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Selective Synthesis of *meso*-Naphthylporphyrins

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A series of novel *meso*-(8-substituted naphth-1-yl)porphyrins has been synthesized creating derivatives with a tight recognition environment above the porphyrin plane. The selective synthesis of single atropisomers is discussed. Condensation of bisnaphthaldehyde **12** with phenyldipyrromethane unexpectedly led to selective synthesis of the α,α-5,10-bridged isomer **14**. A mechanism is proposed for this unusual scrambling, and alternative syntheses of α,α-5,15-bisnaphthylporphyrins are described. Synthesis of 5,15-analogues can be achieved by employing (pentafluorophenyl)-dipyrromethane or via presynthesis of a bis(dipyrromethane) derivative **22** (from bisnaphthaldehyde **12**) and subsequent condensation with benzaldehyde.

Introduction

The synthesis of porphyrins has been widely studied since the first synthesis of hemin by Fisher and Ziele in 1929.[1] Interest often stems from the wide occurrence of porphyrin derivatives in nature combined with the ability of synthetic and natural derivatives to act as models for biological processes (light harvesting, oxygen transport, catalysis, molecular recognition).[2] For some time we have been interested in the construction of useful molecular materials from porphyrins and related macrocycles. As part of a project aimed at construction of molecular recognition hosts based on the metalloporphyrin platform, we targeted *meso*-naphth-1-ylporphyrins[3,4] bearing an additional substituent (suitable for further elaboration) at the 8-position (such naphth-1-ylporphyrins do not interconvert and so give rise to stable atropisomers[5]). We chose to incorporate oxygen at the 8-position (OH) and, to generate a tight recognition cleft above the porphyrin central metal ion, we required pairs of hydroxyl groups located on opposite sides of the porphyrin (5,15- and/or 10,20-) on the same face. The two parent compounds are shown in Figure 1.

The synthesis of symmetrical, tetra-*meso*-substituted porphyrins typically involves condensation of pyrroles with aldehydes or their equivalent.[2,6] Synthesis of unsymmetrically substituted porphyrins using this 4 + 4 approach is possible but usually leads to a statistical distribution of products. A similar statistical distribution is typically observed when atropisomeric porphyrins are synthesized in this way.[7] In our case we realized that statistical condensation of pyrrole with 8-hydroxynaphth-1-aldehyde (or a protected version) would lead to a mixture that comprised 4 atropisomers (Scheme 1). It can be seen that the required α,*β*,α,*β*-atropisomer is expected to be formed as a minor component. Nevertheless, we investigated the statistical synthesis because literature precedent suggested that separation of the atropisomeric mixture produced could prove possible (synthesis and separation of other hydroxynaphthyl porphyrins have been achieved using this strategy[3]).

8-Hydroxynaphthaldehyde was synthesized from 1,8-naphthalic anhydride as shown in Scheme 2.[8] Condensation with pyrrole was attempted using both standard conditions (hot propionic acid[6a]) and boron trifluoride (followed by DDQ),[6b] but the reaction failed to yield any porphyrin product. Condensation of acetate derivative **7** with pyrrole also failed to yield any porphyin.

It was therefore decided to protect the hydroxyl group as its methyl ether (it was known that both 2-methoxy and 7-methoxy-1-naphthaldehyde successfully formed porphyrin derivatives by condensation with pyrrole[3]). 8-Methoxy-1-naphthaldehyde[9] was synthesized by

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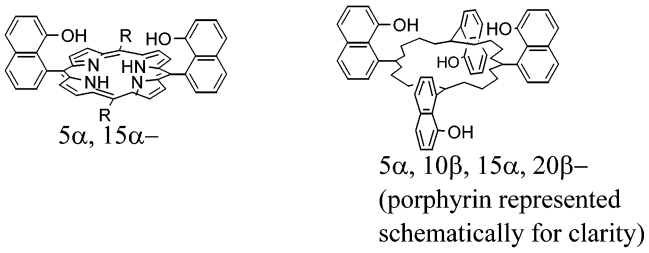

5α, 15α–

5α, 10β, 15α, 20β–
(porphyrin represented
schematically for clarity)

FIGURE 1.

methylation of 8-hydroxy-1-naphthaldehyde using methyl iodide or dimethyl sulfate. However, its synthesis was more conveniently achieved from intermediate diol **4** by methylation of the naphthol followed by oxidation of the primary alcohol. This latter step could be achieved by using a Jones oxidation, but it was found that on a large scale it was more convenient to perform a Swern oxidation (due to simplified workup).

8-Methoxy-1-naphthaldehyde was condensed with pyrrole in hot propionic acid and gave a modest yield of the required porphyrins (6%). The reaction was optimized and a yield of 30% could be obtained using Lindsey's conditions[10] [BF_3·OEt_2, TCQ, PcFe(II)]. The porphyrin was obtained pure (as a mixture of atropisomers) by column chromatography. The product is clearly seen to be a mixture of atropisomers by examination of its ^{1}H NMR spectrum. A set of singlets (MeO) appear at around 2.1−2.3 ppm. These appear at high field (cf. 4.0 ppm for 8-methoxy-1-naphthaldehyde) due to the porphyrin ring current, demonstrating their location above the porphyrin plane. Similarly, a set of signals is clearly observed for 7-H of the *meso*-naphthalenes. Many attempts were made to separate the mixture of atropisomers. Careful recrystallization of the solid (various solvent systems) resulted in product compositions that were essentially unchanged. The mixture proved inseparable by TLC under all combinations of stationary phase (silica, alumina) and mobile phase employed. Analytical HPLC (normal phase) gave similar disappointing results. It was known from the literature that the related 2- and 7-substituted porphyrins could be easily hydrolyzed to give the tetrahydroxide mixtures that were separated using column chromatography. A similar strategy was therefore attempted with **9**. However, it was found that hydrolysis of **9** was extremely difficult in comparison to the other isomers (no doubt due to the extra constraints imposed by 8-substitution) with little or no hydrolysis occurring after treatment with BBr_3 at room temperature for 12 h. Hydrolysis was eventually achieved after treatment for several days with refluxing HBr/glacial acetic acid. Separation of the atropisomeric mixture was again attempted by TLC and HPLC. Unfortunately, no separation could be achieved. Tetramethoxide **9** and tetrahydroxide **10** were converted to their zinc complexes (by treatment with zinc acetate in DMF), but again no separation could be achieved (Scheme 3).

The synthesis was repeated using a longer chain ether (hexyloxynaphthaldehyde) in an attempt to prepare separable atropisomers. The porphyrin mixture was easily isolated (25%) but could not be separated on a preparative scale. In this case, however, analytical HPLC clearly showed the presence of all 4 atropisomers in the mixture.

Single Atropisomer Synthesis from Dialdehydes. At this stage it was decided to alter the synthetic strategy. We reasoned that a less complex mixture of atropisomeric porphyrins would be produced if we started from dialdehydes (i.e., if two naphthaldehydes were linked by a protecting/bridging group). We selected *p*-xylyl as linker,[11] because a simple molecular model indicated that it could bridge across the 5,15-positions easily. Furthermore, we expected its removal (deprotection) would be straightforward. Diol **4** reacted smoothly with α,α-dibromo-*p*-xylene to give bisnaphthyl ether **11**, which was converted to dialdehyde **12** using a Swern oxidation (Scheme 4). Unfortunately reaction between dialdehyde **12** and pyrrole [BF_3·OEt_2, TCQ, PcFe(II)] failed to produce any porphyrin product (polymeric tars and recovered dialdehyde). The conditions were modified but gave similar disappointing results in all cases.

Due to the difficulties experienced with the synthesis and isolation of these single-atropisomer 5,10,15,20-tetranaphth-1-ylporphyrins (which could be elaborated into porphyrins with two identical recognition faces), we decided to instead target derivatives which would, when appropriately modified, bear a single recognition face (i.e. α,α-5,15-bisnaphth-1-ylporphyrins, Figure 1). Such 5,15-disubstituted porphyrins are typically synthesized from a dipyrromethane derivative and an aldehyde.[2,12] In our case, this would be expected to yield a mixture of just two porphyrins (α,α-5,15- and α,*β*-5,15-). Using bridged dialdehyde **12** appeared most attractive, because a single porphyrin product would be expected (the target α,α-5,-15-derivative) (Scheme 5).

Phenyldipyrromethane was therefore prepared and reacted with dialdehyde **12** [both in hot propionic acid and using BF_3·OEt_2, TCQ, PcFe(II)]. A mixture of porphyrins was isolated and separated by column chromatography and found to contain a small amount of tetraphenylporphyrin along with another porphyrin that we expected to be the α,α-5,15-bridged porphyrin **13**. However, identification of this major product was not straightforward. Mass spectrometry gave a molecular ion consistent with **13**, but NMR spectroscopy did not give the simple spectra that we expected. The ^{1}H NMR spectrum in fact shows several interesting features including a broad resonance at 3.9 ppm (which sharpens somewhat at elevated temperatures) and two doublets between 3 and 4 ppm, in addition to a complex set of signals in the aromatic region. The former signal is attributed to the four protons on the bridging xylyl group, and the two doublets are from the inequivalent benzylic protons (geminal coupling). From these data (in conjunction with COESY and DEPT experiments), the major product (15%) was identified as the 5,10-bridged porphyrin **14** (Scheme 6).[13] Crystals suitable for X-ray diffraction

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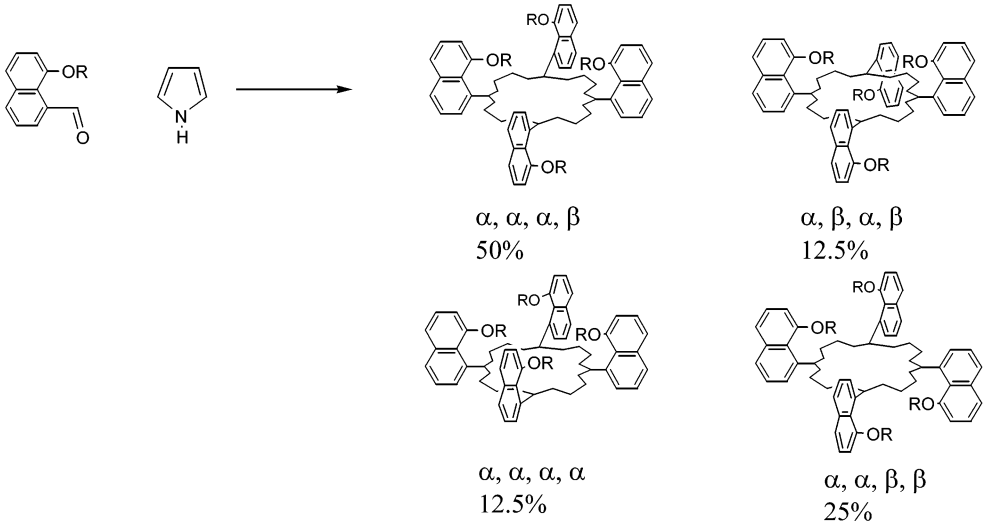
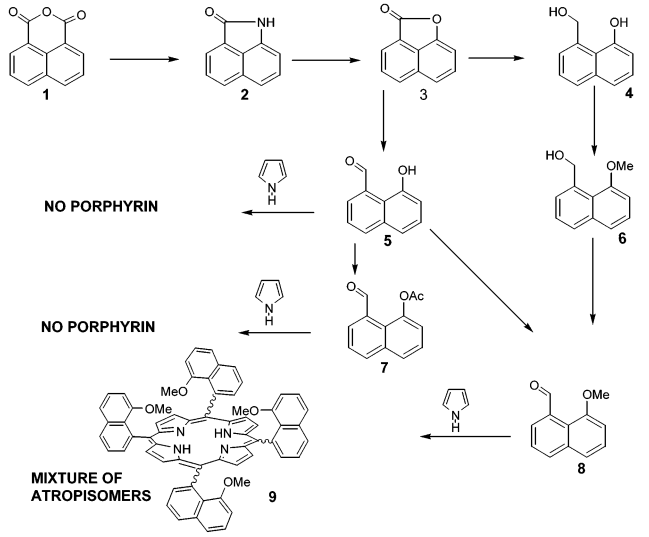
SCHEME 1



SCHEME 2



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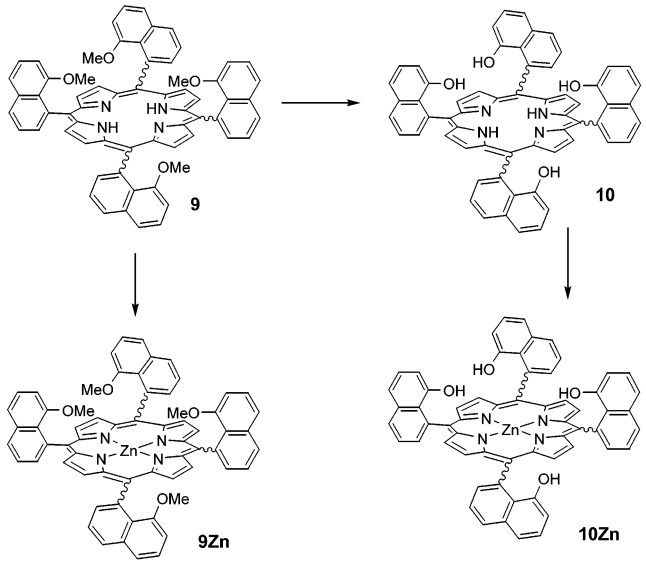

were grown from chloroform/methanol. Careful examination of the products from subsequent reactions allowed trace quantities (2%) of the expected 5,15-isomer to be isolated and characterized. As expected, the ^{1}H NMR spectrum of **13** is uncomplicated and the benzyl and xylyl protons appear as sharp singlets (3.1 and 3.8 ppm).

Scrambling in porphyrin synthesis is commonly observed,[14] but this unprecedented selectivity suggests that a subtle departure from the usual pathway (usually interpreted as arising from breakdown of the dipyrromethane under the acidic conditions and leading to a complex mixture of all possible porphyrins) is occurring. A plausible mechanism is shown in Scheme 7. Following normal electrophilic aromatic substitution at the 5-position of the dipyrromethane, the second aldehyde is added at the 2-position of the same pyrrole unit to give intermediate **15**. Fragmentation can give cyclic 2,5-disubstituted pyrrole **16** and pyrrolic carbocation **17**. Reaction of these two components (directly or sequentially) with another equivalent of dipyrromethane leads to the observed 5,10-bridged isomer **14**.

It can be seen that this mechanism implicates formation of carbocation **17**. We reasoned, therefore, that destabilization of this intermediate (leaving group) would suppress the pathway and favor formation of the 5,15-isomer. Dipyrro(pentafluorophenyl)methane **18**[15] was therefore synthesized and reacted, under the same conditions, with dialdehyde **12** (Scheme 8). This reaction afforded essentially one porphyrin product, which was characterized as the expected 5,15-bridged porphyrin **19**. It has been reported that scrambling during porphyrin synthesis can be reduced if the cyclizations are performed at lower temperatures in the presence of a metal ion template (zinc).[16] These conditions did indeed increase the yield of the reaction, and **19Zn** was isolated in 37% yield. However, the 5,10-bridged isomer was still es-

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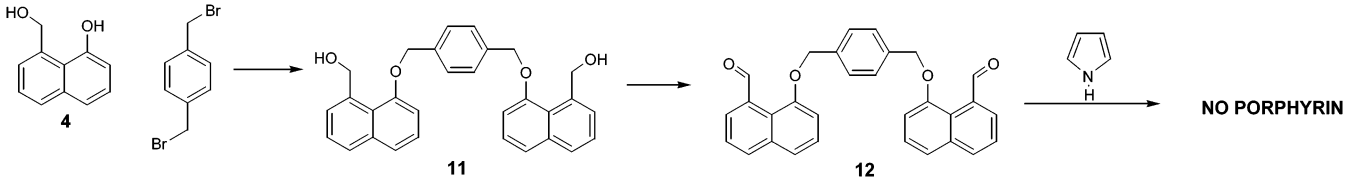
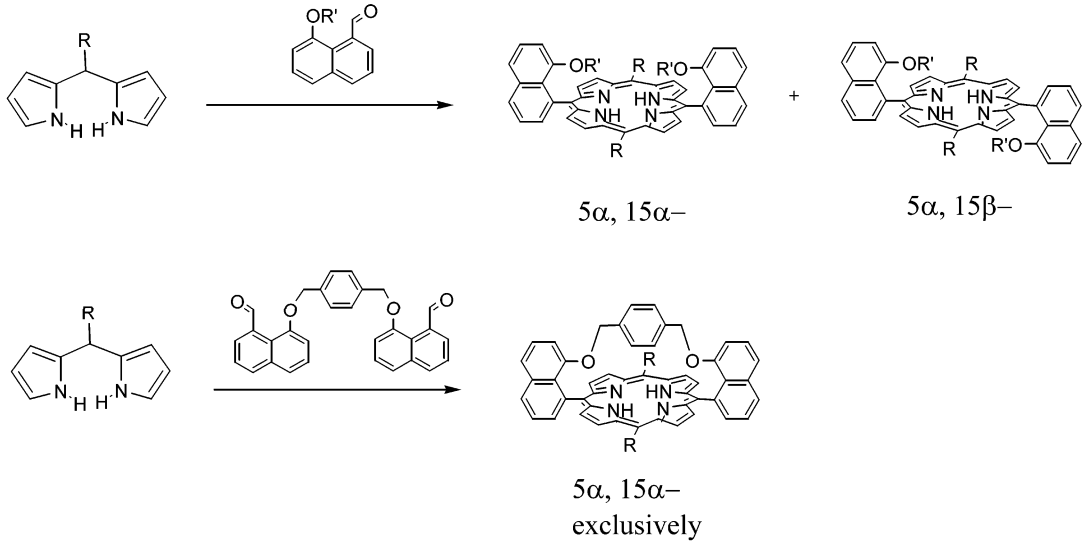
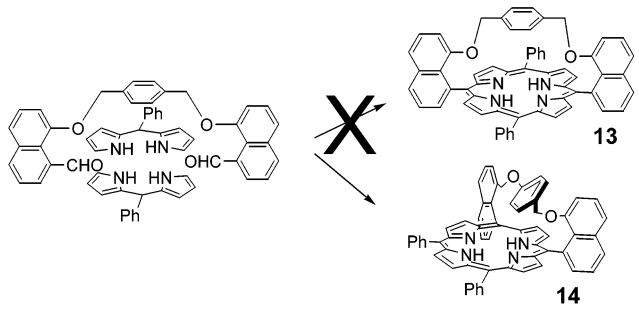
SCHEME 4



SCHEME 5. Expected Outcome from Condensation of Dipyrromethane Derivatives with Naphthaldehydes



SCHEME 6. Unexpected, Selective Scrambling To Give 5,10-Bisnaphthylporphyrin 14



sentially the only isomer observed from the reaction employing dipyrrophenylmethane.

These observations were mirrored when the syntheses of bis(methoxynaphthyl) porphyrins were performed by employing dipyrromethanes and methoxynaphthaldehyde **8**. When dipyrrophenylmethane was employed, a complex mixture of all possible scrambled porphyrin products was obtained (as evidenced by mass spectrometry but not separated). Use of dipyrro(pentafluorophenyl)methane resulted in a clean reaction and isolation of 5,15-bisnaphthylporphyrin as a 1:1 mixture of two atropisomers. Careful crystallization permitted a small quantity of crystalline α,α-isomer (**20**) to be obtained (Scheme 9). Again the yield of (zinc) porphyrin could be improved (50%) using Setsune's conditions. The two atropisomers could be separated by chromatography (as either zinc or metal-free derivatives).

To realize the synthesis of the parent (10,20-diphenyl) porphyrin **13**, an alternative strategy (in which formation of intermediates **15**/**16** and hence **14** was avoided) was devised. Dialdehyde **12** was converted to its bis(dipyrromethane) analogue **22**. Condensation with benzaldehyde proceeded smoothly using Setsune's conditions to produce the desired 5,15-bridged porphyrin (as the zinc derivative). Crystals suitable for X-ray crystallography were obtained from dichloromethane/methanol. A control reaction was carried out under identical conditions to those employed in the synthesis of **14** from dipyrrophenylmethane and **12** (Scheme 10). Compound **13** was the only observed product and this further implies that an alternative mechanism to simple scrambling gives rise to the 5,10-isomer in our previous synthesis.

Conclusions

The controlled synthesis of novel *meso*-naphthylporphyrins (which are suitable for further elaboration into molecular recognition hosts) has been achieved. An unusual "scrambling" mechanism is observed when certain dialdehydes are condensed with dipyrrophenylmethane, leading to essentially exclusive formation of the 5,10-isomer. This scrambling is completely suppressed when dipyrro(pentafluorophenyl)methane is employed (destabilized carbocation leaving group). The α,α-5,15-bridged isomer can be prepared smoothly by conversion of dialdehyde into bis(dipyrromethane) and condensation with benzaldehyde.

Experimental Section

General methods are detailed in the Supporting Information.

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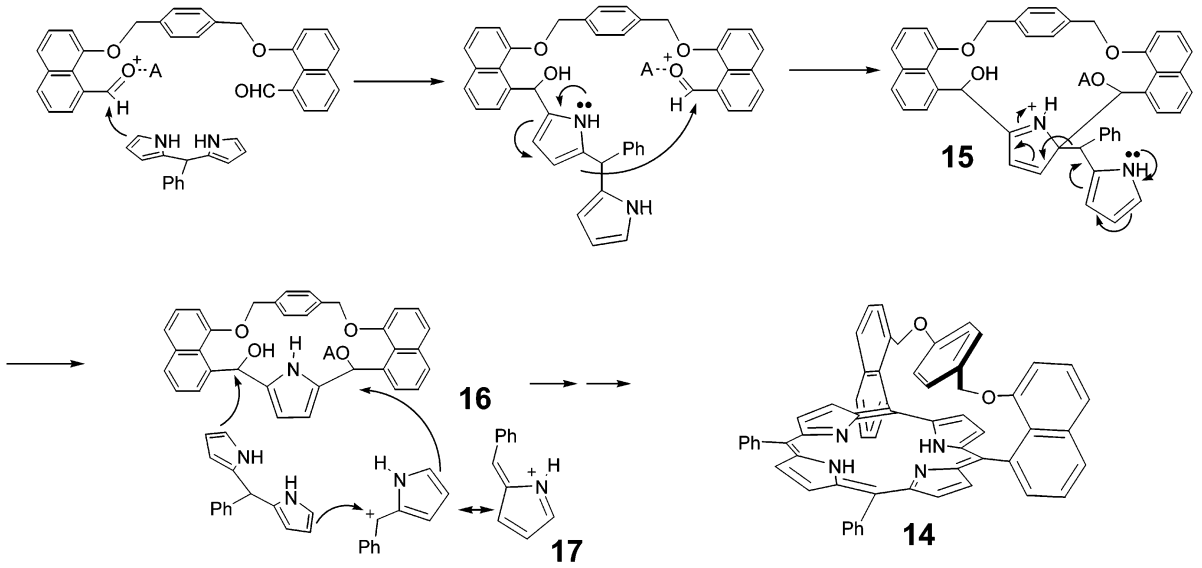
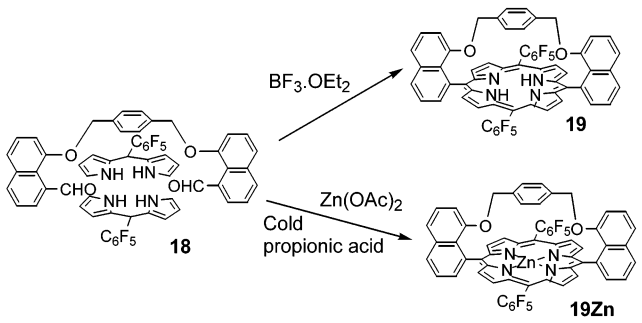
SCHEME 7



SCHEME 8



8-Methoxy-1-naphthaldehyde (8). 8-Hydroxy-1-naphthaldehyde **5**[8] (1.0 g, 5.8 mmol) and potassium hydroxide (0.32 g, 5.8 mmol) were dissolved in ethanol (50 mL). Methyl iodide (1.64 g, 11.6 mmol) was added and the mixture stirred for 4 h. The solvent was evaporated and the residue dissolved in dichloromethane. The solution was washed with water and the solvent evaporated. The resulting solid was recrystallized from methanol to give **8** as white crystals (0.3 g, 28%): mp 87−89 °C (lit.[9] mp 88−90 °C); δ_H (270 MHz, $CDCl_3$) 4.01 (3H, s), 6.97 (1H, dd, J = 7.3, 1.3), 7.42−7.56 (3H, m), 7.91 (1H, dd, J = 7.3, 1.3), 7.96 (1H, dd, J = 8.2, 1.3), 11.15 (1H, s); δ_C (67.9 MHz, $CDCl_3$) 55.61, 106.73, 121.45, 123.28, 125.69, 126.46, 127.20, 133.06, 134.98, 135.25, 156.17, 195.61; *m*/*z* (EI) 186 (M^+).

8-Methoxy-1-naphthaldehyde (8) (Method 2). To a stirred solution of oxalyl chloride (0.63 g, 6.38 mmol) in dry dichloromethane (30 mL) was added anhydrous DMSO (0.49 g, 6.38 mmol) in dry dichloromethane (20 mL) under nitrogen at −50 °C. The reaction mixture was stirred for 30 min and cooled to −78C. After 5 min 8-(hydroxymethyl)naphth-1-yl methyl ether (**6**)[17] (1.0 g, 5.32 mmol) in dry dichloromethane (20 mL) was added (dropwise over 5−10 min). After 10 min TEA (2.15 g, 0.02 mol) was added. The reaction mixture was stirred a further 5 min and allowed to warm to room temperature. The mixture was diluted with water (60 mL), and the layers were separated. The aqueous layer was extracted with dichloromethane. The organic layers were combined and washed with brine, 1% hydrochloric acid, 5% w/v sodium carbonate, and water. The extracts were dried (Na_2SO_4) and the solvents evaporated. The crude product was recrystallized from methanol to give **8** (0.7 g, 70%).

***meso*-Tetrakis(8-methoxynaphth-1-yl)porphyrin (9).** TCQ (0.052 g, 0.215 mmol) and FePc (0.122 g, 0.215 mmol) were mixed under nitrogen. Dry chloroform (550 mL, 0.75% ethanol) was added and the mixture stirred for 10 min. 8-Methoxy-1-naphthaldehyde (**8**) (1.0 g, 5.37 mmol) and pyrrole (0.36 g, 5.37 mmol) were added, followed by $BF_3{\cdot}OEt_2$ (1.32 mL, from 2.5 M stock solution in chloroform, 3.3 mmol). The reaction mixture was stirred for 1 h under nitrogen and an additional 1 h under air. Water (5 mL) was added, and solvents were evaporated to dryness. The residue was dissolved in dichloromethane and purified by flash column chromatography (neutral alumina, dichloromethane). The fast-moving band was collected and evaporation of the solvent gave **9** (0.4 g, 32%): mp >317 °C; λ_{max} (chloroform)/nm (log ϵ) 427 (5.68), 524 (4.22), 560 (4.02), 601 (3.65), 659 (3.72); δ_H (270 MHz, CD_2Cl_2) −2.03 (2H, br s), 2.10−2.29 (12H, 6s), 6.60−6.72 (4H, m), 7.45−7.55 (4H, m), 7.68−7.80 (8H, m), 7.96−8.09 (4H, m), 8.20 (4H, d, J = 8.2), 8.38 (8H, s); δ_C (67.9 MHz; CD_2Cl_2) (most intense peaks) 55.65, 107.8, 121.68, 124.32, 126.89, 128.8, 134.00, 134.10, 135.4, 138.00, 157.60; *m*/*z* (FAB) 935 (M^+ + 1). Found: C, 81.07; H, 4.49; N, 5.72. $C_{64}H_{46}N_4O_4.0.25\ CH_2Cl_2$ requires C, 80.69; H, 4.90; N, 5.86.

***meso*-Tetrakis(8-methoxynaphth-1-yl)porphyrinato Zinc (9Zn).** *meso*-Tetrakis(8-methoxynaphth-1-yl)porphyrin (**9**) (0.5 g, 0.534 mmol) was dissolved in chloroform (50 mL) and zinc acetate dihydrate (excess) added. The reaction mixture was refluxed for 3 h. Water (50 mL) was added and the mixture was extracted with dichloromethane, washed with water, and dried (Na_2SO_4). The solvents were evaporated to give crude compound, which was purified by column chromatography (silica gel, dichloromethane/ethyl acetate, 4:1) to give **9Zn** (0.45 g, 84%): mp >300 °C; λ_{max} (dichloromethane:THF 4:1)/nm (log ϵ) 432 (5.67), 561 (4.27), 604 (3.94); δ_H (270 MHz, $CDCl_3$) 1.89−2.10 (12H, 5s), 6.42−6.55 (4H, m), 7.33−7.43 (4H, m), 7.65−7.70 (8H, m), 8.01−8.13 (8H, m), 8.42 (8H, d, J = 4.6); δ_C (75.4 MHz, $CDCl_3$) 55.34, 55.63, 107.27, 107.69, 121.36, 121.51, 123.07, 123.82, 123.88, 123.98, 126.12, 126.18, 126.21, 126.28, 127.61, 127.74, 128.15, 130.33, 130.36, 130.47, 130.62, 130.74, 133.17, 133.63, 133.69, 134.82, 134.86, 134.89, 138.61, 149.82, 157.43; *m*/*z* (FAB) 996 (M^+); Acc Mass (FAB) found 996.2897 ($C_{64}H_{44}N_4O_4Zn$ = 996.2654). Found: C, 76.80; H, 4.50, N, 5.60. $C_{64}H_{44}N_4O_4Zn{\cdot}0.5CH_2Cl_2$ requires C, 76.98; H, 4.44; N, 5.61.

8-(Hydroxymethyl)naphth-1-yl Hexyl Ether. 8-(Hydroxymethyl)-1-naphthol (**4**) (4.75 g, 27.3 mmol), 1-bromohex-

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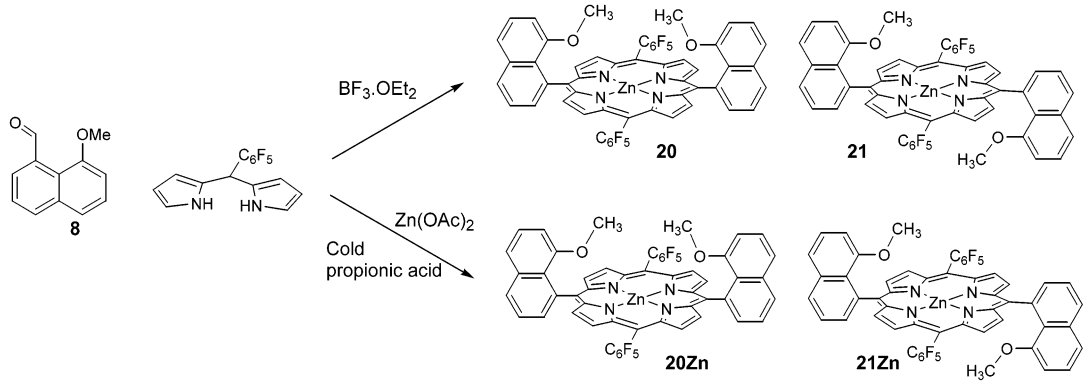
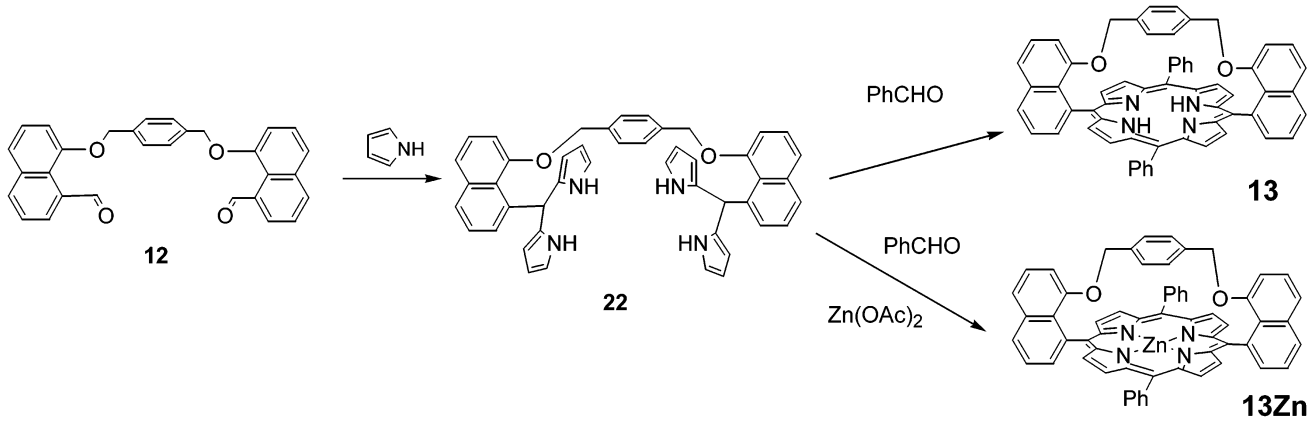
SCHEME 9



SCHEME 10



ane (5.407 g, 32.7 mmol), potassium carbonate (5.65 g, 40.9 mmol), and TBAI (1.0 g, 2.73 mmol) were mixed in MEK (300 mL). The reaction mixture was refluxed under nitrogen for 4 h. The mixture was cooled to room temperature, inorganic materials were removed by filtration, and water (200 mL) was added. The mixture was extracted with dichloromethane and dried (Na_2SO_4). The solvents were evaporated to give crude compound, which was purified by recrystallization from methanol to give the title compound as a white solid (4.0 g, 57%): mp 59−60 °C; δ_H (270 MHz, $CDCl_3$) 0.90 (3H, t, J = 7.1), 1.37−1.43 (4H, m, $-CH_2CH_{2-}$), 1.45−1.61 (2H, m, $-CH_2$), 4.18 (2H, t, J = 6.5, $-OCH_2$), 5.07 (2H, s), 6.92 (1H, d, J = 7.6), 7.35−7.49 (4H, m), 7.74 (1H, dd, J = 8.3, 1.3); m/z (EI) 259 (M^+ + 1). Found: C, 79.09; H, 8.55. $C_{17}H_{22}O_2$ requires C, 79.03; H, 8.58.

8-Hexyloxy-1-naphthaldehyde. Pyridinium chlorochromate (3.57 g, 16.5 mmol) was dissolved in dry dichloromethane (300 mL). 8-(Hydroxymethyl)naphth-1-yl hexyl ether (3.57 g, 13.8 mmol) was added and the mixture stirred for 4 h under nitrogen. The reaction mixture was diluted with ether (300 mL), and inorganic residues were removed by filtration. The solvents were evaporated to give crude product, which was recrystallized from methanol to give the title compound (3.0 g, 85%): mp 34−35 °C; δ_H (270 MHz, $CDCl_3$) 0.86 (3H, t, J = 7.0), 1.32−1.40 (4H, m), 1.43−1.53 (2H, m), 1.85−1.95 (2H, m), 4.12 (2H, t, J = 6.6), 6.94 (1H, dd, J = 7.4, 1.2), 7.39−7.54 (3H, m), 7.87 (1H, dd, J = 7.0, 1.2), 7.94 (1H, dd, J = 8.3, 1.3), 11.11 (1H, s); δ_H (67.8 MHz, $CDCl_3$) 13.91, 22.46, 25.80, 29.05, 31.41, 69.04, 107.27, 121.15, 125.53, 126.45, 127.00, 132.92, 135.16, 135.23, 155.52, 195.39; m/z (EI) 256 (M^+). Found: C, 79.61; H, 7.95. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86.

***meso*-Tetrakis(8-hexyloxynaphth-1-yl)porphyrin.** TCQ (0.038 g, 0.156 mmol) and PcFe(II) (0.088 g, 0.156 mmol) were mixed under nitrogen. Dry chloroform (390 mL 0.75% ethanol) was added and the mixture stirred for 10 min. 8-Hexyloxy-1-naphthaldehyde (1.0 g, 3.9 mmol) and pyrrole (0.26 g, 3.9 mmol) were added, followed by $BF_3{\cdot}OEt_2$ (2.6 mL, from 2.5 M stock solution in chloroform, 6.3 mmol). The reaction mixture was stirred for 1 h under nitrogen and an additional 1 h under air. Water (5 mL) was added, and solvents were evaporated to dryness. The residue was dissolved in dichloromethane and purified by flash column chromatography (neutral alumina, dichloromethane). The fast-moving band was collected and evaporation of the solvent gave the title porphyrin (0.3 g, 25%): mp 198−200, 239−240, 245−250, 265−268 °C; λ_{max} (dichloromethane)/nm (log ϵ) 427 (5.31), 522 (4.32), 558 (4.13), 601 (3.76), 659 (3.90); δ_H (270 MHz, $CDCl_3$) −2.01 (2H, s), −1.5−0.16 (32H, m), −0.13 (12H, t, J = 6.9), 2.57−2.89 (8H, m), 6.55 (4H, 2d, J = 6.9, 8.3), 7.40 (4H, t, J = 8.0), 7.57−7.72 (8H, m), 7.87 (4H, dd, J = 7.3, 1.3), 8.12 (4H, dd, J = 8.2, 1.3), 8.22 (8H, m); δ_C (67.4 MHz, $CDCl_3$) 12.14−12.85, 20.72−22.67, 23.75−24.60, 26.52−27.02, 29.59−30.85, 67.18−67.69, 107.00−107.38, 121.09−121.18, 122.64, 123.98−124.29, 126.84, 127.63, 127.70, 128.66, 128.75, 130.13, 133.69, 133.94, 134.12, 134.46, 134.75, 135.43, 138.85, 156.80. m/z FAB 1216 (M^+). Found: C, 82.66; H, 7.18, N, 4.53. $C_{84}H_{86}N_4O_4$ requires C, 82.99; H, 7.13; N, 4.60.

5,15-Bis(8-methoxy-1-naphthyl)-10,20-bis(pentafluorophenyl)porphyrin (20, 21). TCQ (0.0196 g, 0.096 mmol) and PcFe(II) (0.045 g, 0.096 mmol) were mixed under nitrogen and degassed for 10 min. Dry chloroform (100 mL 0.75% ethanol) was added and the solution stirred for 10 min. 8-Methoxy-1-naphthaldehyde **8** (0.178 g, 0.95 mmol) in dry chloroform (10 mL) and dipyrro(pentafluorophenyl)methane (0.30 g, 0.95 mmol) in dry chloroform (10 mL) were added. After 15 min, $BF_3{\cdot}OEt_2$ (0.1 mL, from 2.5 M stock solution in chloroform, 0.25 mmol) was added and the reaction mixture stirred for a further 1 h under nitrogen. Air was bubbled through the mixture for an additional 1 h. The reaction was quenched with water and evaporated to dryness. The crude

residue was purified (as a mixture) by column chromatography (silica gel, pet. ether/dichloromethane 50:50, then 100% dichloromethane). The major components were isolated as a mixture of α,α- and α,*β*-isomers (0.2 g, 43%). This mixture was recrystallized (from dichloromethane/methanol) to give powder and crystals. A crystal was carefully removed and X-ray analysis proved it to be the α,α-isomer **20**. See below for characterization data for each isomer.

5,15-Bis(8-methoxynaphth-1-yl)-10,20-bis(pentaflorophenyl)porphyrinato Zinc (20Zn and 21Zn). Dipyrro(pentafluorophenyl)methane (0.335 g, 1.07 mmol) and an excess of zinc acetate dihydrate were added to stirring propionic acid (50 mL) and cooled to 0 °C. 8-Methoxy-1-naphthyldehyde **8** (0.20 g, 1.07 mmol) in dry dichloromethane (20 mL) was added (dropwise over 1 h) and the mixture stirred for 2 h at 0 °C then 12 h at room temperature. The reaction mixture was refluxed for 2 h, and the solvents were evaporated. The crude was dissolved in dichloromethane (100 mL), and the zinc salts were removed by filtration, neutralized by excess aqueous ammonia, and dried (Na_2SO_4). TLC analysis showed that two porphyrin products were present. The mixture was purified by flash column chromatography (neutral alumina, dichloromethane) to give **20Zn** and **21Zn** (0.26 g, 48%) as a mixture of isomers. These isomers were separated by careful column chromatography (silica gel, dichloromethane/pet. ether 70:30); first fraction (**20Zn**) (0.15 g): mp >300 °C; λ_{max} (dichloromethane)/nm (log ϵ) 420 (5.61), 545 (4.20), 600 (3.77); δ_H (270 MHz; $CDCl_3$) 2.22 (6H, s), 6.67 (2H, d, J = 7.9), 7.52 (2H, t, J = 7.9), 7.73 (2H, d, J = 8.3), 7.79 (2H, t, J = 7.8), 7.98 (2H, dd, J = 6.9, 1.0), 8.25 (2H, d, J = 8.3), 8.72−8.78 (8H, dd, J = 4.6, 1.3); δ_C (69.7 MHz; $CDCl_3$) 55.50, 107.44, 121.45, 124.00, 125.21, 126.70, 127.26, 128.78, 129.47, 133.06, 134.25, 134.91, 137.28, 148.78, 151.14, 157.01; *m/z* (FAB) 1018 (M^+). Second fraction (**21Zn**) (0.1 g): mp >300 °C; λ_{max} (dichloromethane)/nm (log ϵ) 420 (5.57), 545 (4.19), 600 (3.77); δ_H (270 MHz; $CDCl_3$) 2.04 (6H, s), 6.60 (2H, d, J = 7.3), 7.50−7.57 (2H, t, J = 7.8), 7.75 (2H, d, J = 7.6), 7.80 (2H, d, J = 8.3), 8.03 (2H, t, J = 7.3), 8.26 (2H, d, J = 8.3), 8.72−8.81 (8H, m); δ_C (69.7 MHz; $CDCl_3$) 54.93, 107.13, 116.71, 121.34, 126.90, 127.33, 127.45, 128.76, 129.00, 130.02, 131.10, 131.55, 133.71, 149.29, 149.55, 149.90, 151.44, 156.85; *m/z* (FAB) 1018 (M^+).

5,15-Bis(8-methoxynaphth-1-yl)-10,20-bis(pentaflorophenyl)porphyrin (20 and 21). 5,15-Bis(8-methoxynaphth-1-yl)-10,20-bis(pentaflorophenyl)porphyrinato zinc (**20Zn** and **21Zn**) (0.01 g, 1×10^{-6} mol) was dissolved in dichloromethane (50 mL) and concentrated hydrochloric acid (5 mL) added. The solution was stirred vigorously for 4 h at room temperature. The organic layer was separated, washed with excess aqueous ammonia, and dried (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane) to give **20** (0.0054 g, 57%) and **21** (0.0035 g, 37%). **20**: λ_{max} (dichloromethane)/nm (log ϵ) 420 (5.39), 515 (4.25), 550 (3.87), 594 (3.66), 650 (3.87); δ_H (270 MHz; $CDCl_3$) −2.42 (2H, s), 2.24 (6H, s), 6.66 (2H, d, J = 7.6), 7.51 (2H, t, J = 8.1), 7.70 (2H, d, J = 7.3), 7.76 (2H, t, J 7.3), 7.92 (2H, dd, J = 8.3, 1.2), 8.23 (2H, d, J = 7.9), 8.59−8.65 (8H, dd, J = 4.6, 1.3); δ_C (75.3 MHz; $CDCl_3$) 54.31, 106.41, 120.58, 123.32, 123.45, 126.03, 126.39, 128.19, 133.53, 134.18, 135.82, 156.15; *m/z* Acc Mass (calcd $M^+ + 1$) (FAB) 955.2131, (found), 955.2172. **21**: λ_{max} (dichloromethane)/nm (log ϵ) 419 (5.21), 515 (4.23), 550 (3.87), 594 (3.60), 650 (3.91); δ_H (270 MHz; $CDCl_3$) −2.65 (2H, br s), 2.08 (6H, s), 6.59 (2H, d, J = 7.9), 7.49−7.56 (2H, m), 7.73−7.81 (4H, m), 7.97 (2H, d, J = 5.9,), 8.24 (2H, d, J = 7.6), 8.60−8.69 (8H, m); δ_C (69.7 MHz; $CDCl_3$) 54.77, 54.82, 106.97, 121.15, 121.22, 124.06, 124.27, 126.73, 126.86, 127.00, 128.98, 129.21, 133.89, 134.89, 136.53, 156.63; *m/z* FAB 955 ($M^+ + 1$).

α,α′-Bis(8-hydroxymethylnaphth-1-yloxy)-*p*-xylene (*11*). 8-(Hydroxymethyl)-1-naphthol 4 (5.19 g, 29.8 mmol), α,α′-dibromo-*p*-xylene (3.983 g, 15.0 mmol), potassium carbonate (10.36 g, 74.9 mmol), and TBAI (1.108 g, 3.0 mmol) were stirred in MEK (400 mL) and refluxed for 5 h in the dark under nitrogen. The reaction mixture was cooled to room temperature. Water (200 mL) was added and the mixture was extracted with dichloromethane and then dried (Na_2SO_4). The solvents were evaporated to give crude product, which was recrystallized (dichloromethane/hexane) to give **11** (4.0 g, 60%): mp 222−223 °C; δ_H (270 MHz; $CDCl_3$) 3.69 (2H, br s), 4.98 (4H, s), 5.27 (4H, s), 7.02 (2H, dd, J = 7.6, 1.0), 7.38−7.53 (8H, m), 7.60 (4H, s), 7.47−7.78 (2H, dd, J = 7.9, 1.7), δ_C (75.4 MHz, $CDCl_3$) 66.67, 71.42, 121.57, 122.73, 124.30, 125.26, 125.76, 126.42, 127.10, 128.70, 130.51, 133.64, 136.74, 153.43; *m/z* Acc Mass (EI) (calcd M^+) 450.1831, (found) 450.1828.

α,α′-Bis(8-formylnaphth-1-yloxy)-*p*-xylene (12). Pyridinium chlorochromate (5.746 g, 26.6 mmol) was dissolved in dry dichloromethane (300 mL). Compound **11** (4.0 g, 8.88 mmol) was added and the mixture was stirred for 24 h under nitrogen. The reaction mixture was diluted with dry ether (600 mL), and the inorganic salts were removed by filtration. The solvents were evaporated to give crude product, which was purified by column chromatography (silica gel, dichloromethane) and recrystallization from dichloromethane/pet. ether to give **12** (3.0 g, 76%): mp 242−244 °C; δ_H (300 MHz, $CDCl_3$) 5.32 (4H, s), 7.07 (2H, d, J = 7.9), 7.43 (2H, t, J = 7.9), 7.50 (4H, s), 7.53−7.58 (4H, m), 7.93 (2H, dd, J = 7.2, 1.3), 7.99 (2H, dd, J = 8.9, 1.2), 11.10 (2H, s); δ_C (75.4 MHz, $CDCl_3$) 70.89, 108.30, 121.92, 125.80, 126.48, 127.47, 128.01, 133.13, 135.11, 135.43, 136.19, 155.14, 195.47; *m/z* (EI) 446 (M^+). Found: C, 80.47; H, 4.82. $C_{30}H_{22}O_4$ requires C, 80.70; H, 4.96.

Xylyl-Bridged Porphyrins 13, 14. TCQ (0.015 g, 0.063 mmol) and PcFe(II) (0.035 g, 0.063 mmol) were mixed under nitrogen. Dry chloroform (400 mL 0.75% ethanol) was added and the mixture stirred for 10 min. Compound **12** (0.35 g, 0.7838 mmol) and dipyrrophenylmethane (0.348 g, 1.56 mmol) were added, followed by $BF_3{\cdot}OEt_2$ (1.3 mL, from 2.5 M stock solution in chloroform, 3.3 mmol). The reaction mixture was stirred for 1 h under nitrogen and an additional 1 h under air. Water (5 mL) was added, and the solvents were evaporated to dryness. The black residue was dissolved in dichloromethane. TLC analysis indicated that at least three porphyrins were present. Separation by column chromatography (silica gel, dichloromethane/pet. ether 5:1) gave **14** (0.1 g, 15%), TPP (0.02 g, 4%), **13** (0.015 g, 2%). **14**: mp> 300 °C; λ_{max} (dichloromethane)/nm (log ϵ) 425 (5.79), 520 (4.41), 557 (4.18), 597 (3.81), 653 (3.78); δ_H (270 MHz, $CDCl_3$)(at 24 °C) −2.49 (2H, br s), 3.52 (2H, d, J = 10.2), 3.91−3.94 (4H, br s), 4.13 (2H, d, J = 10.2), 6.79 (2H, d, J = 7.6), 7.53 (2H, t, J = 7.6), 7.62−7.79 (10H, m), 7.93 (2H, d, J = 6.9), 8.07 (2H, m), 8.17 (2H, d, J = 4.6), 8.33 (2H, m), 8.55 (2H, s), 8.59 (2H, d, J = 4.6), 8.85 (2H, s); δ_C (67.4 MHz, $CDCl_3$) 69.63, 106.27, 119.19, 120.70, 123.16, 124.18, 126.36, 126.55, 127.45, 127.96, 128.28, 129.56, 133.76, 134.41, 134.62, 0.134.96, 137.80, 142.55, 156.04; *m/z* Acc Mass (calcd) 848.315127 (M^+), (found) 848.3171 (M^+). **13**: mp >300 °C, λ_{max} (dichloromethane)/nm (log ϵ) 426 (5.78), 521 (4.40), 556 (4.17), 598 (3.80), 654 (3.77); δ_H (270 MHz, $CDCl_3$) −3.11 (2H, s,), 3.16 (4H, s), 3.63 (4H, s), 6.48 (2H, d, J = 7.6), 7.34 (2H, t, J = 7.9), 7.61 (6H, m), 7.73 (2H, d, J = 8.3), 7.81 (2H, t, J = 7.6), 8.04 (2H, m), 8.10 (2H, m), 8.20 (2H, d, J = 8.3), 8.45 (2H, d, J = 7.9), 8.48 (4H, s, d, J = 4.62), 8.56 (4H, d, J = 4.62); δ_C (67.4 MHz, $CDCl_3$) 69.34, 77.19, 109.57, 120.18, 122.30, 123.32, 124.09, 126.48, 127.20, 128.50, 128.89, 130.99, 131.44, 132.95, 134.28, 134.93, 138.38, 143.16, 149.21, 149.86, 155.81.

Bis(dipyrromethane) Derivative 22. Compound **12** (0.5 g, 0.73 mmol) in dry dichloromethane (100 mL) was added to stirring pyrrole (1.96 g, 29.28 mmol) at room temperature under nitrogen. $BF_3{\cdot}OEt_2$ (0.0157 g, 0.222 mmol) was added and the reaction mixture stirred for 45 min. The mixture was diluted with dichloromethane (50 mL), washed with 0.1 N sodium hydroxide and water, and then dried (Na_2SO_4). The solvent and pyrrole were removed by vacuum distillation to give a sticky brown solid, which was purified by column chromatography (silica gel, dichloromethane) to give **22** as an

off white solid (0.45 g, 56%): mp 208−210 °C; δ_H (270 MHz, $CDCl_3$) 5.05 (4H, s), 5.67 (4H, s), 6.04 (4H, m), 6.48 (4H, d, J = 1.3), 6.86 (2H, d, J = 7.6), 7.01 (2H, s), 7.06 (2H, d, J = 7.3), 7.20 (4H, s), 7.28−7.35 (4H, m), 7.43 (2H, d, J = 8.3), 7.51 (4H, br s), 7.67 (2H, d, J = 8.2); δ_C (75.4 MHz, $CDCl_3$) 41.63, 70.60, 106.97, 107.51, 108.16, 116.29, 116.47, 122.24, 124.06, 125.28, 125.91, 127.65, 128.66, 134.33, 136.40, 136.72, 139.37, 156.11; *m*/*z* Acc Mass (EI) (calcd M^+) 678.2995, (found) 678.2993.

5,15-Xylyl-Bridged 10,20-Diphenylporphyrin 13Zn. Compound **22** (0.2 g, 0.294 mmol) was dissolved in propionic acid (50 mL), and zinc acetate dihydrate (excess) was added. The mixture was cooled to 0 °C under nitrogen. Benzaldehyde (0.078 g, 0.73 mmol) in dichloromethane (50 mL) was added dropwise over 1 h and the mixture stirred for a further 2 h at 0 °C under nitrogen and then 12 h at room temperature. The reaction mixture was refluxed for 2 h, then the solvents were evaporated. The black solid was dissolved in dichloromethane, and inorganic salts were removed by filtration. The solution was treated with aqueous ammonia and water and dried (Na_2SO_4). The solvents were removed in vacuo. The crude product was purified by column chromatography (neutral alumina, dichloromethane). The fast-moving dark red fraction was collected, and the solvents were evaporated to give **13Zn** (0.1 g 37%): mp >300 °C; λ_{max} (dichloromethane)/nm (log ϵ) 426 (5.37), 553 (3.92), 595 (3.34); δ_H (270 MHz, $CDCl_3$) 3.07 (4H, s), 3.68 (4H, s), 6.51 (2H, d, J = 7.6), 7.38 (2H, t, J = 8.1), 7.68 (6H, m), 7.79 (2H, d, J = 8.6), 7.87 (2H, t, J = 7.8), 8.15 (4H, m), 8.25 (2H, d, J = 8.3), 8.51 (2H, d, J = 6.9), 8.62 (4H, d, J = 4.6), 8.74 (4H, d, J = 4.6); δ_C (75.4 MHz, $CDCl_3$) 69.34, 77.19, 109.57, 120.18, 122.30, 123.07, 123.32, 124.09, 126.28, 126.48, 127.20, 128.50, 128.89, 130.99, 131.44, 132.95, 134.28, 134.93, 138.38, 143.16, 149.21, 149.86, 155.81; *m*/*z* (FAB) 912 (M^+). **13Zn** was recrystallized from dichloromethane/methanol to obtain crystals for X-ray diffraction.

5,15-Xylyl-Bridged 10,20-Bis(pentafluorophenyl)porphyrin 19. TCQ (0.0196 g, 0.08 mmol) and PcFe(II) (0.045 g, 0.08 mmol) were mixed under nitrogen for 10 min. Dry chloroform (300 mL, 0.75% ethanol) was added and the mixture was stirred for 10 min. **12** (0.178 g, 0.4 mmol) and dipyrro(pentafluorophenyl)methane (0.25 g, 0.8 mmol) were added, followed by $BF_3{\cdot}OEt_2$ (0.2 mL, from 2.5 M stock solution in chloroform, 0.5 mmol). The reaction mixture was stirred for 1 h under nitrogen and an additional 1 h under air. Water (5 mL) was added and the solvents were evaporated to dryness. The residue was separated by column chromatography (silica gel, dichloromethane/cyclohexane, 40:60) to give **19** (0.025 g, 6.1%): mp >320 °C; λ_{max} (dichloromethane)/nm (log ϵ) 422 (5.37), 516 (4.16), 551 (3.79), 595 (3.68), 652 (3.69); δ_H (270 MHz, $CDCl_3$) −3.33 (2H, s), 3.06 (4H, s), 3.67 (4H, s), 6.48 (2H, d, J = 7.6), 7.37 (2H, t, J = 7.9), 7.75 (2H, d, J = 7.9), 7.85 (2H, t, J = 7.6), 8.23 (2H, d, J = 7.8), 8.43 (2H, d, J = 6.9), 8.50 (8H, dd, J = 4.6, 4.3); δ_C (67.4 MHz, $CDCl_3$) 69.27, 77.20, 108.78, 122.03, 123.55, 123.73, 124.09, 126.66, 128.42, 129.03, 131.71, 131.93, 134.93, 136.92, 155.50; *m*/*z* Acc Mass (FAB) (calcd M^+) 1028.2209, (found) 1028.2201.

5,15-Xylyl-Bridged 10,20-Bis(pentafluorophenyl)porphyrinato Zinc(II) 19Zn (Method 1). Dipyrro(pentaflorophenyl)methane (0.28 g, 0.896 mol) and zinc acetate dihydrate (excess) were mixed in propionic acid (50 mL), and the solution was cooled to 0 °C under nitrogen. Compound **12** (0.20 g, 0.448 mmol) in dry dichloromethane (50 mL) was added dropwise over 1 h and the mixture stirred a further 2 h at 0 °C. Air was then bubbled through the reaction mixture overnight at room temperature. The mixture was refluxed for 2 h, and the solvents were evaporated. The crude solid was dissolved in dichloromethane, and zinc acetate was removed by filtration, washed with aqueous ammonia and water, and dried (Na_2SO_4). The solvents were evaporated to give crude product, which was purified by column chromatography (neutral alumina, dichloromethane) to give **19Zn** as red/purple solid (0.12 g, 37%): mp >310 °C; λ_{max} (dichloromethane)/nm (log ϵ) 423 (5.38), 550 (4.16), 596 (3.72); δ_H (300 MHz, $CDCl_3$) 3.04 (4H, s), 3.69 (4H, s), 6.54 (2H, d, J = 7.6), 7.44 (2H, t, J = 7.9), 7.84 (2H, d, J = 8.5), 7.92 (2H, t, J = 7.7), 8.32 (2H, d, J = 8.2), 8.52 (2H, d, J = 7.0), 8.70−8.77 (8H, dd, J = 4.7, 4.1); δ_C (75.3 MHz, $CDCl_3$) 69.04, 77.18, 109.27, 122.21, 123.52, 124.07, 124.43, 126.55, 128.75, 128.84, 129.23, 131.32, 132.63, 132.75, 134.87, 137.52, 148.46, 150.63, 155.47; *m*/*z* Acc Mass (FAB) (calcd M^++1) 1091.1422, (found) 1091.1425.

5,15-Xylyl-Bridged 10,20-Bis(pentafluorophenyl)porphyrinato Zinc(II)19Zn (Method 2). Compound **22** (0.10 g, 0.147 mmol) and zinc acetate dihydrate (excess) were mixed in propionic acid (50 mL) and cooled to 0 °C under nitrogen. To the mixture was added pentafluorobenzaldehyde (0.057 g, 0.294 mmol) in dry dichloromethane (50 mL) (dropwise over 1 h). The mixture was stirred for 2 h at 0 °C then at room temperature for an additional 12 h under air. The reaction mixture was refluxed for 2 h, and solvents were evaporated to dryness. The residue was dissolved in dichloromethane, treated with aqueous ammonia, washed with water, and dried (Na_2SO_4). The solvents were evaporated to give crude product, which was purified by column chromatography (neutral alumina, dichloromethane). The fast-moving dark red band was collected, and evaporation of the solvent gave **19Zn** as red/purple solid (0.04 g, 25%).

5,15-Xylyl-Bridged 10,20-Bis(pentafluorophenyl)porphyrin 19. Compound **19Zn** (0.01 g, 0.0091 mmol) was dissolved in dichloromethane (50 mL), and concentrated hydrochloric acid (5 mL) was added. The mixture was stirred at room temperature for 4 h. Water (100 mL) was added, and the layers were separated. The organic phase was washed with aqueous ammonia and water and then dried (Na_2SO_4). The solvents were evaporated to give crude product, which was purified by column chromatography (silica gel, dichloromethane) to give **19** (0.008 g, 85%).

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Supporting Information Available: Further experimental details and comparison of synthetic methods, synthesis of starting materials, MS, NMR spectra, HPLC profile for *meso*-tetrakis(8-hexyloxynaphth-1-yl)porphyrin, and X-ray crystallographic details for **14**, **13Zn**, and **20**. This information is available free of charge via the Internet at http://pubs.acs.org.

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