iso}(H)$ = 1.5eq(C)). Full-matrix least-squares refinement on F^2 led to convergence, $(\Delta/\sigma)_{max}$ = 0.000, $(\Delta/\sigma)_{mean}$ = 0.0000, with R_1 = 0.0475 and wR_2 = 0.1305 for 4316 data with $F_o^2 > 2\sigma(F_o^2)$ using 0 restraints and 363 parameters. A final difference Fourier synthesis showed features in the range of $\Delta\rho_{max}$ = 1.51 $e^-/Å^3$ to $\Delta\rho_{min}$ = −1.411 $e^-/Å^3$. Some positional disorder (<10%) appears to exist; however, the structure models best without inclusion of the disorder. Molecular diagrams were generated using ORTEP-3.[51] CCDC 824680 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information. ORTEP III and POV Ray figures for the X-ray structure of **16**, and selected ^1H NMR, $^1H-^1H$ COSY, HMQC, ^{13}C NMR, MS, and UV−vis spectra are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

Notes

[†]Part 56 in the series "Conjugated Macrocycles Related to the Porphyrins". For part 55, see: Jain, P.; Ferrence, G. M.; Lash, T. D. *J. Org. Chem.* **2010**, *75*, 6563−6573.

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