Oxypyriporphyrin, the First Fully Aromatic Porphyrinoid Macrocycle with a Pyridine Subunit**

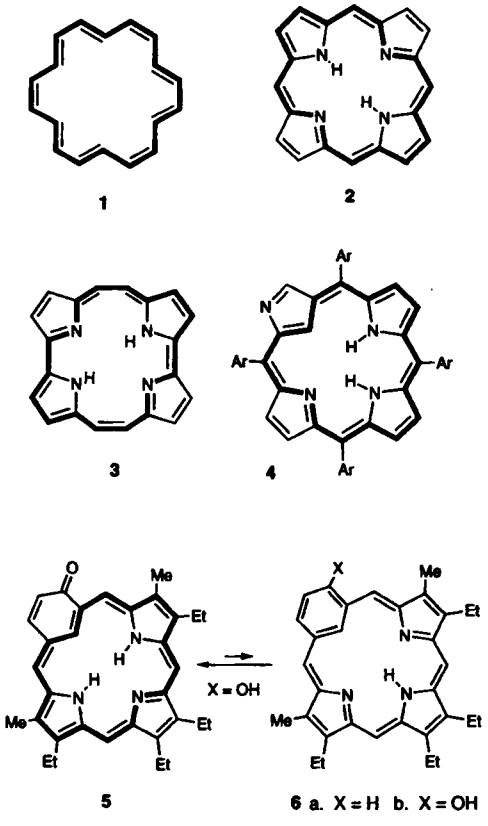
Timothy D. Lash* and Sun T. Chaney

Abstract: The synthesis of the first example of an aromatic pyridine-containing porphyrinoid **10** has been accomplished in excellent yields by the acid-catalyzed "3+1" condensation of 3-hydroxypyridinedicarboxaldehyde (**8**) with tripyrrane **9**. The key intermediate **8** was obtained by the selenium dioxide oxidation of the known biscarbinol **7**. The aromaticity of "oxypyriporphyrin" **10** has been confirmed by MS, NMR, IR, and UV/Vis spectroscopy. This system afforded a monocation in 0.2% TFA–chloroform, and a dication was observed in 2% TFA–chloroform; these species also retained macrocyclic aromaticity. Oxypyriporphyrin readily formed the corresponding metal chelates **14a–c** by reaction with zinc, copper(II), or nickel(II) acetate, and this observation suggests that there are extensive possibilities for the use of **10** in coordination chemistry. Oxypyriporphyrin and the related semiquinone system oxybenziporphyrin represent the first two members of a new class of aromatic porphyrinoids.

Keywords
aromaticity · porphyrins · pyridones · MacDonald condensation · tautomerizations

Introduction

Ever since benzene was first isolated by Michael Faraday in 1825 from the illuminating fuel used in London gaslights, the chemistry of "aromatic" systems has fascinated chemists and stimulated major advances in the field of organic chemistry.[2] Hückel's development of a molecular orbital description for aromatic ring systems[3] encouraged chemists to investigate the synthesis and properties of potentially aromatic cyclic polyenes. Sondheimer's ground-breaking synthesis of [18]annulene (**1**) provided the first example of a continuously conjugated monocyclic 18 π-electron system, and the aromatic nature of this structure furnished strong evidence in support of Hückel's theories.[4] Although Hückel's rule is not valid for multiring systems, the identity of an aromatic species can usually be predicted based upon the presence of a conjugative pathway with $4n+2$ π electrons within the structure. The porphyrin ring system **2** is a particularly important example of a naturally occurring structure[5] with 18 π-electron delocalization pathways and can effectively be considered to be nature's [18]annulene.[6] Apart from their biological significance, porphyrins also have a number of potential applications, ranging from photodynamic therapy (porphyrins preferentially associate with malignant tissue and when irradiated with laser light can generate singlet oxygen, which destroys the cancerous cells[7]), to highly selective catalysts and organic electrical conductors. Aromatic structures related to the porphyrins also have many useful properties and have been extensively investigated.[8] However, novel structural motifs are still being uncovered, and these new discoveries are stimulating major advances in this area. In particular, the synthesis of porphycene (**3**) by Vogel and co-workers in 1986,[9] and the serendipitous discovery of inverted porphyrins **4** by two



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[**] Conjugated Macrocycles Related to the Porphyrins, Part 6. Part 5: ref. [1].

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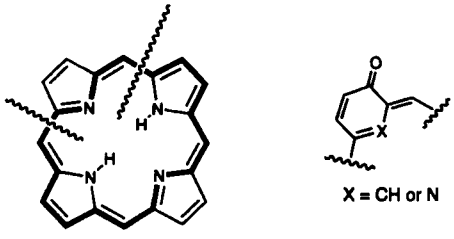
independent groups in 1994,[10] have refocused the field of porphyrin chemistry and opened up new avenues of research that will be pursued well into the 21st century.

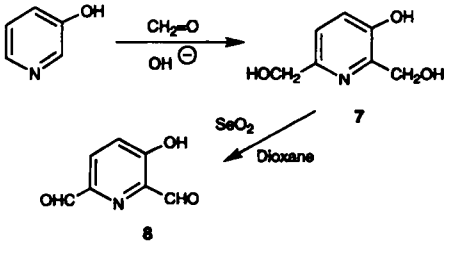
Results and Discussion

In a recent paper,[1] we described the synthesis of the first example of an aromatic porphyrinoid macrocycle **5** containing a benzene ring in place of a pyrrolenic subunit. Although a nonaromatic system termed "benziporphyrin" (**6a**) had been described prior to this,[11] the new system overcame the problems associated with attaining 18 π-electron delocalization pathways by the introduction of a suitably placed hydroxyl unit (structure **6b**). This allowed a favorable keto–enol tautomerization to occur which gave the novel aromatic porphyrinoid oxybenziporphyrin **5**. In a conceptual sense, a pyrrolenic ring has been replaced by a semiquinone unit (Scheme 1), although it is clear that other substitutions are also feasible.



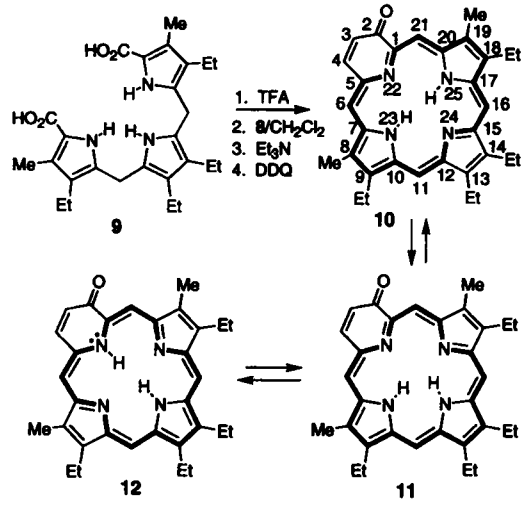
Scheme 1. Replacement of pyrrolenic subunits with semiquinone or pyridone moieties gives a new family of porphyrinoid macrocycles.

We now report the synthesis of a pyridine-containing porphyrin analogue[12] by applying the same "3+1" strategy used in the earlier preparation of **5**.[1,13] Reaction of 3-hydroxypyridine with formaldehyde in the presence of sodium hydroxide gives the biscarbinol **7** (Scheme 2).[14] However, initial attempts to oxidize **7** to the corresponding dialdehyde **8** were



Scheme 2. Synthesis of 3-hydroxy-2,6-pyridinedicarboxaldehyde **8**.

largely unsuccessful. Traditional oxidants such as manganese dioxide and pyridinium chlorochromate failed to give the required diformylpyridine, and the Swern oxidation was similarly unsuccessful. However, oxidation with selenium dioxide[15] in refluxing dioxane was found to give the dialdehyde **8** in excellent yields (Scheme 2). Acid catalyzed condensation with tripyrrane **9**[16] (Scheme 3), followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and chromatography on neutral alumina, gave a deep green fraction that crystallized from chloroform–methanol as dark bluish purple crystals in 67% yield. Spectroscopic characterization of this brightly colored compound, named oxypyriporphyrin, demonstrated that it



Scheme 3. Synthesis of oxypyriporphyrin **10**.

favors a fully aromatic structure. The major tautomer for oxypyriporphyrin is almost certainly structure **10**, although several other species with 18 π-electron delocalization pathways can also be achieved. Structure **11** is less likely to be favored due to the increased level of steric interactions between the two internal hydrogens, and tautomers with the lone pair electrons of pyridine contributing to the porphyrinoid delocalization pathway (e.g., **12**) are relatively unlikely. The proton NMR spectrum for oxypyriporphyrin in deuteriochloroform (Fig. 1)

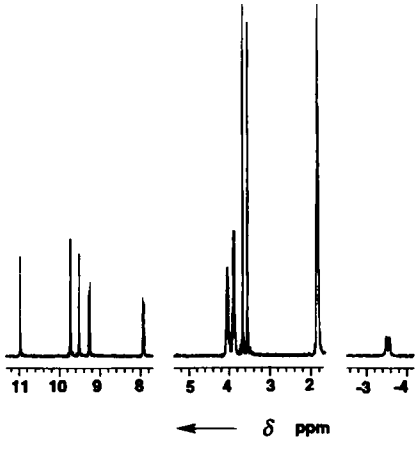


Fig. 1. 300 MHz ^{1}H NMR spectrum of oxypyriporphyrin **10** in deuteriochloroform.

was consistent with structure **10**, showing two broad resonances for the internal NH's upfield at $\delta = -3.6$ and -3.7. The external *meso*-CH's were highly deshielded by the aromatic ring current and appeared as four singlets between $\delta = 9.5$–11.0 (the bridge methine at C-21 is significantly downfield from the other three due to its proximity to the carbonyl unit). The CH=CH component of the pyridone subunit gave a pair of doublets at $\delta = 7.93$ (H_α) and 9.25 (H_β); these data are also in accord with this unit not being directly involved with an aromatic delocalization pathway. The ^{13}C NMR spectrum for **10** was well resolved showing all 20 of the anticipated carbon resonances in the aromatic/olefinic region, and the carbonyl moiety appeared in the usual range for a conjugated ketone at $\delta = 185$. The IR spectrum showed a strong band at 1629 cm^{-1}, which further confirmed

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the presence of the cross-conjugated carbonyl unit. The 70 eV electron impact mass spectrum gave the anticipated strong molecular ion at *m/z* 478 (Fig. 2), as would be expected for a stable aromatic system, and minor benzylic fragmentation ($[M - CH_3]^+$) was observed as well as expulsion of CO to give a porphyrin radical cation (*m/z* 450; Scheme 4). In common

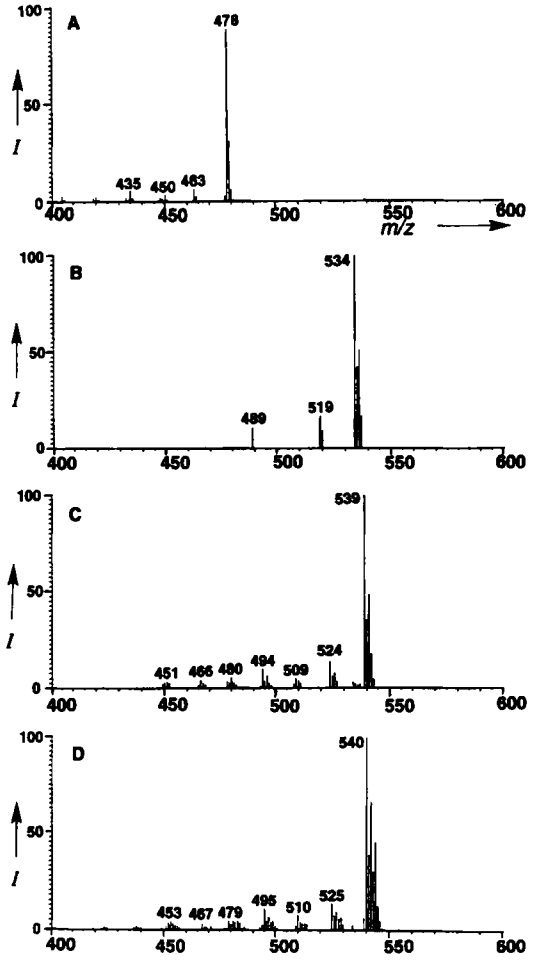
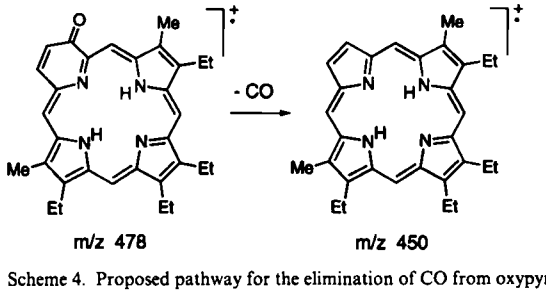


Fig. 2. Electron impact mass spectra (70 eV) for oxypyriporphyrin **10** (A), nickel(II) oxypyriporphyrin **14c** (B), copper(II) oxypyriporphyrin **14b** (C), and zinc oxypyriporphyrin **14a** (D).



Scheme 4. Proposed pathway for the elimination of CO from oxypyriporphyrin in electron impact mass spectrometry.

with true porphyrins,[17] doubly charged ions, including $[M]^{2+}$ and $[M - CO]^{2+}$, made varying contributions to the EI mass spectra. A small cluster of peaks was also observed with masses 61–64 units higher than the molecular ion, presumably due to the presence of transition metal contaminants.[18] The UV/Vis spectrum of **10** in chloroform was porphyrin-like, showing a strong Soret band at 422 nm and several smaller absorptions at

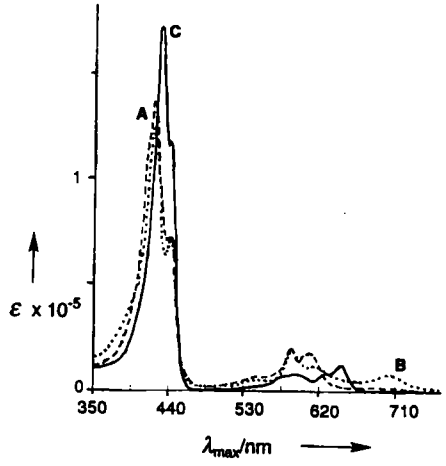
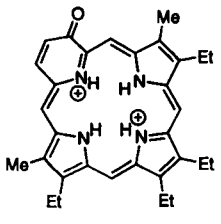


Fig. 3. Electronic absorption spectra of oxypyriporphyrin **10**. A: in chloroform; B: in 0.2% TFA-chloroform (monocation); C: dication **13** in 2% TFA-chloroform.

higher wavelengths (Fig. 3). In 0.2% trifluoroacetic acid–chloroform, a distinct species with a long wavelength absorption at 704 nm was observed; this was attributed to the formation of a monocation (several structures are possible). In 2% trifluoroacetic acid–chloroform, the Soret band underwent significant batho- and hyperchromic shifts that presumably corresponded to the formation of the oxypyriporphyrin dication **13**. The retention of strong Soret bands in the UV/Vis spectra for the mono- and dications suggested that these species also favor macrocyclic aromaticity. This conjecture was further supported for the dication by the ^1H and ^{13}C NMR data for **10** in trifluoroacetic acid–deuteriochloroform.[19]



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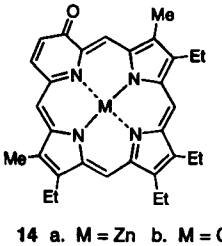

14 a. M = Zn b. M = Cu c. M = Ni

Oxypyriporphyrin readily formed the related zinc, copper(II), and nickel(II) complexes.[20] The zinc and copper chelates, **14a** and **14b**, were easily obtained by simply refluxing the free base **10** with a solution of excess metal acetate in chloroform–methanol; this failed in the case of the nickel(II) complex, although **14c** was obtained in good yields when the reaction was carried out in refluxing *N,N*-dimethylformamide.[21] The structures of **14a–c** were confirmed by electron impact mass spectrometry (Fig. 2). Interestingly, while benzylic fragmentation was still observed for these metal chelates, the CO expulsion pathway was no longer discernible for either the singly or doubly charged ions. UV/Vis spectroscopy indicated that these chelates retained the aromatic electronic configuration; ^1H NMR spectroscopy confirmed this supposition for the diamagnetic complex **14c**, although the zinc complex **14a** gave anomalous data. The zinc complex was only sparingly soluble in deuteriochloroform, but it was possible to obtained ^1H NMR spectra in this solvent. Although most of the ^1H NMR resonances were in accord with the expected values, the downfield *meso*-proton corresponding to 21-H, which appears near $\delta = 11$

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for **10** and **14c**, was replaced by a broad signal near $\delta = 7.0$. In addition, the doublet for the α enone proton, which should have been evident near $\delta = 8$, was replaced by a broad resonance at $\delta = 4.85$. Addition of trace amounts of pyrrolidine greatly increased the solubility of **14a**, and the abnormal signals shifted to $\delta = 10.96$ and 8.12, respectively, in the presence of this secondary amine. These data suggest that the zinc complex strongly aggregates in solution through an intermolecular interaction between the carbonyl units (Fig. 4). This arrangement places the aberrant protons at positions 3 and 21 within the shielding zone for the interacting macrocycle, and this leads to the unexpected upfield shifts that were observed. Presumably pyrrolidine disrupts macrocyclic aggregation by hydrogen bonding to the carbonyl unit and this both increases the solubility of the chelate as well as allowing full spectroscopic characterization. As porphyrins have a strong tendency to aggregate in solution, these results are not particularly unexpected. Overall, the preliminary results for metal chelates **14a–c** suggest that oxypyriporphyrin could have as versatile and extensive a coordination chemistry as tetrapyrrolic porphyrins.

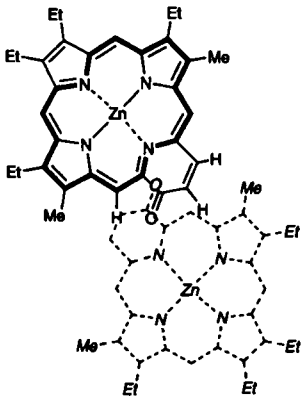

Fig. 4. Proposed intermolecular interaction/aggregation of zinc oxypyriporphyrin **14a** in chloroform solution.

Conclusion

Although it has been over 170 years since the first isolation of benzene, the nature of aromaticity continues to fascinate organic chemists. Oxybenzi- and oxypyriporphyrins represent the first two members of a fundamentally new class of aromatic porphyrinoids, and this work is likely to provide the foundations for many related studies in this area. These macrocycles also show the potential for chemical modifications (derivatization of the carbonyl moiety, functionalization of double bonds, Diels–Alder cycloaddition chemistry, etc.) and these studies will provide access to other highly conjugated aromatic systems.

Experimental Procedure

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR Spectrometer, and UV spectra were obtained on a Beckmann DU-40 spectrophotometer. NMR spectra were recorded on a Varian Gemini-300 NMR spectrometer. Mass spectral data were obtained from the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, supported in part by a grant from the National Institute of General Medical Sciences (GM 27029). Elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

3-Hydroxy-2,6-pyridinedicarboxaldehyde (8): A solution of 2,6-bis(hydroxymethyl)-3-hydroxypyridine [14] (1.00 g) in dioxane (32 mL) was stirred under reflux with selenium dioxide (0.75 g) for 12 h. The dioxane was removed under reduced pressure and the residue steam distilled. The distillate was extracted with chloroform (3 × 200 mL), and the combined organic solutions were dried over sodium sulfate and evaporated under reduced pressure to give **8** as off-white crystals (0.50 g; 51%), m.p. 145–146 °C. Sublimation gave an analytical sample as small white needles, m.p. 148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.51$ (1 H, d, $J = 8.7$ Hz, 4-H), 8.14 (1 H, d, $J = 8.7$ Hz, 5-H), 10.01 (1 H, s), 10.15 (1 H, s) (2 × CHO), 11.17 (1 H, s, OH); ^{13}C NMR ($CDCl_3$): $\delta = 127.23$, 128.19, 136.68, 146.90, 161.90, 191.20, 198.53; IR (KBr; selected absorptions): $\tilde{\nu} = 3209$ ($\tilde{\nu}_{OH}$), 1706, 1666 cm^{-1} (2 × $\tilde{\nu}_{C=O}$); MS (EI, 70 eV): *m/z* (%): 151 (100) [M^+], 123 (100), 122 (30), 96 (16), 95 (15), 94 (22), 77 (13), 68 (30), 67 (52), 66 (17), 58 (23), 52 (15), 43 (83); HRMS: calculated for $C_7H_5NO_3$: *m/z* 151.02694; found: 151.02689; elemental analysis for $C_7H_5NO_3$: calcd C 55.63, H 3.33, N 9.27; found C 55.28, H 3.19, N 8.94.

Oxypyriporphyrin 10: Tripyrranedicarboxylic acid **9** (200 mg) was stirred with TFA (2 mL) under an atmosphere of nitrogen for 10 min. Dichloromethane (38 mL) was added, followed immediately by 3-hydroxy-2,6-pyridinedicarboxaldehyde (67 mg), and the mixture was stirred under nitrogen for a further 2 h. After neutralization by the dropwise addition of triethylamine, DDQ (102 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 alumina, eluting first with dichloromethane and then with chloroform. A deep green fraction was collected and recrystallized from chloroform–methanol to give the porphyrin analogue (144 mg; 67%) as dark purple crystals, m.p. > 300 °C; UV/Vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 422 (5.24), 436 (sh, 4.95), 548 (3.86), 586 (4.40), 609 (4.34), 661 nm (3.09); UV/Vis (0.2% TFA–$CHCl_3$; monocation): λ_{max} ($\log_{10}\varepsilon$) = 422 (5.19), 442 (4.96), 543 (3.84), 588 (4.38), 615 (4.18),704 nm (3.98); UV/Vis (2% TFA–$CHCl_3$; dication **13**): λ_{max} ($\log_{10}\varepsilon$) = 429 (5.34), 442 (infl, 5.22), 576 (sh, 4.02), 591 (4.08), 625 (4.09), 647 nm (4.28); IR (KBr): $\tilde{\nu}$ = 3364, 3039, 2961, 2924, 2866, 1629, 1594, 1549, 1447, 1412, 1391, 1370, 1311, 1269, 1237, 1223, 1164, 1139, 1111, 1055, 1013, 988, 950, 880, 835, 775, 740, 694, 680, 663, 615, 566, 530, 474 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -3.66$ (1 H, s), −3.59 (1 H, s) (2 × NH), 1.7–1.9 (12 H, 4 overlapping triplets, 4 × CH_2CH_3), 3.53 (3 H, s), 3.66 (3 H, s) (2 × pyrrole-CH_3), 3.87 (6 H, q), 4.01 (3 H, q), 4.04 (3 H, q) (4 × CH_2CH_3), 7.93 (1 H, d, $J = 9.6$ Hz, 3-H), 9.25 (1 H, d, $J = 9.6$ Hz, 4-H), 9.48 (1 H, s), 9.70 (1 H, s), 9.72 (1 H, s) (3 × *meso*-H), 10.96 (1 H, s, 21-H); ^{1}H NMR (300 MHz, TFA–$CDCl_3$): $\delta = -1.2$ (4 H, br, 4 × NH), 1.6–1.75 (12 H, 4 overlapping triplets, 4 × CH_2CH_3), 3.50 (3 H, s), 3.54 (3 H, s) (2 × pyrrole-CH_3), 3.9–4.1 (8 H, 4 overlapping quartets, 4 × CH_2CH_3), 8.72 (1 H, d, $J = 10$ Hz, 3-H), 9.84 (1 H, d, $J = 10$ Hz, 4-H), 10.16 (1 H, s), 10.38 (1 H, s), 10.39 (1 H, s) (3 × *meso*-H), 11.10 (1 H, s, 21-H); ^{13}C NMR (75.46 MHz, $CDCl_3$): $\delta = 11.18$, 11.64, 17.20, 18.31, 19.46, 19.58, 19.70, 95.98, 96.36, 103.43, 107.97, 131.14, 133.55, 135.08, 135.69, 137.27, 137.79, 138.22, 138.90, 138.99, 139.56, 144.14, 145.20, 145.36, 145.56, 155.13, 155.66, 184.88; ^{13}C NMR (75.46 MHz, TFA–$CDCl_3$): $\delta = 11.55$, 11.66, 16.41, 16.45, 17.40, 19.79, 98.78, 103.55, 108.21, 132.24, 135.02, 137.56, 139.03, 140.10, 140.87, 141.98, 143.13, 143.23, 144.28, 145.22, 148.25, 177.82; MS (EI, 70 eV): *m/z*(%): 479 (35), 478 (100) [M^+], 463 (7) [$M^+ - CH_3$], 450 (4) [$M^+ - CO$], 239 (4) [M^{2+}], 225 (5) [$(M - CO)^{2+}$]; HRMS: calculated for $C_{31}H_{34}N_4O$: *m/z* 478.27326; found: 478.27336; elemental analysis for $C_{31}H_{34}N_4O$: calcd C 77.79, H 7.16, N 11.70; found C 77.53, H 7.07, N 11.62.

Zinc complex 14a: A saturated solution of zinc acetate in methanol (3 mL) was added to a solution of oxypyriporphyrin (10 mg) in chloroform (10 mL), and the mixture was stirred under reflux for 1 h. The mixture was washed with water and evaporated under reduced pressure. The residue was chromatographed on neutral alumina (Grade 3) eluting with 1% methanol–chloroform and recrystallized from chloroform–methanol to give the zinc complex (10 mg; 88%) as blue crystals, m.p. > 300 °C; UV/vis (2% pyrrolidine–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 418 (sh, 4.60), 440 (5.35), 458 (5.14), 555 (sh, 3.61), 583 (4.075), 627 (sh, 4.29), 636 nm (4.46); UV/vis (DMF): λ_{max} ($\log_{10}\varepsilon$) = 411 (sh, 4.58), 431 (5.32), 449 (5.03), 546 (sh, 3.45), 578 (4.045), 627 nm (4.40); IR (KBr): $\nu_{C=O} = 1604$ cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ + 1 drop pyrrolidine): $\delta = 1.75–1.87$ (12 H, 4 overlapping triplets, 4 × CH_2CH_3), 3.49 (3 H, s), 3.56 (3 H, s) (2 × pyrrole-CH_3), 3.88–4.02 (8 H, 4 overlapping quartets, 4 × CH_2CH_3), 8.12 (1 H, d, $J = 9.3$ Hz, 3-H), 9.44 (1 H, d, $J = 9.3$ Hz, 4-H), 9.50 (1 H, s), 9.72 (2H, s) (3 × *meso*-H), 10.96 (1 H, s, 21-H); ^{13}C NMR (75.46 MHz, $CDCl_3$ + 1 drop pyrrolidine): $\delta = 11.60$, 11.87, 17.65, 17.70, 18.50, 19.69, 19.92, 97.27, 97.30, 103.48, 108.24, 130.84, 135.97, 137.43, 139.51, 142.97, 143.22, 143.50, 143.69, 145.01, 147.58, 149.46, 150.31, 150.83, 150.94, 151.32, 184.81; MS (EI, 70 eV): *m/z* (%): 546 (4.7), 545 (12), 544 (45), 543 (30), 542 (66), 541 (38), 540 (100), 539 (6.4), 529 (6.2), 528 (5.4), 527 (9.1), 526 (7.3), 525 (13), 510 (7.4); HRMS: calculated for $C_{31}H_{32}N_4O_{64}Zn$ *m/z* 540.18676; found: 540.18726.

Copper(II) complex 14b: A saturated solution of copper(II) acetate in methanol (3 mL) was added to a solution of **10** (10 mg) in chloroform (10 mL), and the mixture was stirred under reflux for 1 h. The mixture was washed with water, the solvent evaporated under reduced pressure and the residue chromatographed on neutral alumina (Grade 3) eluting with chloroform. Recrystallization from chloroform–methanol gave the copper(II) complex (11 mg; 96%) as purple crystals, m.p. > 300 °C; UV/vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 427 (5.30), 438 (sh, 5.11), 575 (3.76), 601 (sh, 3.90), 620 nm (4.30); IR (KBr): $\nu_{C=O} = 1624$ cm^{-1}; MS (EI, 70 eV): *m/z* (%): 543 (4.8), 542 (17), 541 (48), 540 (35), 539 (100), 526 (7.8), 525 (6.2), 524 (13), 510 (3.8), 509 (5.1), 508 (2.2), 496 (6.0), 495 (4.0), 494 (9.7), 481 (2.9), 480 (5.5), 479 (3.1), 478 (3.3), 467 (2.5), 466 (4.2), 452 (2.8), 451 (3.4), 450 (3.1), 270 (4.9), 269 (12); HRMS: calculated for $C_{31}H_{32}N_4O^{63}Cu$ *m/z* 539.18721; found: 539.18693.

Nickel(II) complex 14c: A mixture of oxypyriporphyrin (10 mg) and nickel(II) acetate tetrahydrate (26 mg) in DMF were stirred under reflux for 1 h. The solution was diluted with chloroform, washed with water, and evaporated under reduced

pressure. The residue was chromatographed on Grade 3 alumina, eluting first with dichloromethane and then with chloroform, and the product was collected as a deep green fraction. Recrystallization from chloroform–methanol afforded the nickel complex (7 mg; 64%) as bluish purple crystals, m.p. 237–238 °C; UV/vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 436 (5.07), 578 (3.98), 619 nm (4.40); IR (KBr): $\nu_{C=O}$ = 1622 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.62–1.74 (12H, 4 overlapping triplets, 4 × CH_2CH_3), 3.19 (3H, s), 3.23 (3H, s) (2 × pyrrole-CH_3), 3.62–3.74 (8H, 4 overlapping quartets, 4 × CH_2CH_3), 7.84 (1H, d, J = 10 Hz, 3-H), 8.59 (1H, s, *meso*-H), 9.10 (1H, d, J = 10 Hz, 4-H), 9.14 (1H, s), 9.15 (1H, s) (2 × *meso*-H), 9.67 (1H, s, 21-H); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 11.05, 11.33, 17.08, 17.92, 19.51, 19.58, 97.57, 104.81, 104.90, 129.72, 130.09, 137.27, 138.37, 139.21, 139.35, 141.33, 141.46, 141.69, 141.99, 144.55, 145.01, 145.67, 146.04, 147.68, 189.11; MS (EI, 70 eV): *m/z* (%): 537 (17), 536 (51), 535 (42), 534 (100), 520 (9), 519 (17), 489 (10), 268 (13), 267 (20), 233 (12), 222 (8.5); HRMS: calculated for $C_{31}H_{32}N_4O^{58}Ni$ *m/z* 534.19296; found: 534.19352.

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